THE POLYMERIZATION OF ACRYLONITRILE WITH FERRIC CHLORIDE AS PHOTOINITIATOR.

A thesis submitted to the University of Glasgow in accordance with the regulations for the award of the degree of Doctor of Philosophy

by

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SUMMARY.

A detailed kinetic study has been made of the photosensitized polymerization of acrylonitrile in dimethyl formamide solution with ferric chloride as both catalyst and terminating agent.

It has been shown that ferric chloride readily forms complexes with solvents containing atoms which act as electron donors, and that a complex exists between ferric chloride and dimethyl formamide which probably involves co-ordination via carbonyl oxygen atoms.

There is evidence also that two species of ferric chloride exist in dimethyl formamide, and that one of these is more readily reduced by absorption of light or reaction with free radicals than the other.

Notwithstanding the complex nature of these solutions, it appears that the process whereby free radicals are obtained on photolysis with u.v. light primarily involves a relatively simple reaction, namely electron transfer from chlorine to iron to form chlorine atoms. These atoms, however, do not initiate polymerization directly; it is probable that the solvent is attacked to produce further radicals which react with monomer to initiate chains.

The extinction coefficient of ferric chloride in dimethyl formamide at 3650Å is 5 x 10^3 litre mole^{-1} cm.^{-1}, such that absorption of irradiation at this wavelength in reaction vessels of 2 cm. diameter containing chloride concentrations greater than ca. 3 x 10^{-4} mole litre^{-1} is virtually complete. It is shown that under these conditions the rate of production of ferrous iron, and consequently the rate of initiation, is independent of ferric chloride concentration. At concentration greater than ca. 2 x 10^{-3} mole litre^{-1}, termination occurs by reaction of growing radicals with ferric chloride. To describe this system, a simple kinetic scheme is postulated which indicates that, under stationary state conditions, rates of polymerization and initiation should be given by the expressions

$$\text{Rate}_p = \frac{k_p k_i I_o [M]}{k_t [FeCl_3]} \qquad \text{.....(1)}$$

and

$$I_n = k_i I_o \qquad \text{.....(2)}$$

where k_p and k_t are the velocity coefficients of propagation and termination, k_i is the constant relating the rate of initiation, I_n, to the intensity of irradiation, I_o, and $[M]$ and $[FeCl_3]$ represent the monomer and ferric chloride concentrations.

I_n, as measured by titration for ferrous iron with ceric ammonium sulphate, is $1{\cdot}64 \times 10^{-7}$ mole litre^{-1} sec^{-1}, and by substitution of this value for k_1I_o in equation (1), a value of 0·078 is obtained for k_p/k_t at 25°C. This is somewhat smaller than that obtained by Bamford and co-workers, namely 0·33 at 60°C (29). The difference is due in part to the difference in temperature; the overall activation energy is ca. 2 kcal mole^{-1}. It may also however, be due to a lower efficiency of initiation for the radicals derived from ferric chloride than for cyanoisopropyl radicals.

Kinetic observations, in general, are in agreement with the scheme postulated, though the intensity exponent is lower than expected. A tentative theory has been put forward to explain this.

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CHAPTER 1.

INTRODUCTION

1.1. The Polymerization of Vinyl Compounds by Free Radical Mechanisms; The Homogeneous Polymerization of Acrylonitrile.

The first observation of the polymerization of vinyl monomers was made as early as 1839 by Simon (1), who reported the conversion of styrene to a gelatinous mass. In 1910, Stobbs and Posnjak (2) postulated that polystyrene was a "colloidal body", but almost immediately Lebedev (3) showed that polymers had high molecular weights. Lebedev's suggested mechanism for the growth process however, involved intermolecular association. This was nevertheless, an advance on the prevailing ring theories of Harries (4) and earlier of Lebedev himself (5).

The first major advance in the elucidation of the mechanism of polymerization of vinyl monomers is to be found in an all important paper by Staudinger in 1920 (6) in which he suggested a chain mechanism, the formula of the intermediates being written with free valances at both ends of the molecule. He considered that activation of the monomer molecule resulted in the opening of the double bond, and that the activated molecule then reacted with successive monomer units to give intermediates similar to those described above. He assumed also that termination occurred by deactivation of the radical by virtue of its long chain length. These discussions however, were rather vague and imprecise, and the first complete free radical mechanism for a polymerization reaction was given by Taylor and Jones in 1930 (7).

Another mechanism was suggested by Whitby and Katz (8) who, although accepting the idea of linear polymeric molecule, did not agree with Staudinger's concept of free radical intermediates. They postulated a mechanism involving successive hydrogen transfer between a polymeric molecule and the vinyl monomer. Even in 1936, at a symposium on polymerization (9), both free radical and stepwise hydrogen transfer mechanisms were discussed.

Thus the theory that polymerization could occur by free radical chain mechanisms was not universally accepted for almost another decade. It was finally accepted when it was shown that polymerizations could be initiated by substances which were known to give radicals on decomposition or by photo-exitation. Detailed kinetic analyses of vinyl polymerizations also gave results which could be correlated to a radical mechanism. This latter evidence was slow in forthcoming since the influence of impurities on a reaction involving radical intermediates was not fully appreciated.

The normal kinetic scheme is now taken to be:-

Initiation $$C \longrightarrow R_c \quad ....(1.1.)$$

$$M + R_c \longrightarrow R_1 \quad ....(1.2.)$$

Propagation $$R_n + M \xrightarrow{k_p} R_{n+1} \quad ....(1.3.)$$

Termination $$R_n + R_m \xrightarrow{k_t} \text{Polymer} \quad ....(1.4.)$$

where C and M are molecules of initiator and monomer, R_c is a radical derived from the initiator, R represents a growing radical chain, the subscripts refer to the number of units in the chain, and k_p and k_t are velocity coefficients. This simple scheme gives rise, under steady state conditions, - (the full assumptions involved are discussed in Chapter 5) - to the following rate equation:-

$$\text{Rate} = k_p[C]^{0\cdot5}[M]^{1\cdot0}$$

On addition of a substrate X which can terminate free radicals, the additional termination step:-

$$R + X \xrightarrow{k_t'} \text{Polymer} \qquad \text{....(1.5.)}$$

should be included in the scheme. If this reaction is significant compared to (1.4.) the effect on the rate equation is to raise the initiator exponent and in the extreme case where all termination of radicals is by (1.5.) the equation becomes:-

$$\text{Rate} = \frac{k_p [M] I_n}{k_t' [X]}$$

where I_n, the rate of initiation may be proportional to initiator concentration, or light intensity, or both.

The first detailed results for the polymerization of acrylonitrile by free radicals were published in 1953 by Bamford et. al. (10, 11), but not until 1955 were results published on the homogeneous polymerization of this monomer (12). In dimethyl formamide solution, at 60°C, kinetic orders in initiator and monomer concentration are 0·5 and 1·5 respectively, but in the photosensitized polymerization at 25°C (13) the rate is proportional to $(\text{light intensity})^{0\cdot6}$ and $[M]^{1\cdot3}$. A kinetic scheme in which relatively inactive radicals are formed by transfer to solvent has been proposed to account for the unusual kinetic orders observed.

1.2. Effect of Added Substrates; the Role of Transition Metal Salts in Free Radical Reactions.

The role of metal salts with variable valance in reactions involving free radical intermediates has been widely studied in both aqueous and non-aqueous media. Work in each media is considered separately.

1.2.1. Reactions of Metal Salts in Aqueous Media

From an examination of the u.v. spectra of various salts and bases of multi-valent ions, Rabinowitch et. al. (14, 15), postulated the existence of ion pair complexes of the type $(M^{z+}X^{y-})$ in aqueous solution with varying degrees of stability, and maintained that the high molecular extinction coefficient was to be associated with electron transfer from anion to cation. Evans et. al. (16, 17) subsequently showed that u.v. irradiation of aqueous solutions of ferric perchlorate in perchloric acid produced free radicals, and this was considered to involve electron transfer within the active species $(Fe^{3+}OH^-)$

$$Fe^{3+}OH^- \xrightarrow{h\nu} Fe^{2+}OH \longrightarrow Fe^{2+} + OH$$

In presence of halogen ions, the species $(Fe^{3+}Cl^-)$ or

($Fe^{3+}Br^-$) could become active by regulation of pH such that the ($Fe^{3+}OH^-$) concentration was minimal. The radicals produced (OH, Cl, or Br), were shown to initiate the polymerization of acrylonitrile.

Another aqueous system capable of producing free radicals on photolysis is that containing the oxalato complex $\left[M\ (C_2O_4)_3\right]^{3-}$. This reaction has been studied by Porter et. al. (18) and it has been shown that $\left[Mn(C_2O_4)_3\right]^{3-}$ and $\left[Fe(C_2O_4)_3\right]^{3-}$ produce free radicals which can initiate the polymerization of acrylonitrile (19, 20). The active radical is said to be the $C_2O_4^-$ radical-ion produced by electron transfer to the metal ion.

The second role of transition metal salts in aqueous solutions containing radicals is that of termination. That water soluble free radicals could reduce metal ions in solution has been shown by Hains and Waters (21), Dainton et. al. (22, 23, 24, 25) and others. Again in the ion pair ($Fe^{3+}OH^-$) is postulated as the active species with a contribution from ($Fe^{3+}H_2O$)

$$Fe^{3+}OH^- + R \longrightarrow ROH + Fe^{2+}$$

$$Fe^{3+}H_2O + R \longrightarrow ROH + Fe^{2+} + H^+$$

In their study of the polymerization of acrylonitrile mentioned above, Evans and co-workers assumed that termination was by interaction of radicals and postulated considerable back reaction of the type

$$Fe^{2+} + OH \longrightarrow Fe^{3+}OH^{-}$$

to explain certain kinetic characteristics. Dainton and Tordoff in a study of the polymerization of acrylamide initiated photochemically by ($Fe^{3+}OH^{-}$) (26) point out that, at the monomer concentration used by Evans, this is extremely unlikely, and moreover, at the ferric ion concentrations used, (up to 10^{-2} mole litre^{-1}), at least some, if not all, termination of radicals would be effected by electron transfer to metal ions. Some confirmation for these claims is to be seen in earlier work on the photochemical oxidation of aromatic substrates in aqueous solution in presence of ferric ion by Bates and Uri (27) and Baxendale and Magee (28). For example, although diphenyl is formed on photolysis of ($Fe^{3+}OH^{-}$) in presence of benzene, phenol is also formed, and the yield can be increased by increasing the ($Fe^{3+}OH^{-}$) concentration. Dainton, then, postulates that, at relatively high ferric concentrations, the rate of polymerization for steady state conditions is given by the expression

$$\text{Rate} = \frac{\phi_{OH}\, I_{abs.}\, [M]\, k_p}{k_4[Fe^{3+}H_2O] + k_5[Fe^{3+}OH^{-}]}$$

where k_p, k_4 and k_5 are velocity coefficients, ϕOH is the quantum yield from the initial photolysis, $[M]$ is the acrylamide concentration and Iabs. is the actual intensity of light absorbed for any one ferric ion concentration. The rate of production of ferrous iron is given by

$$\frac{d\,[Fe^{2+}]}{dt} = 2\,\phi OH\ \text{Iabs.}$$

It was found that the intensity exponent was only less than unity when the total ferric ion concentration was less than 4×10^{-4} mole litre^{-1} such that termination is exclusively first order above this concentration. ϕOH was found to be approximately $0{\cdot}2$ while the values of k_4 and k_5 were 2×10^{-3} and $1{\cdot}5 \times 10^{-4}$ litre $\text{mole}^{-1}\text{second}^{-1}$ respectively.

1.2.2. Reactions of Metal Salts in Non-Aqueous Media

Little was known of the interaction of free radicals and metal salts in non-aqueous solution prior to 1957 when Bamford et. al. (29) investigated the thermal polymerization of acrylonitrile in dimethyl formamide solution initiated by azobisbutyronitrile in presence of ferric chloride. At chloride concentrations of about 10^{-2} mole litre^{-1} and above, the salt was found to be an efficient retarder, and from the kinetic scheme postulated it was shown that the rate of initiation could be obtained by measuring the rate of production of ferrous iron via the reaction

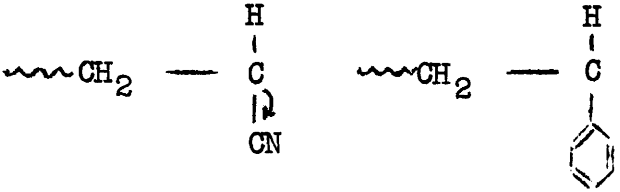
$$R + FeCl_3 \longrightarrow \text{Polymer} + FeCl_2$$
$$k_t = 6 \times 10^3 \text{ l.mole}^{-1}\text{sec}^{-1}.$$

Subsequently Cherniak et. al. (30) have pointed out the usefulness of ferric chloride as a scavenger for radicals formed during the radiolysis of organic compounds. Products of reaction or radical intermediates could be identified in this way. More recently Monteiro (31) has shown cupric chloride to be an inhibitor in the polymerization of acrylonitrile in dimethyl formamide, the process

$$R + CuCl_2 \longrightarrow \text{Polymer} + CuCl$$

being even more efficient than the corresponding reaction with ferric chloride.

Bamford et. al. have made an extensive study of the nature of the reaction between polymer radicals and ferric chloride in dimethyl formamide solution. It was observed initially that polystyrene radicals were considerably more reactive to the ferric salt than polyacrylonitrile radicals. This unexpected result was explained in terms of inductive effects. The electron attracting - CN group in polyacrylonitrile radicals would tend to oppose transfer of charge to metal cations more than the phenyl group in polystyrene radicals



Thus, even though the polystyrene radical is more "resonance stabilised" it reacts more rapidly with metal cations because the reaction involves charge transfer. This study was extended to a series of monomers (32) and the order of reactivity of radicals to ferric chloride was found to be:-

Vinyl Acetate > Styrene > Methyl Acrylate > Acrylonitrile
> Methyl Methacrylate > Methacrylonitrile

The reactivity to metal cations then is governed by two factors:-

(a) Resonance stabilisation, a relative measure of which can be obtained from the radicals' reactivity to non-polar toluene.

(b) Electron donating ability of the radical.

The transition state in the radical-ion reaction may be vizualised as involving partial transference of an electron from radical to ion. That the transition state could be associated with contributions from polar structures had been observed as early as 1948 (33), but Bamford et. al. go much further than other workers by separating the general reactivities of radicals from their polar properties in a mathematical treatment which correlates each of these with measurable quantities (34,35). Most recent work (36) presents tabulation of all results, and the presentation, on nomogram-type plots, of the whole of copolymerization monomer reactivity and transfer reagent reactivity.

Electron transfer then, is a prime factor in the radical-ion reaction, but in 1960 Entwhistle studied the reaction from a new angle (37). The reactivities of a series of ferric salts to polymethylmethacrylate radicals were examined and it was found that these varied greatly. The order of reactivity is

Bromide > Chloride > Benzoate > Perchlorate

Entwhistle observes that this is also the order of decreasing tendency to hydrolyse and concludes that the bond strength of the ferric salt is an important factor in determining its reactivity to polymer radicals. Also Watanabe and Kiuchi (38) have shown that cupric salts have a similar order of reactivity to polyacrylonitrile radicals as that found for ferric salts to polymethylmethacrylate radicals. These results would appear to favour the "bridged activated complex for electron transfer reactions" theory postulated by Taube and Meyers (39) with the reaction proceeding via the transition state shown below.

$$R + M^{n}X_{n} \longrightarrow \left[R\ldots\overset{-}{X}\ldots M^{n}X_{n-1}\right] \longrightarrow RX + M^{n-1}X_{n-1}$$

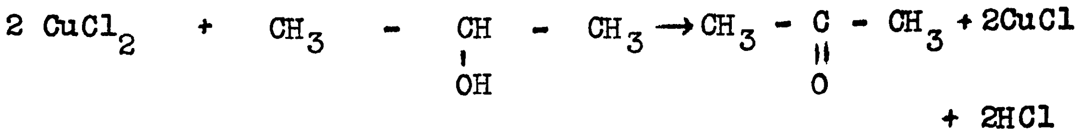
These authors quote, as evidence for this, the oxidation of chromous ion by chloro pentammino cobalt ion

$$\left[Co\,(NH_3)_5Cl\right]^{2+} + Cr^{2+} \longrightarrow \left[Co\,(NH_3)_5\right]^{2+} + \overset{2+}{CrCl}$$

Quantitative transfer of a chlorine atom to the reducing agent takes place with no exchange with chlorine ions in solution. Thus it is maintained that reaction takes place only through the formation of a chlorine bridged transition state.

In the final analysis then, the facts would appear to indicate that reaction between free radicals and metal salts involves "electron flow through a bridged activated complex".

Little is recorded in the literature of the photolysis of metal salts in non-aqueous media. Kochi has studied the effect of u.v. irradiation on solutions of cupric chloride in organic solvents (40) and describes the reactions as the addition and abstraction reactions of chlorine. For example, in isopropyl alcohol, acetone is formed by abstraction of two hydrogen atoms



$$2\,CuCl_2 + CH_3 - \underset{\displaystyle OH}{\underset{|}{CH}} - CH_3 \rightarrow CH_3 - \underset{\displaystyle O}{\underset{\|}{C}} - CH_3 + 2CuCl + 2HCl$$

No attempt has been made, as yet, to study the photolysis of solutions of ferric chloride in dimethyl formamide. McIntosh (41) in 1960 observed that radicals were formed from this reaction which could initiate polymerization of acrylonitrile. The exact nature of these radicals is unknown however. Ferric chloride complexes strongly with dimethyl formamide as postulated by Bamford (29) and substantiated by McIntosh, whilst Nortia (42) describes complexes of the type

$$\left[M\ (HCONMe_2)_6\right](ClO_4)_3$$

where M is Copper, Nickel or Cobalt. Thus it appears likely that the complex

$$\left[Fe(HCONMe_2)_6\right]Cl_3$$

might exist in dimethyl formamide, though this has not, as yet, been shown. Nor is it known whether different species of ferric ion analogous to thos found in aqueous solutions exist in dimethyl formamide.

Thus the process whereby free radicals are formed on photolysis of the ferric chloride - dimethyl formamide complex with possible d^2sp^3 octahedral co-ordination is almost certainly more complex than that represented by the simple equation

$$FeCl_3 \xrightarrow{h\nu} FeCl_2 + Cl$$

The purpose of the present work is to examine this reaction with particular reference to its role in the polymerization of acrylonitrile in the region of ferric chloride concentration where both initiation and termination are effected by the ferric salt, and to compare the kinetics and kinetic parameters of this system with those obtained with aqueous solutions of ferric ions by Dainton and Tordoff in the polymerization of acrylamide (26), and also with those obtained by Bamford et. al. in the thermal polymerization of acrylonitrile in dimethyl formamide (29). In this way it is hoped to establish a better understanding of the nature of ferric chloride solutions in dimethyl formamide, and other non-aqueous media.

CHAPTER 2.

EXPERIMENTAL

2.1. Materials

2.1.1. Ferric Chloride

Anhydrous ferric chloride is supplied to the laboratory by B.D.H. as the reagent grade, and the following experiments were carried out in an attempt to purify this grade

(a) sublimation under vacuum; it was found that heating under high vacuum caused breakdown of ferric chloride presumably to ferrous chloride and chlorine.

(b) sublimation in a stream of pure dry nitrogen; McIntosh (41) describes this as a satisfactory method for the purification of anhydrous ferric chloride, but it was found that breakdown here was even more prevalent than in (a) with additional formation of red and brown crystals.

It was now decided to prepare the anhydrous salt from the elements and A.R. iron filings were heated in a stream of dry chlorine. This method yielded no more satisfactory results, the solid being found to form in layers containing varying amounts of red, brown and darker crystals.

Variations of all three methods described above were employed without success.

It has been suggested that the red or brown materials formed might be intermediate hydrates of ferric chloride, but this seems unlikely since their formation occurs in similar proportions whether the chlorine is dried carefully or not, and, on exposure to the atmosphere, no formation of the hexahydrate by further absorption of moisture is observed. No attempt has been made to identify these products.

In all experiments what appeared to be pure anhydrous, (deep purple), crystals of ferric chloride did sublime near the area of application of heat, but to recover these crystals without contamination from other materials and products, particularly before hydrolysis of the chloride, was found to be virtually impossible.

In view of the above, it was decided to use the relatively pure B.D.H. reagent grade of ferric chloride without further purification.

2.1.2. N.N. - Dimethyl Formamide (DMF)

The solvent, as supplied by Eastman Kodak, was shaken up for five 1 - hourly treatments with phosphorus pentoxide, then distilled at atmospheric pressure, and the fraction boiling at 153°C collected.

2.1.3. Acrylonitrile (AN)

The monomer, (supplied by G. Light & Co.), was dried over calcium chloride for twenty four hours, then filtered off and distilled at atmospheric pressure. The fraction boiling at 77·3°C was collected.

This pure acrylonitrile was poured into a distillation flask, a little azobisisobutyronitrile added and the flask connected to the vacuum line. The solution was degassed, then photochemically polymerized to about 20% conversion. Pure unreacted monomer was now distilled off into another compartment on the line, and reaction vessels could be filled direct from this reservoir.

2.2. Apparatus

2.2.1. High Vacuum Line

This consisted of a series of traps and vacuum tested taps in Pyrex glass connected via a mercury diffusion pump to an Edwards rotary high vacuum pump. Cold traps were placed immediately before and after the mercury diffusion pumps, and a Drikold-Acetone mixture was used as coolant in both traps. All taps and joints were greased with Apiezon high vacuum greases. A manometer connected to the system allowed approximate measurement of the vacuum, and could be used to detect slow air leaks, which in turn, could be located by observing the discharge of a high voltage coil activated close to the line. A pressure of about 10^{-4} mm. of mercury was easily attained.

2.2.2. Reaction Vessels.

All reactions were carried out in Pyrex glass dilatometers. The design of these was as illustrated in Figure (1). The vessels were made from tubing of 2 cm. bore giving a capacity of some 12 to 13 ml., and a magnetic follower, encased in glass, was incorporated into the bulb to allow stirring. Stems were of Veridia tubing of 1 mm. bore, and the use of a side arm facilitates degassing and distillation procedures.

2.2.3. Thermostatically Controlled Tank

All experiments were carried out under standard conditions in a cylindrical glass tank. This was surrounded by an aluminium jacket with observation and irradiation windows. The annular space between the

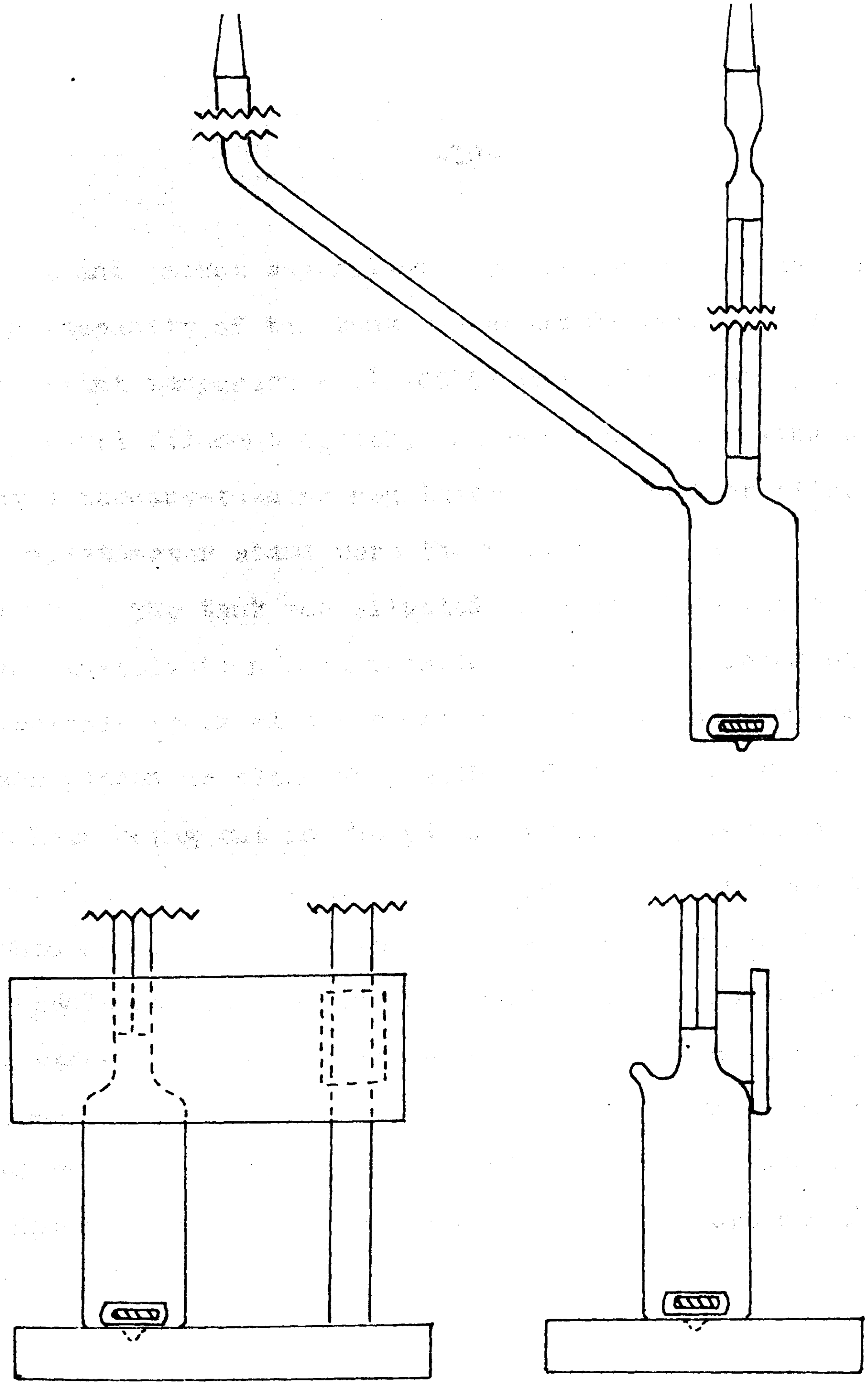


fig 1

tank and jacket was filled with asbestos wool lagging. The capacity of the tank was about 25 litres, and a constant temperature ($\pm 0{\cdot}02^{\circ}C$) was maintained by a relay operated filament heater, the relay circuit being actuated by a mercury-toluene regulator. A propellor stirror and a dilatometer stand were the only other contents of the tank. The tank was situated on a platform which allowed the introduction of a rotating magnet, (operated by a variable speed electric motor), underneath. The magnet was placed as close as possible to the base of the tank, a hole being cut in the platform directly beneath the dilatometer stand for this purpose. The rotation of this magnet was used to induce stirring in reaction vessels by means of the enclosed magnetic followers. A strip of brass was attached to the dilatometer stand some 4 cm. above the base to ensure that the surface area of reaction vessel being irradiated was the same in all experiments. To this end also, dilatometers had flat bottoms.

2.2.4. Irradiation

The source of irradiation was a 125 w. Osira high pressure mercury vapour lamp. To smooth out variations in the applied current, the lamp was connected to a capacitator and choke. The emitted light was filtered through a Chance OX_1 filter such that 3650Å was the predominant wavelength of light.

2.3. Procedure

2.3.1. Calibration of Dilatometers

The volume of the bulbs was found by filling with A.R. acetone from a burette graduated in 0·05 ml. divisions, and Veridia tubing, (bore known), was used for the stem.

2.3.2. Filling of Dilatometers

The calculated volume of ferric chloride - DMF solution to be used was measured into the cleaned dilatometer before connecting to the vacuum line. (DMF distils only very slowly on the line). Degassing was carried out as follows:- The dilatometer was immersed in a Drikold-Acetone mixture before opening to vacuum. The air in the vessel was pumped off for thirty minutes, then the isolating tap was closed. Reactants were warmed to 25°C, then immersed in coolant, before opening the tap to vacuum. The above cycle was repeated three times.

The dilatometer was now sealed off from the side arm at the constriction joining of the two, the bulb being immersed in a small beaker of coolant.

Monomer was distilled directly from a reservoir on the line into the dilatometer, and this was sealed off at the constriction.

2.3.3. Rate Measurement

The filled dilatometers were completely immersed in the thermostat at the required temperature and allowed twenty minutes to come to thermal equilibrium with the surroundings before irradiation commenced. The rate of polymerization was obtained by measuring the rate of fall of the meniscus level in the dilatometer stem using a cathetometer. From a knowledge of the densities of reactants and products, the rate of fall of meniscus can be directly correlated to the rate of reaction.

CHAPTER 3.

The Extinction of Ferric Chloride in DMF.

3.1. Theory

For the absorption of light by a substance in solution, the relationship between the incident and transmitted radiations is given by Beer's law, one form of which states that

$$I = I_0 10^{-\varepsilon cd} \qquad \ldots.(III.1.)$$

where I_0 = Intensity of Incident Light
I = Intensity of Transmitted Light
ε = Extinction Coefficient
c = Concentration of solution
d = Length of light path through solutions.

Obviously the intensity of the incident light will decrease on passing through depth d, but if this decrease is no greater than 10%, the irradiation can be considered approximately uniform. Thus it was required to find what concentration of ferric chloride in DMF would allow transmission of at least 90% of the incident light of wavelength 3650Å.

Equation III.1. can be written:-

$$\log \frac{I_0}{I} = \varepsilon cd \qquad \ldots.(III.2.)$$

$\log {}^{I_o}/_{I}$ is known as the optical density, (O.D.) and this can be read directly against wavelength on a spectrophotometer. A plot of O.D. against concentration for any one wavelength will have a slope equal to εd from which ε can be estimated. Knowing ε for any wavelength, we can estimate the percentage light transmitted for any concentration or alternatively the concentration for any transmission or optical density.

3.2. Experimental

Measurements of O.D. were made on a Unicam spectrophotometer, (S.P. 500), and cells of 1 cm. thickness were used. The O.D. was measured between wavelengths 3000Å and 6000Å for a range of concentrations of ferric chloride in DMF, from 1×10^{-3} moles litre^{-1} downwards, with DMF as blank.

A set of readings of O.D. for various concentrations was also taken for the wavelength 3650Å for estimation of ε.

The effect of time on the O.D. of solutions was also investigated. Little or no difference was found for solutions of various concentrations on standing in air for up to seven days.

3.3. Results

Figs. (2) and (3) show two sample plots of O.D. against wavelength of light. Fig. (2) is for a concentration of $2{\cdot}02 \times 10^{-5}$ moles litre^{-1} and the value of 0·0625 for O.D. at 3650Å shows that this concentration is quite close to that which would allow 90% transmission for 1 cm. vessels. Fig. (3) is for a considerably higher concentration.

The slope from Fig. (4) gives the value of εd at 3650Å.

$$\varepsilon d \quad = \quad 4{\cdot}96 \times 10^{3} \text{ litre mole}^{-1}$$

Thus $$\varepsilon \quad = \quad \underline{4{\cdot}96 \times 10^{3}} \text{ litre mole}^{-1}\text{cm}^{-1}$$

3.4. Discussion

Most of the polymerizations described in the chapters following have been carried out in cells of 2 cm. diameter. Thus the value of ferric chloride concentration for which transmission is 90% is $\dfrac{OD}{\varepsilon d}$

$$= \frac{0{\cdot}046}{4{\cdot}96 \times 10^{3} \times 2{\cdot}0}$$

$$= 4{\cdot}64 \times 10^{-6} \text{ mole litre}^{-1}$$

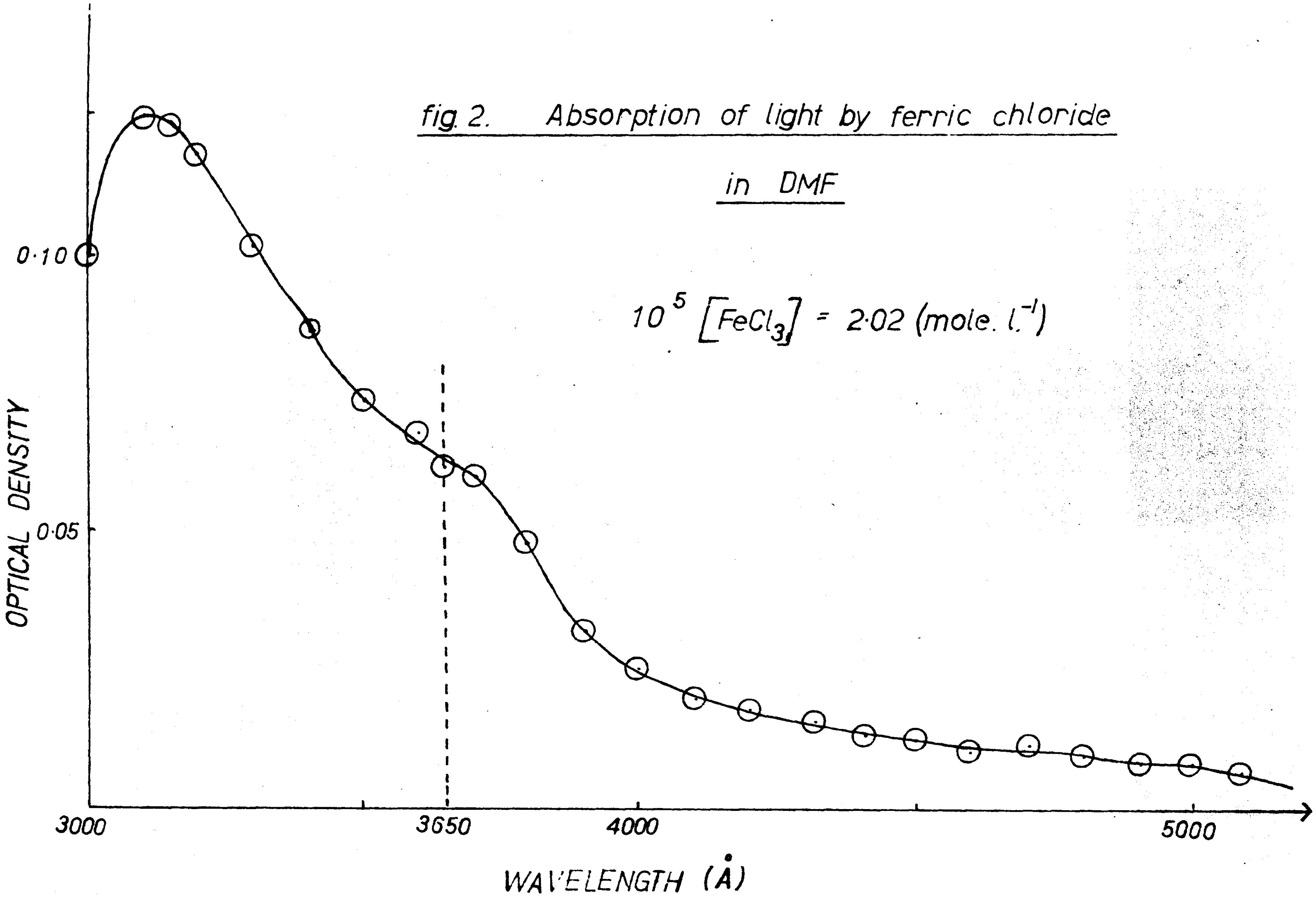


fig. 2. Absorption of light by ferric chloride in DMF

$10^5 [FeCl_3] = 2{\cdot}02$ (mole. $l.^{-1}$)

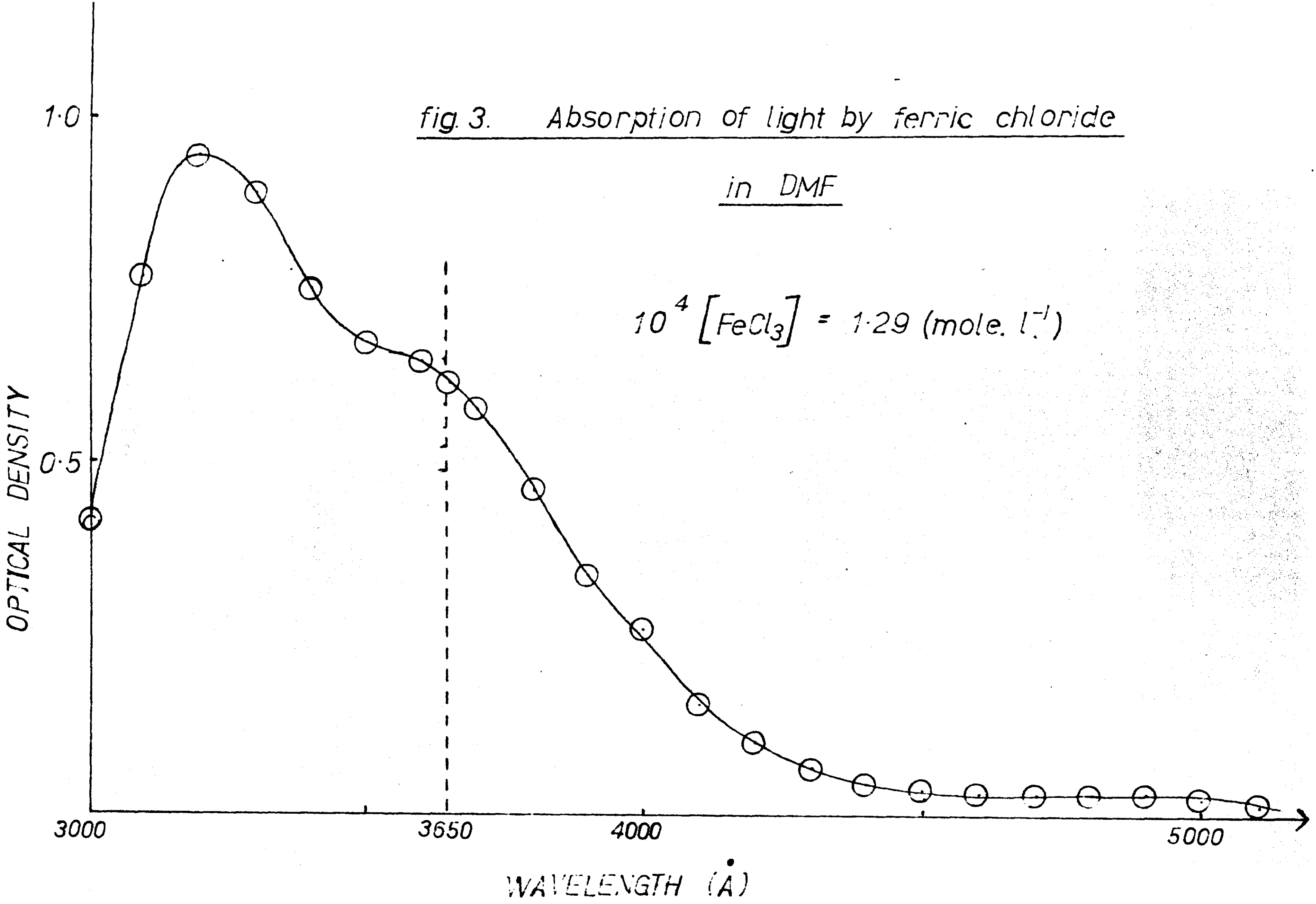


fig. 3. Absorption of light by ferric chloride in DMF

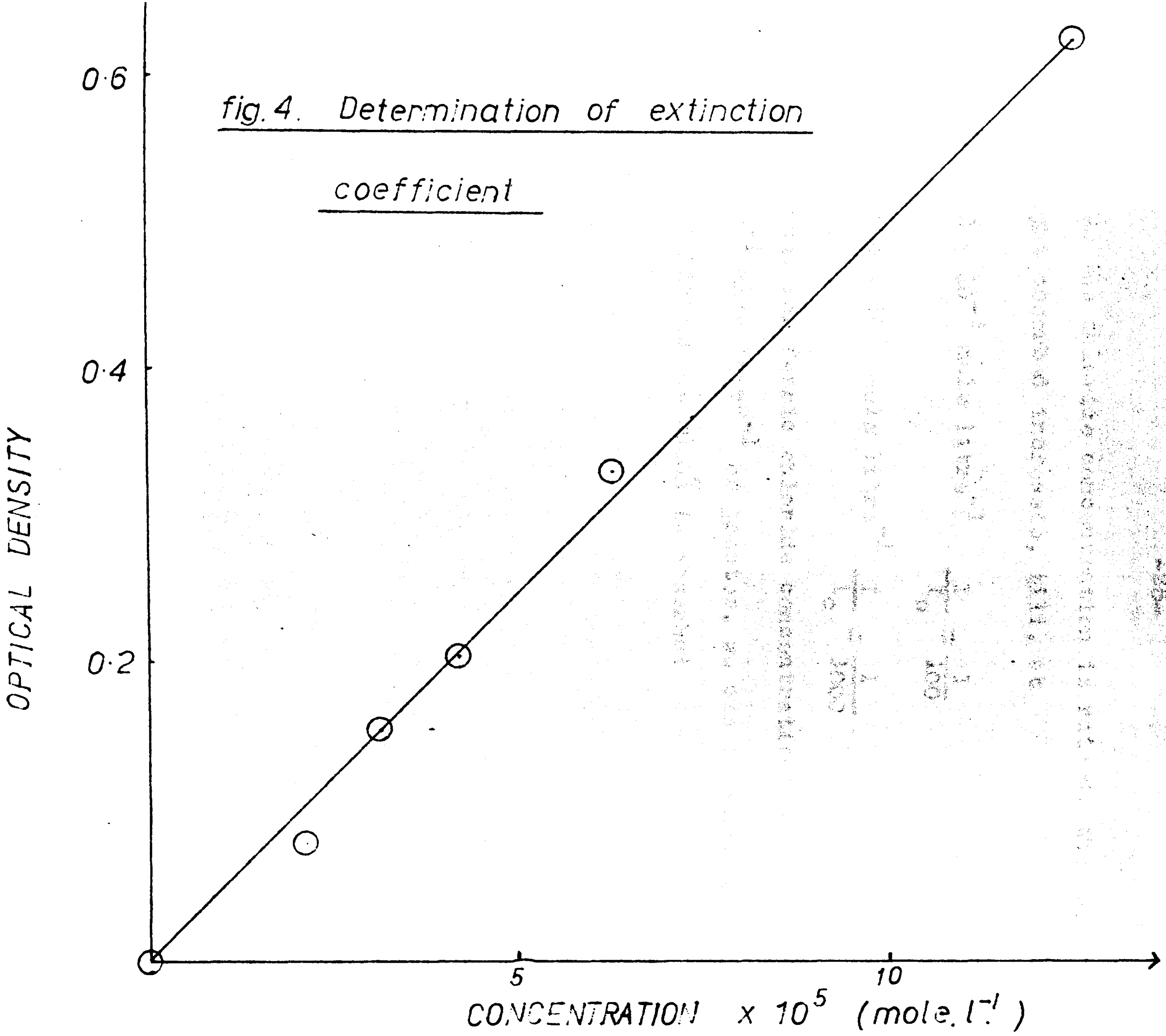


fig. 4. Determination of extinction coefficient

As the chloride concentration is raised, the amount of light absorbed increases, till, at

2×10^{-4} mole litre^{-1} $\frac{I}{I_o} = \frac{1}{100}$

and at 3×10^{-4} mole litre^{-1} $\frac{I}{I_o} = \frac{1}{1000}$

Thus for ferric chloride concentrations of 3×10^{-4} mole litre^{-1} or greater, we can consider that all irradiation at 3650Å is absorbed.

CHAPTER 4.

Estimation of Ferrous Iron in Presence of DMF.

The most obvious method of estimating ferrous iron is titration with a standard oxidising solution using a redox indicator. Bamford et. al. (29, 43) used Ceric Ammonium Sulphate (C.A.S.) with dipyridyl as indicator, but McIntosh (41) found this method unreliable in presence of DMF, and made use of potentiometric titrations. It was decided to carry out a series of experiments on the applicability of titrants Potassium Dichromate (P.D.) and C.A.S. with redox indicators for the estimation of ferrous iron and to compare this with the use of potentiometric titrations for this estimation.

4.1. Materials

4.1.1. Ceric Ammonium Sulphate (C.A.S.)

The B.D.H. Laboratory reagent grade contains anything from 95% to 105% Ceric cerium. The molecular weight is 632·6, so about 6·4 - 6·6 gm. are dissolved in 500 ml. of 2N sulphuric acid, then made up to 1 litre with water. This gives a N/100 solution suitable for measuring the low concentrations of Fe^{++} ion produced during polymerization.

Standardization is against weighed portions of A.R. sodium oxalate.

1 ml. N/100 C.A.S. $\equiv$ 10^{-5} moles ferrous iron.

4.1.2. Potassium Dichromate (P.D.)

The A.R. grade has a purity not less than 99·9%. An exactly N/100 solution can be made up by weighing out 0·4904 gm. of the salt and dissolving in 1 litre of water.

as above,

1 ml. N/100 P.D. $\equiv$ 10^{-5} moles ferrous iron.

4.1.3. Redox Indicator

N - phenyl anthranilic acid indicator solution is made up by weighing 1·07 gm. and dissolving this in 20 ml. of 5% sodium carbonate solution, then making up to 1 litre with water. About 0·5 ml. is used in a titration.

4.2. Results

A standard solution of ferrous sulphate ($FeSo_4 7H_2O$) was made up in water. Portions of this were titrated with standard P.D. solution (N/100) using N - phenyl anthranilic acid indicator. Each titration was diluted with about 15-20 ml. 2N sulphuric acid. Presence of DMF in small amounts was found to have little effect on the titration, yet larger amounts prevented any colour change completely. A series of titrations was carried out with increasing amount of DMF. A plot of volume of titrant against amount of DMF added is shown in Fig. (5). The volume of P.D. required falls linearly, and after the addition of 10 ml. of DMF no colour change is observed. This effect was observed for titrations of P.D. (N/100), from a few ml. to about 20 ml. Thus potassium dichromate could not be used in presence of DMF.

The above experiment was repeated with C.A.S. in place of P.D. Although the same effect was not observed, reproduceability was not entirely satisfactory since, in presence of more than 10-12 ml. DMF, the titrations of C.A.S. were sometimes about 0·5 ml. greater or less than the values expected.

The reproduceability of potentiometric titrations with P.D. and C.A.S. in presence of DMF was next investigated. It was found that results were consistant no matter how much DMF was added, and it appears that the solvent has little or no effect on this type of titration.

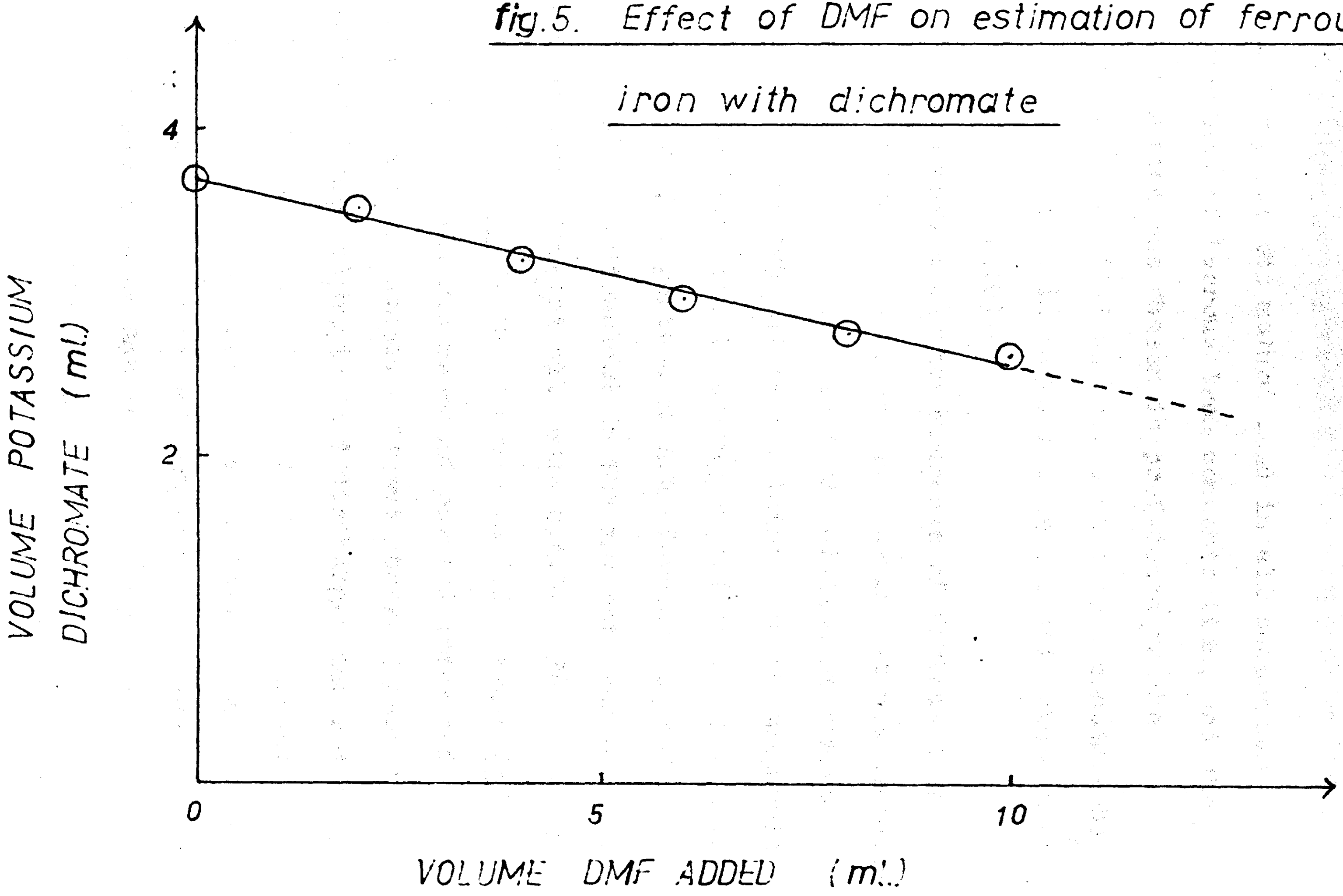
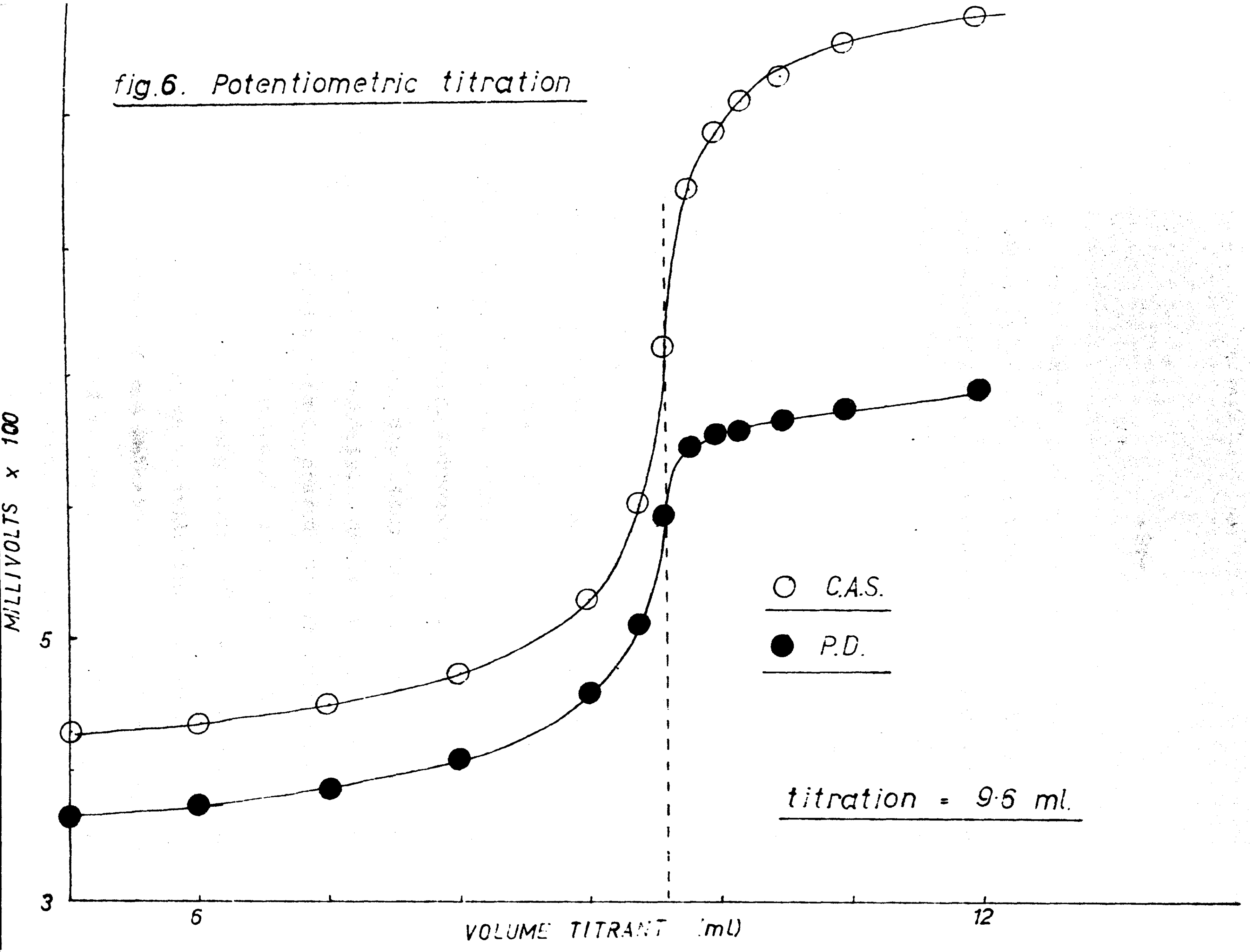


fig.5. Effect of DMF on estimation of ferrous iron with dichromate

This, then, was the method used in all subsequent measurements of ferrous iron concentration, and the ceric solution was chosen in preference to the dichromate since its' use gives rise to a considerably greater difference in potential at the end point as can be seen from Fig. (6).

Before making any measurements of ferrous iron produced during polymerization, however, it was decided to test the method on a standard solution of ferrous iron made up in DMF and then diluted with 2N sulphuric acid to simulate actual working conditions. For this purpose a weighed portion of A.R. ferrous sulphate, ($FeSo_4 7H_2O$), was dissolved in DMF and portions of this titrated potentiometrically with C.A.S. For expected titrations of 10 ml. the results varied between 0•7 ml. and 1•5 ml. This was repeated several times and similar results obtained. It was observed here that addition of the sulphuric acid discharged the red colour of the solution. A solution of $FeSo_4 7H_2O$ in water gave consistant 10 ml. titrations as expected. The sulphate dissolves only slowly in DMF and in view of the apparent disappearance of over 80% of the Fe^{++} ions, it was thought that oxidation by air might be responsible.

fig.6. Potentiometric titration



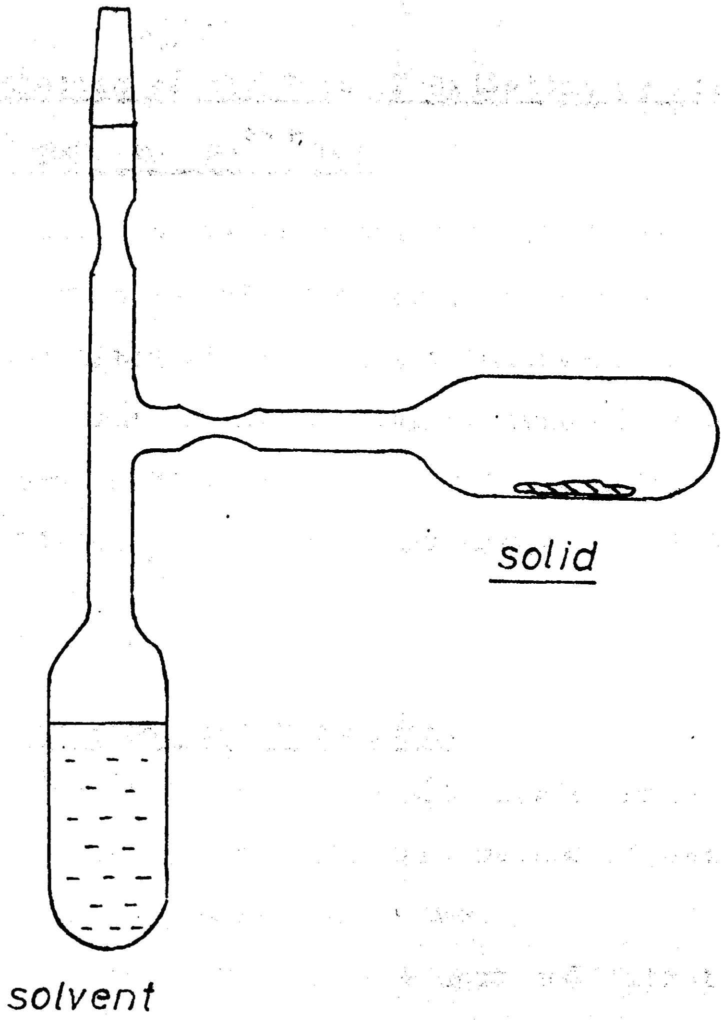


fig 7

the air.

Estimation of the Rate of Oxidation by Air of Fe^{++}/DMF to Fe^{+++}/DMF.

A solution of ferrous chloride ($FeCl_2 4H_2O$) was made up under vacuum in DMF as before, the vessel broken open and samples titrated after noted intervals of time. A plot of volume of C.A.S. against time of standing in air is shown in Fig. (8). The rate of oxidation under these conditions is constant and occurs at 68·8% per hour.

4.3. Conclusions and Discussion

Potentiometric titration with ceric ammonium sulphate is the most satisfactory method of estimation of ferrous iron in presence of DMF.

That addition of sulphuric acid and titration immediately on breaking open of dilatometers will give reliable results, is illustrated by the experiments carried out on ferrous chloride solutions, and is verified by the constant and relatively slow rate of oxidation of ferrous iron in DMF on standing in air.

Ferrous sulphate is a light green salt and the solution made up in colourless DMF is reddish brown.

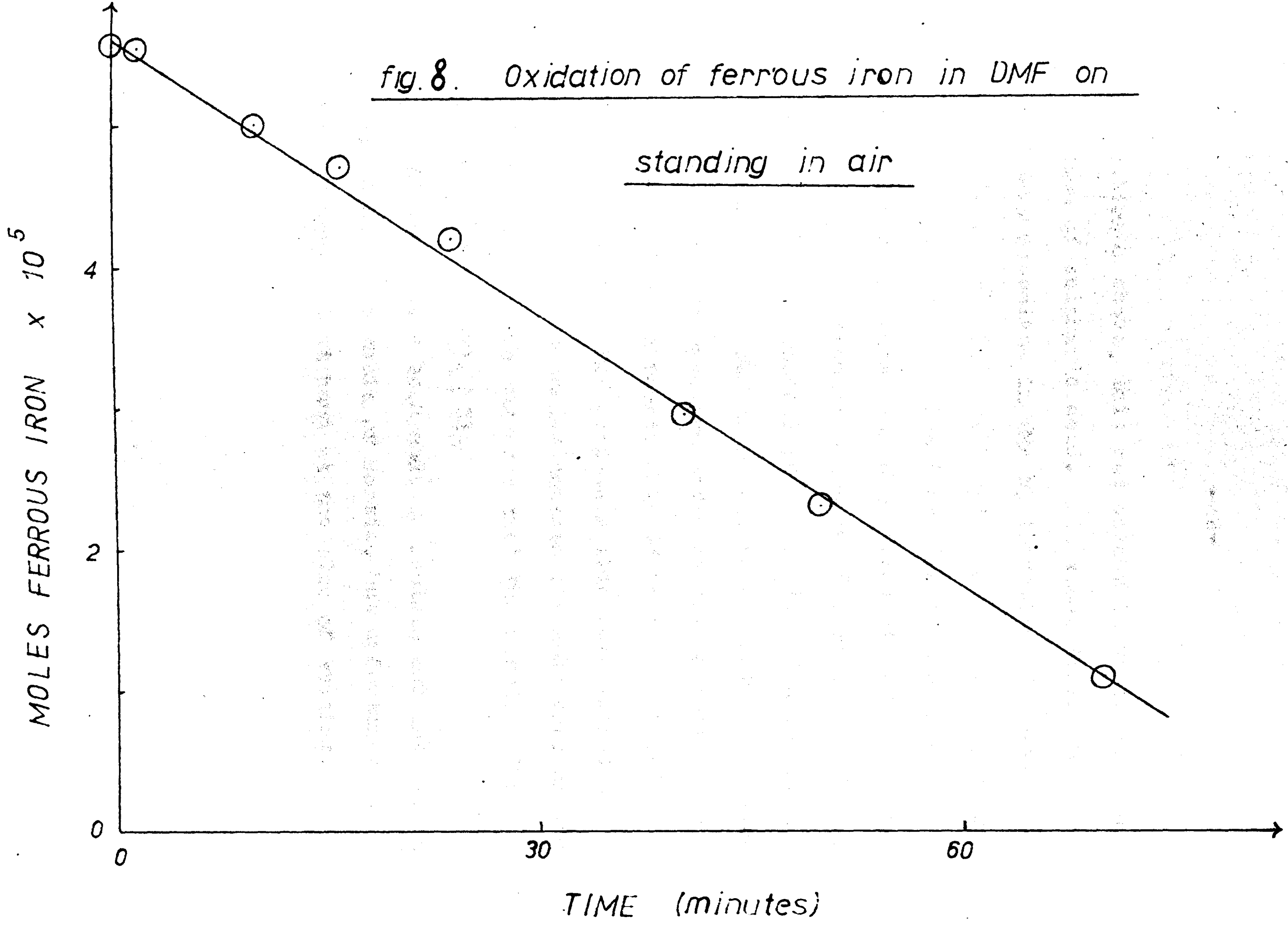


fig. 8. Oxidation of ferrous iron in DMF on standing in air

As mentioned above, this red colour is discharged on addition of sulphuric acid. It seems likely that the salt only dissolves in DMF by formation of a complex which is relatively easily oxidised by air. Bamford et. al. suspected complex formation in the light of optical measurements and the effect of DMF on the rate of AN polymerization in presence of ferric chloride (29) and McIntosh, on removal of DMF by distillation from a ferric chloride - DMF solution, found that the residue had an infra-red spectrum which exhibited peaks corresponding neither to ferric chloride nor to DMF (41). Nortia found that DMF complexes with some transition metals of the iron series contain six molecules of the solvent (42), which suggests that the ferric - DMF complex might be $\left[Fe\ (DMF)_6\right]Cl_3$

Attempts have been made to isolate and analyse the complex by the methods of Nortia, but unfortunately results were not at hand at the time of writing.

CHAPTER 5.

Rate Dependences, Rate of Initiation and Evaluation of Velocity Coefficients for the Polymerization of Acrylonitrile in DMF solution with Ferric Chloride as Photoinitiator.

The complete kinetic scheme for a polymerization reaction is extremely complex and it is normal to make the following simplifying assumptions.

(a) The reactivity of the growing chain is independent of chain length.

The reactive radical intermediates in vinyl polymerizations are all of a similar type, containing varying numbers of the same structural unit. The kinetic treatment must consider radicals of all sizes, and it is generally assumed that the reactivity of any given type of radical is independent of its length.

(b) Monomer is removed in the propagation step only.

The rate of polymerization is generally taken to be equal to the rate of removal of monomer in the propagation step, neglecting any consumption of monomer in initiation or transfer reaction.

(c) A stationary state for radicals is rapidly established.

It is assumed that the concentration of radical intermediates remains constant during the polymerization.

5.1. Kinetic Scheme

Making full use of the assumptions outlined above, the simplest kinetic scheme for a photoinitiated polymerization by free radicals is as follows:-

$$\begin{array}{ll} & \underline{\text{Rate}} \\ \left.\begin{array}{l}\text{Catalyst} \xrightarrow{h\nu} R_c \\ R_c + M \longrightarrow R_1\end{array}\right\} & I_n \\ R_n + M \longrightarrow R_{n+1} & k_p[R][M] \\ R_n + R_m \longrightarrow \text{Polymer} & k_t'[R]^2 \end{array}$$

where R_c is a radical derived from the initiator, R_n is a growing radical with n monomer units, M is a molecule of monomer, and k_p and k_t are velocity coefficients for propagation and termination respectively.

$$\text{For } \frac{d[R]}{dt} = 0 \;, [R]_s = \sqrt{\frac{I_n}{k_t'}}$$

$$\text{and Rate}_p = -\frac{d[M]}{dt} = k_p\sqrt{\frac{I_n}{k_t'}}\,[M]$$

$$\text{Hence if } I_n \propto [\text{Catalyst}]$$

$$\text{Rate}_p \propto [\text{Catalyst}]^{\frac{1}{2}}$$

These relationships will hold where illumination of reaction vessels is uniform.

Applying this mechanism to a system with ferric chloride as catalyst, and for convenience, assuming that the initiation process commences with simple fracture of an Fe - Cl bond, we have:-

Rate

$$\left.\begin{array}{l} FeCl_3 \xrightarrow{h\nu} FeCl_2 + Cl \\ Cl + M \longrightarrow R_1 \end{array}\right\} \qquad I_n \qquad .....(V.1.)$$

$$R_n + M \longrightarrow R_{n+1} \qquad k_p[R][M] \qquad .....(V.2.)$$

$$R_n + R_m \longrightarrow \text{Polymer} \qquad k_t'[R]^2 \qquad .....(V.3.)$$

$$R_m + FeCl_3 \longrightarrow \text{Polymer} + FeCl_2 \qquad k_t[R][FeCl_3]...(V.4.)$$

where (V.4.) is an additional termination step allowing for the ability of ferric chloride to react with free radicals. Thus termination will involve either or both of reactions (V.3.) or (V.4.)

From absorption measurements, (Chapter 3.) it was found that only for concentrations of ferric chloride in DMF of 5 x 10^{-6} moles litre^{-1} or less would irradiation be uniform for a path length, (or dilatometer diameter), of 2 cm. Unfortunately, using concentrations of this order does not allow polymerizations to be followed for very long before the catalyst is used up. Apart from this, it is extremely difficult to reproduce such low concentrations with any great accuracy since successive dilutions are required. Thus to obtain reproducible rate measurements over reasonable periods of time, higher catalyst concentrations must be used.

We would expect the relationship Rate $\propto [FeCl_3]^{\frac{1}{2}}$ to hold for $FeCl_3 \leqslant 5 \times 10^{-6}$ mole $litre^{-1}$ where not only will illumination be uniform, but where termination by (V.4.) will almost certainly be negligible.

As the chloride concentration is increased however, the value of I as governed by the equation

$$I = I_0 \, 10^{-\varepsilon cd} \qquad \text{.....(III.1.)}$$

will begin to fall, illumination can no longer be considered uniform, and a point will soon be reached where I is negligible compared to I_0. (In Chapter 3, we saw that this point was found to correspond to a ferric chloride concentration of about 3×10^{-4} mole $litre^{-1}$ for d = 2 cm.)

For all concentrations beyond the point where I is negligible compared to I_0 we can consider that all the irradiated light is absorbed.

Let the actual intensity of light absorbed = I'.

I' will be proportional to $\int_0^d I\,dx$

Using the form of Beer's law,

$$I = I_o e^{-2\cdot3\,\varepsilon cd}$$

we have $I' \propto I_o \int_0^d e^{-2\cdot3\,\varepsilon cd}\,dx$

For any concentration C,

$$I' \propto - \frac{I_o}{\varepsilon c} \left[e^{-2\cdot3\,\varepsilon cd} \right]_o^d$$

$$\propto \frac{I_o}{\varepsilon c} \left[1 - e^{-2\cdot3\,\varepsilon cd} \right]$$

$\varepsilon = 5\cdot0 \times 10^3$ and $d = 2\cdot0$ Thus $e^{-2\cdot3\,\varepsilon cd}$ is negligible compared to unity for $c \geqslant 3 \times 10^{-4}$.

The rate of initiation, I_n, is proportional to I' and to catalyst concentration C.

i.e. $I_n \propto I' c$

$\therefore$ $I_n \propto \frac{I_o}{\varepsilon}$ where all light is absorbed

Thus $I_n = k_i I_o$ ....(V.5.)

where k_i is a constant.

Thus for ferric chloride concentrations greater than 3×10^{-4} mole litre^{-1}, I_n should be independent of catalyst concentration and should depend only on the intensity of the incident light.

Coupled with this, termination by (V.4.) will become increasingly important till a point is reached, as the chloride concentration is increased, where termination by (V.3.) is negligible compared with (V.4.)

Assuming a stationary state for radicals in this region, we have:-

$$I_n = k_t [R_s][FeCl_3]$$

$$R_s = \frac{I_n}{k_t [FeCl_3]}$$

$$\text{Rate} = \frac{k_p I_n [M]}{k_t [FeCl_3]} \qquad \text{....(V.6.)}$$

$$= \frac{k_p k_i I_o [M]}{k_t [FeCl_3]} \qquad \text{....(V.7.)}$$

and, since initiation will produce ferrous chloride at the same rate as termination,

$$I_n = \frac{1}{2} \frac{d [FeCl_2]}{dt} \qquad \text{....(V.8.)}$$

Furthermore, the kinetic chain lifetime $\tau = \frac{[R_s]}{I_n}$

$$\tau = \frac{1}{k_t [FeCl_3]}$$

$$\text{or } [FeCl_3] = \frac{1}{\tau k_t}$$

Substituting in (V.6.) for $\left[FeCl_3\right]$

$$\text{Rate} = k_p I_n [M] \tau$$

$$\therefore \frac{1}{I_n \tau} \times \frac{\text{Rate}}{[M]} = k_p$$

$$\text{or} \quad \frac{\text{Fractional Rate}}{I_n \tau} = k_p \qquad \text{....(V.9.)}$$

From the above discussion of the various regions of ferric chloride concentration, it can be seen that a plot of log Rate against log $\left[FeCl_3\right]$ should have a slope of 0•5 at very low concentrations where irradiation is uniform, and a slope of -1 for high concentrations where all irradiation is absorbed, and termination is all first order with respect to $[R]$. It is difficult to predict what might happen in the intermediate region where fractions of light absorbed will vary from 10% to 100% though some sort of gradual changeover would not be unexpected.

5.2. Preliminary Investigation; Rate Dependence on Ferric Chloride Concentration

A series of dilatometric measurements of rate of polymerization was carried out at 20°C with reaction mixtures containing varying amounts of ferric chloride.

The monomer concentration was held constant at 3·02 mole litre^{-1}, (20% by volume), small cells were used, (about 5 ml. capacity), and the ultra-violet irradiation was unfiltered.

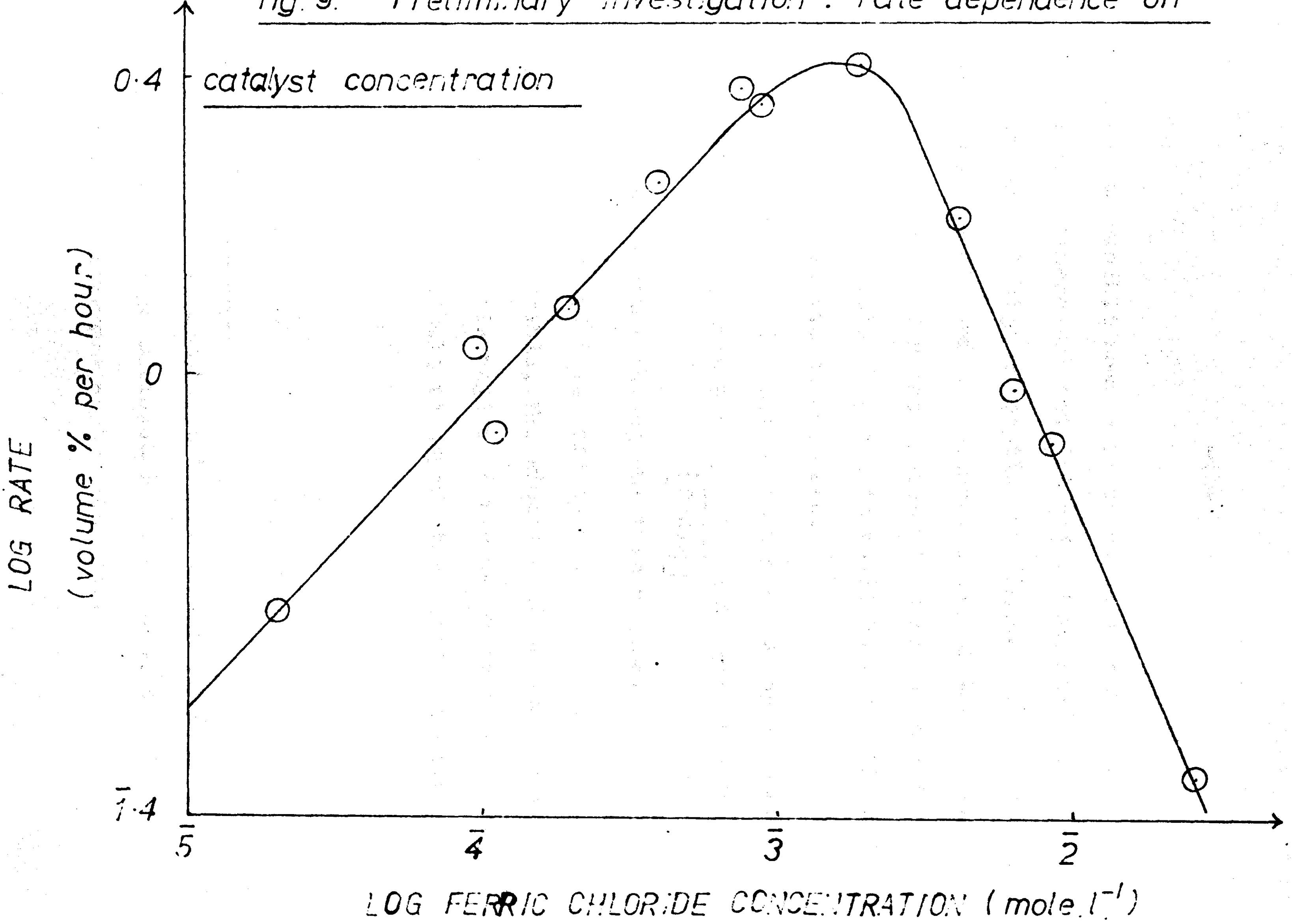
5.2.1. Results

The results of this preliminary series are shown in Fig. (9). This is a plot of log Rate against log $[FeCl_3]$ and shows nothing very definite below a concentration of 1×10^{-3} mole litre^{-1}. It was found almost impossible to reproduce rates below a concentration of 1×10^{-5} mole litre^{-1}, probably because of the successive dilutions required. The region of concentration where irradiation is not uniform but where some light is transmitted, (in this system between 1×10^{-5} and about 6×10^{-4} mole litre^{-1}) shows a scatter of points through which a line of slope 0·42 has been drawn.

Above 2×10^{-3} mole litre^{-1}, the plot slopes downwards with a gradient of -0·97 or very nearly unity.

5.2.2. Discussion

The region of ferric chloride concentration between 10^{-5} mole litre^{-1} and 10^{-3} mole litre^{-1} might be fig. 9. Preliminary investigation : rate dependence on catalyst concentration



expected to exhibit some sort of curve to mark the transition between 2nd and 1st order termination, and between low and high absorption of light. Such a curve might well exist, and a prolonged study of the region with many repeats for each point might serve to detect a non-linear relationship but it would be very difficult to ascribe a kinetic scheme here.

The slope of -1 obtained at higher chloride concentrations verifies that Rate $\propto \frac{1}{[FeCl_3]}$ and indicates that I_n remained constant throughout this region.

The purpose of this work is now to study, as completely as possible, the kinetics of polymerization of AN in DMF in this region of ferric chloride concentration where the salt is apparently initiating and terminating the reaction.

5.3. Experimental

5.3.1. Apparatus

For rate measurements, this was as described in Chapter 2. For potentiometric titrations, a Pt^{+} $Calomel^{-}$ electrode system was used.

5.3.2. Rate Dependences

A series of polymerizations was carried out at 25°C, (i) using reaction mixtures containing varying quantities of ferric chloride, the AN-DMF proportion being held constant at 20% - 80% such that $[M] = 3{\cdot}02$ mole litre^{-1}. (ii) using reaction mixtures containing varying proportions of AN-DMF and with constant ferric chloride concentration, $[FeCl_3] = 2 \times 10^{-3}$ mole litre^{-1}.

5.3.3. Rate of Initiation

Quantities of ferrous iron produced during polymerizations were estimated by potentiometric titration using C.A.S. as oxidant. For the Ce^{3+} - Ce^{4+} system in contact with a platinum electrode, $E_0 = 1{\cdot}61$ volts, while the corresponding value for the Fe^{2+}- Fe^{3+} system is 0•77 volts (44). Consequently end points are marked with an easily detectable rise in potential. (see Fig. (6), Chapter 4.)

From the above, rate dependences on ferric chloride and monomer were obtained and the rate of initiation was estimated.

5.3.4. Factors used in Calculations

Bore of Veridia tubing = 1·0 mm.

Volume of tubing/cm.length = $7{\cdot}85 \times 10^{-3}$ ml.

Density of AN = $0{\cdot}8004$ gm.ml^{-1} (45)

Density of poly-AN = $1{\cdot}19$ gm.ml^{-1} (13)

Thus for conversion of AN to poly-AN,

1% volume decrease $\equiv$ 3·05% polymerization

$$\text{Rate (mole litre}^{-1}\text{sec}^{-1}\text{)} = \text{Rate(volume \% hour}^{-1}\text{)} \times (2{\cdot}559 \times 10^{-5})$$

The use of density differences to correlate volume change with rate of polymerization is generally considered to be an approximation, but experiments involving precipitation of polymer were carried out which showed that their use for the polymerization of AN in 20% AN - 80% DMF mixtures is justified. This is in agreement with work by Bevington and Eaves (46).

5.4. Results

5.4.1. Rate Dependence on Catalyst Concentration

Fig. (10) shows the plot of log Rate against log ferric chloride concentration. The gradient is - 1·03.

5.4.2. Rate Dependence on Monomer Concentration

Fig. (11) shows that the rate of polymerization is directly proportional to monomer concentration.

5.4.3. Rate of Initiation

Fig. (12) shows that the rate of production of ferrous chloride is constant. The points represent concentrations of ferric chloride ranging from 2 x 10^{-3} mole litre^{-1} up to 1·6 x 10^{-2} mole litre^{-1}. From the slope,

$$I_n = \frac{1}{2}\frac{d\left[FeCl_2\right]}{d_t} = \frac{1\cdot64 \times 10^{-7}}{\text{mole litre}^{-1}\text{sec}^{-1}}$$

5.5. Evaluation of Ratio k_p/k_t.

It would appear from the results above that the equation

$$\text{Rate} = \frac{k_p}{k_t} \times \frac{I_n\left[M\right]}{\left[FeCl_3\right]} \qquad ....(V.6.)$$

where I_n is a constant, holds for $\left[FeCl_3\right]$ above 2 x 10^{-3} moles litre^{-1}. The constancy of I_n, while $\left[FeCl_3\right]$ is changed, is shown by the observation that Rate = $\frac{k}{\left[FeCl_3\right]}$ and is verified by the observation that the rate of production of ferrous iron is independent of $\left[FeCl_3\right]$

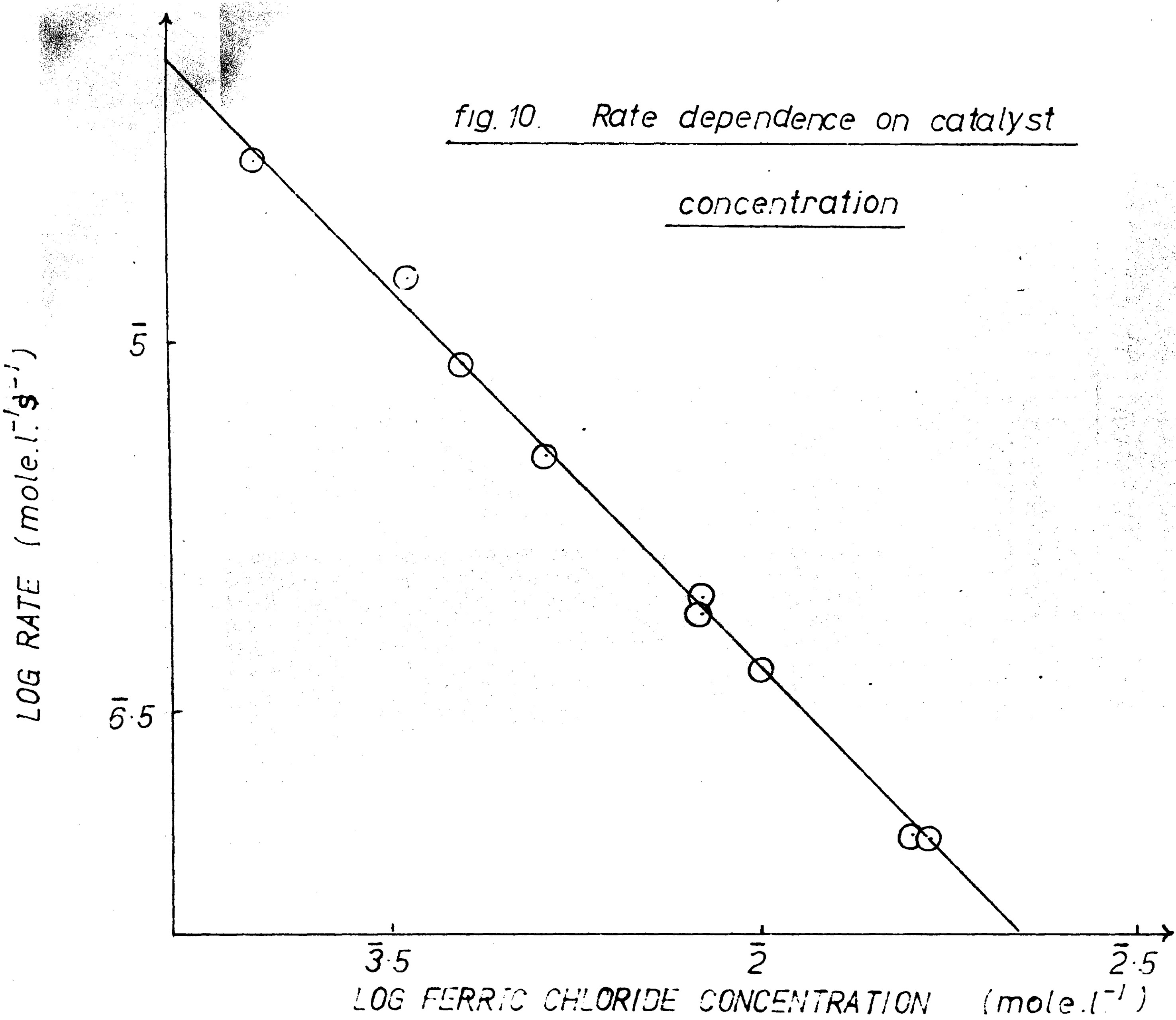


fig. 10. Rate dependence on catalyst concentration

fig. 11. Rate dependence on monomer concentration

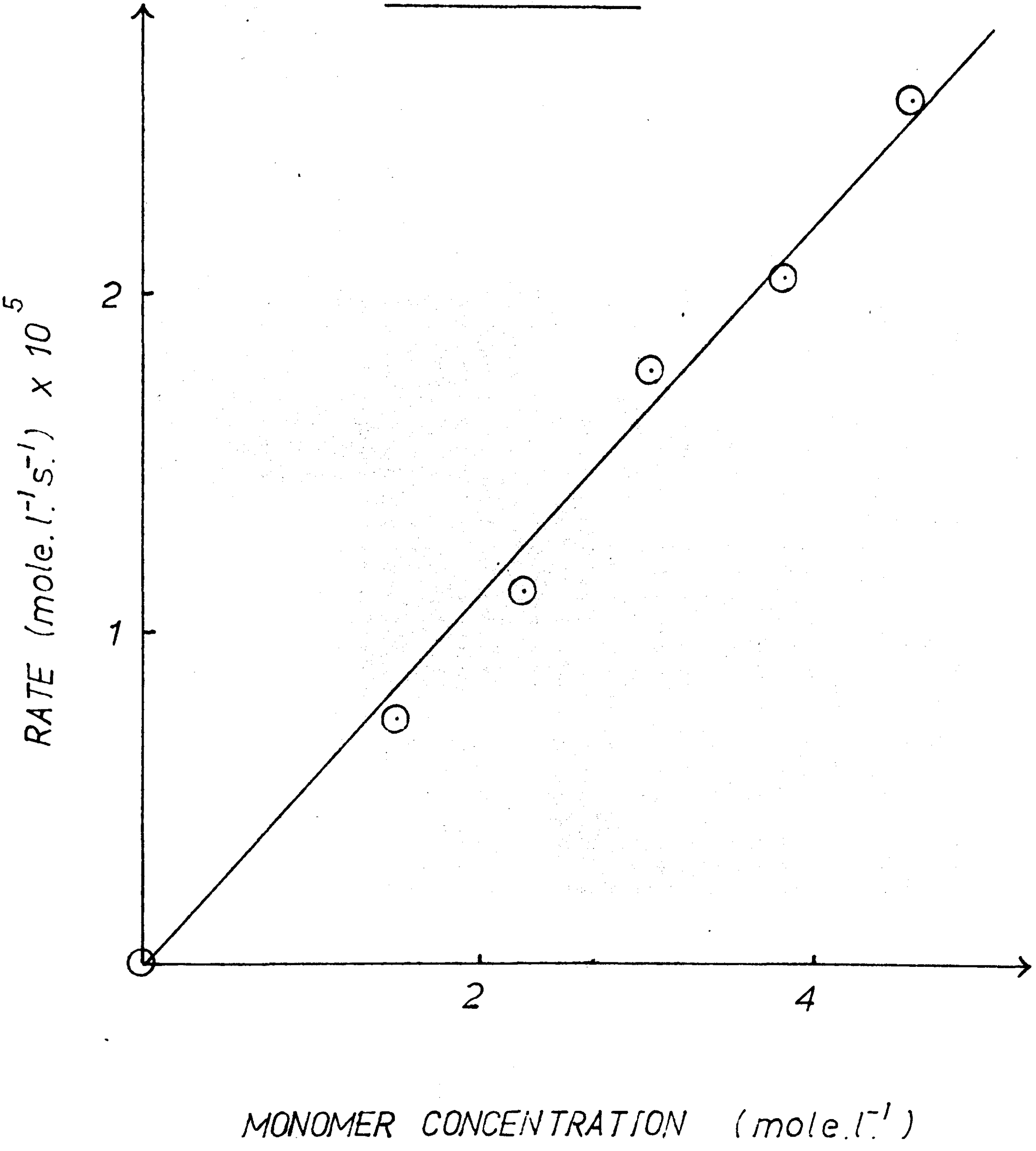


fig. 12. Ferrous iron produced during polymerization

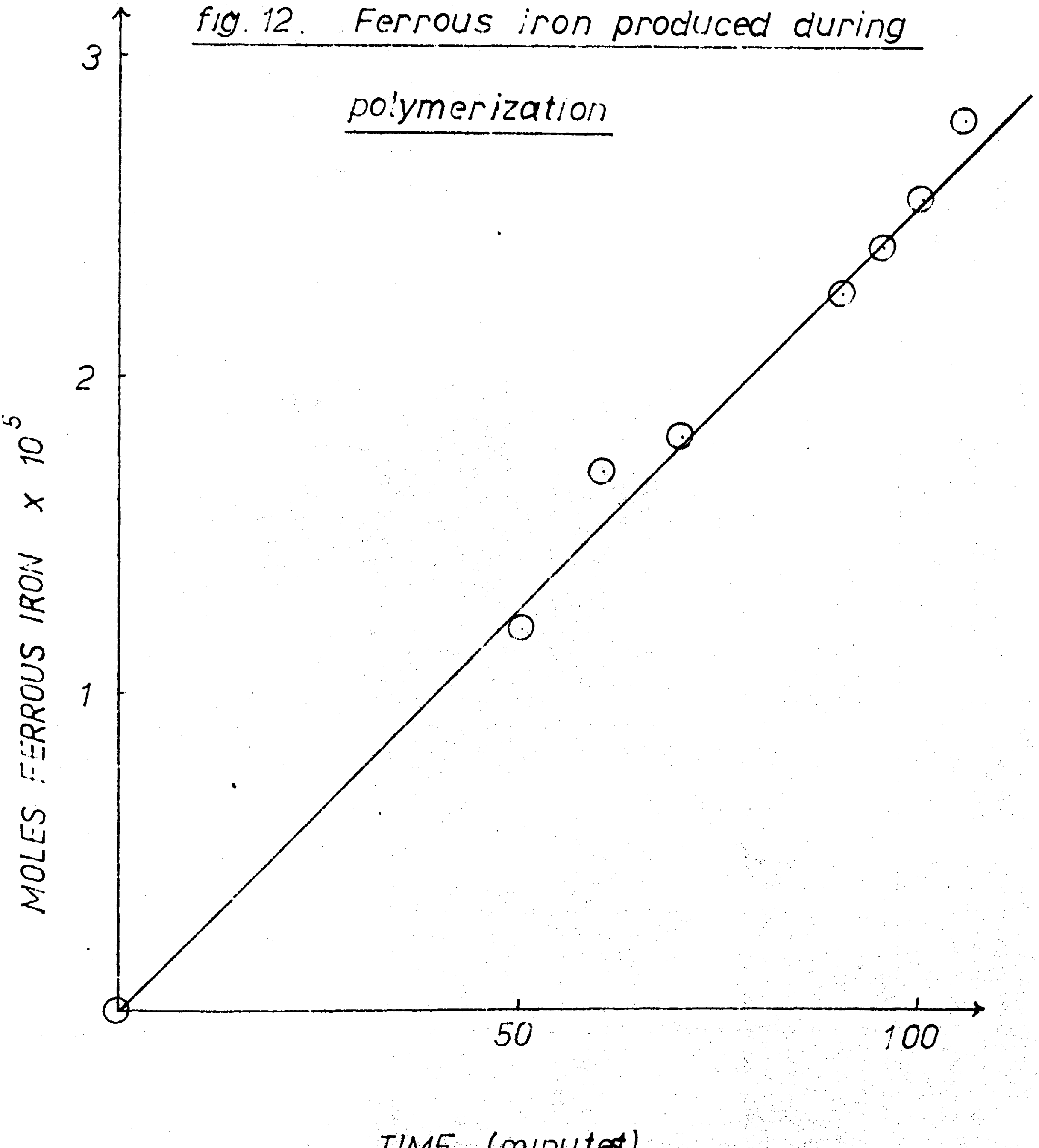
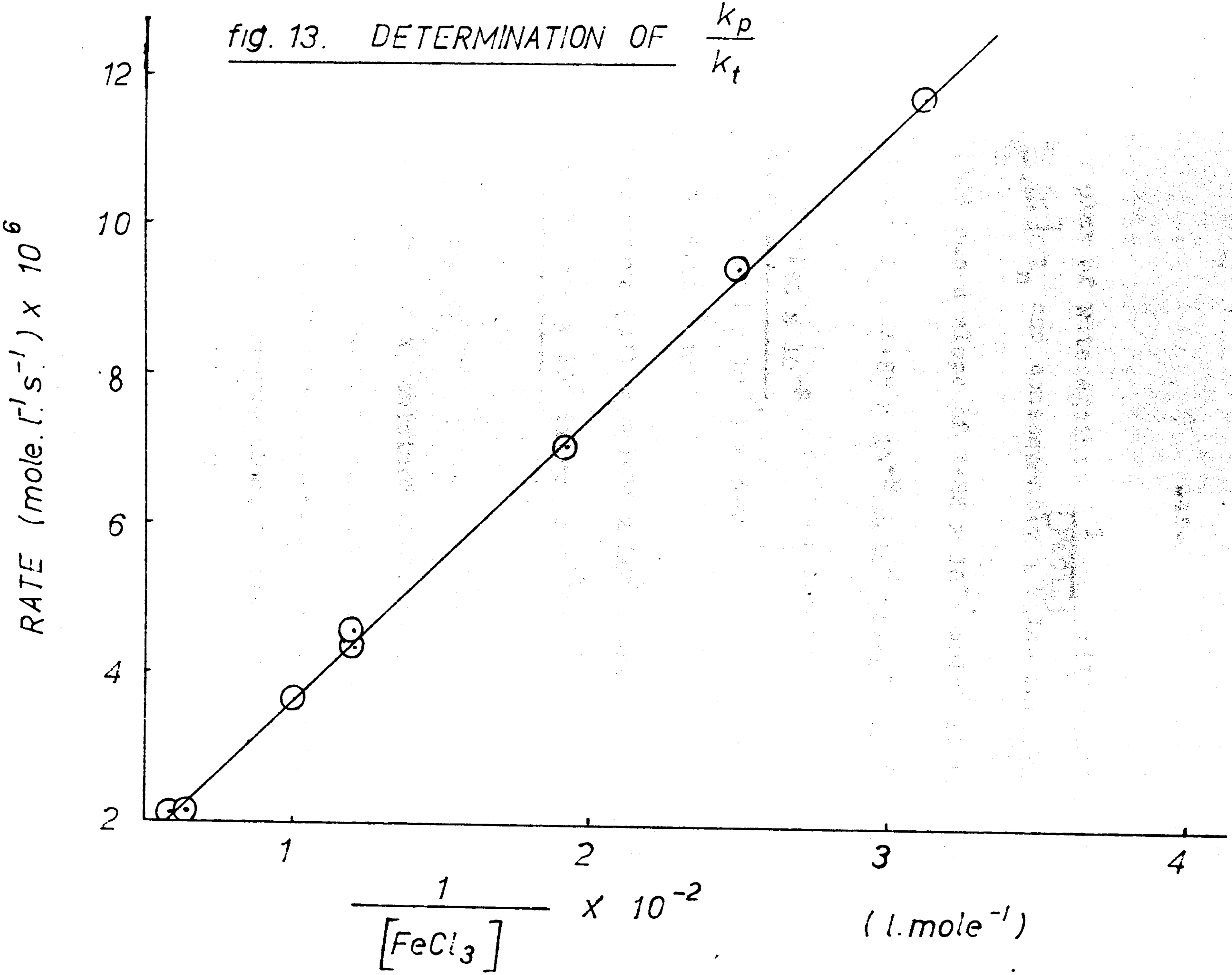


fig. 13. DETERMINATION OF $\frac{k_p}{k_t}$



Thus a plot of Rate against $\frac{1}{[FeCl_3]}$ will yield a slope of $\frac{k_p}{k_t}[M]. I_n$ and consequently a value for $\frac{k_p}{k_t}$

Fig. (13) has a slope of $3{\cdot}85 \times 10^{-8}$ mole^2 litre^{-2}sec^{-1}

$$\therefore \frac{k_p}{k_t}[M]\ I_n = 3{\cdot}85 \times 10^{-8} \text{ mole}^2 \text{ litre}^{-2} \text{sec}^{-1}$$

$$\therefore \frac{k_p}{k_t} = \frac{3{\cdot}85 \times 10^{-8}}{(1{\cdot}64 \times 10^{-7}) \times 3{\cdot}02}$$

$$= 7{\cdot}77 \times 10^{-2}$$

From literature (41) $k_p = 3{\cdot}39 \times 10^3$ litre mole^{-1}sec^{-1}

$$\therefore \underline{k_t = 4{\cdot}36 \times 10^4} \text{ litre mole}^{-1}\text{sec}^{-1}$$

5.6. Discussion

The value of k_t obtained above is small compared to that for systems where termination is between two radicals. This is expected, since, for this system, termination, like propagation, is brought about by interaction of a radical and a molecule. Thus k_p and k_t are of approximately the same order.

Equation (V.9.) gives an expression relating the kinetic chain lifetime, τ, and k_p such that k_p could be determined independently if a method of measuring τ

could be found. (A plot of Rate against τ would have $I_n\ k_p$ as gradient). Now, the value of τ at $[FeCl_3] = 10^{-3}$ mole litre^{-1} is $\frac{1}{40}$ second, $\left(\frac{1}{k_t[FeCl_3]}\right)$ and of course as $[FeCl_3]$ is raised, τ becomes even smaller. Thus τ could not be measured by the usual non-stationary state techniques, and, since termination is first order, the sector method could not be used. Thus it appears that the ratio k_p/k_t can only be separated into k_p and k_t by taking a literature value of k_p as above.

The value of k_p/k_t obtained in this work is low compared to the value of 0·33 obtained by Bamford et. al. (29). There is, in fact, a fourfold difference, but two factors should be considered at this point:- (a) Bamford's constant was obtained from work at 60°C while ours was from work at 25°C. Consequently, if our system has a positive activation energy, then our value of k_p/k_t will be higher at 60°C.

(b) In evaluating k_p/k_t above, the value of I_n used is that obtained by halving the total rate of production of ferrous iron. This presumes an initiator efficiency of 100%. It may well, of course, be lower which would mean the true value of k_p/k_t would be higher.

A fuller discussion of these points, on receipt of further results, is given in Chapter 12.

CHAPTER 6.

An Examination of Reaction Characteristics at Later Stages

6.1. Acceleration in Rate of Polymerization as Reaction Proceeds

In all references to "Rate of Reaction" in Chapter 5, the rate indicated is that of consumption of monomer in the initial stages of reaction, i.e. at less than 1% conversion of monomer to polymer. If however the reaction is allowed to continue, a gradual acceleration is observed. A series of experiments has been carried out to study this effect.

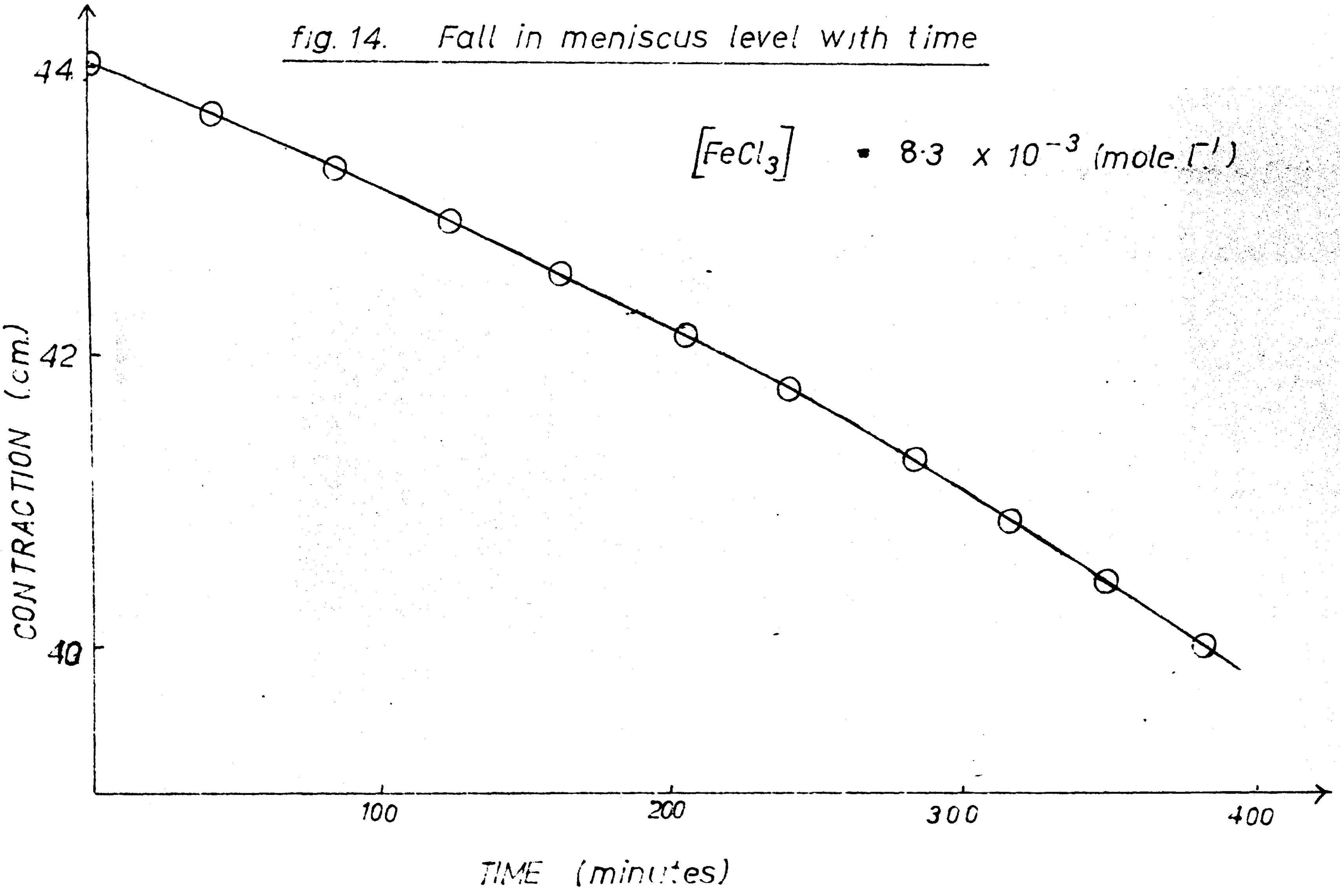
6.1.1. Results

Examples are shown in Figs. (14) to (18). These are for initial ferric chloride concentrations of $8{\cdot}3 \times 10^{-3}$, $5{\cdot}2 \times 10^{-3}$, 2×10^{-3}, $1{\cdot}4 \times 10^{-3}$ and 5×10^{-4} mole litre^{-1} with monomer concentration at 3·02 mole litre^{-1}. The latter three runs have been taken to completion, and, following the acceleration, a marked decrease in rate is observed.

6.1.2. Discussion

The acceleration in rate can be explained quite simply.

fig. 14. Fall in meniscus level with time



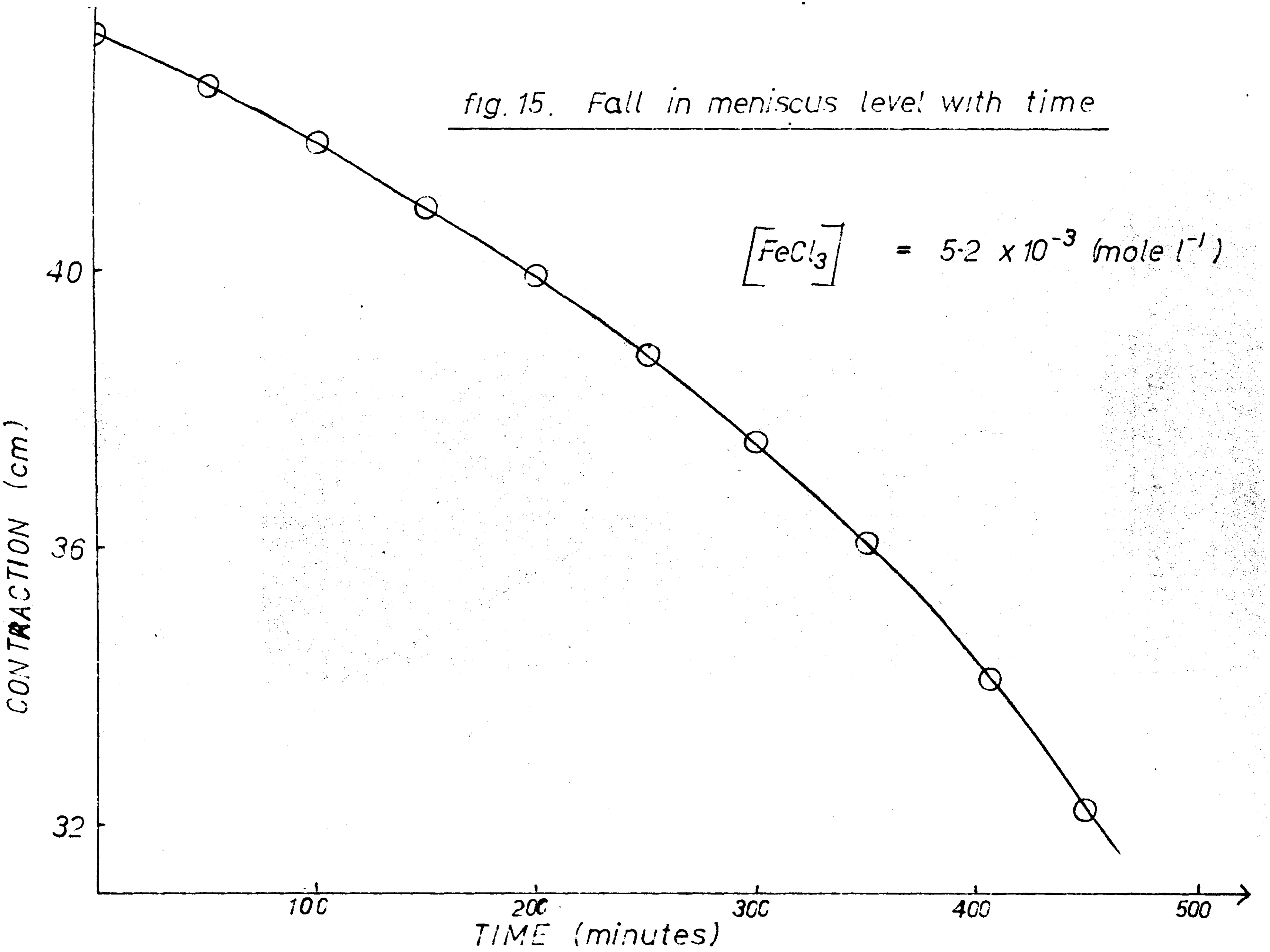
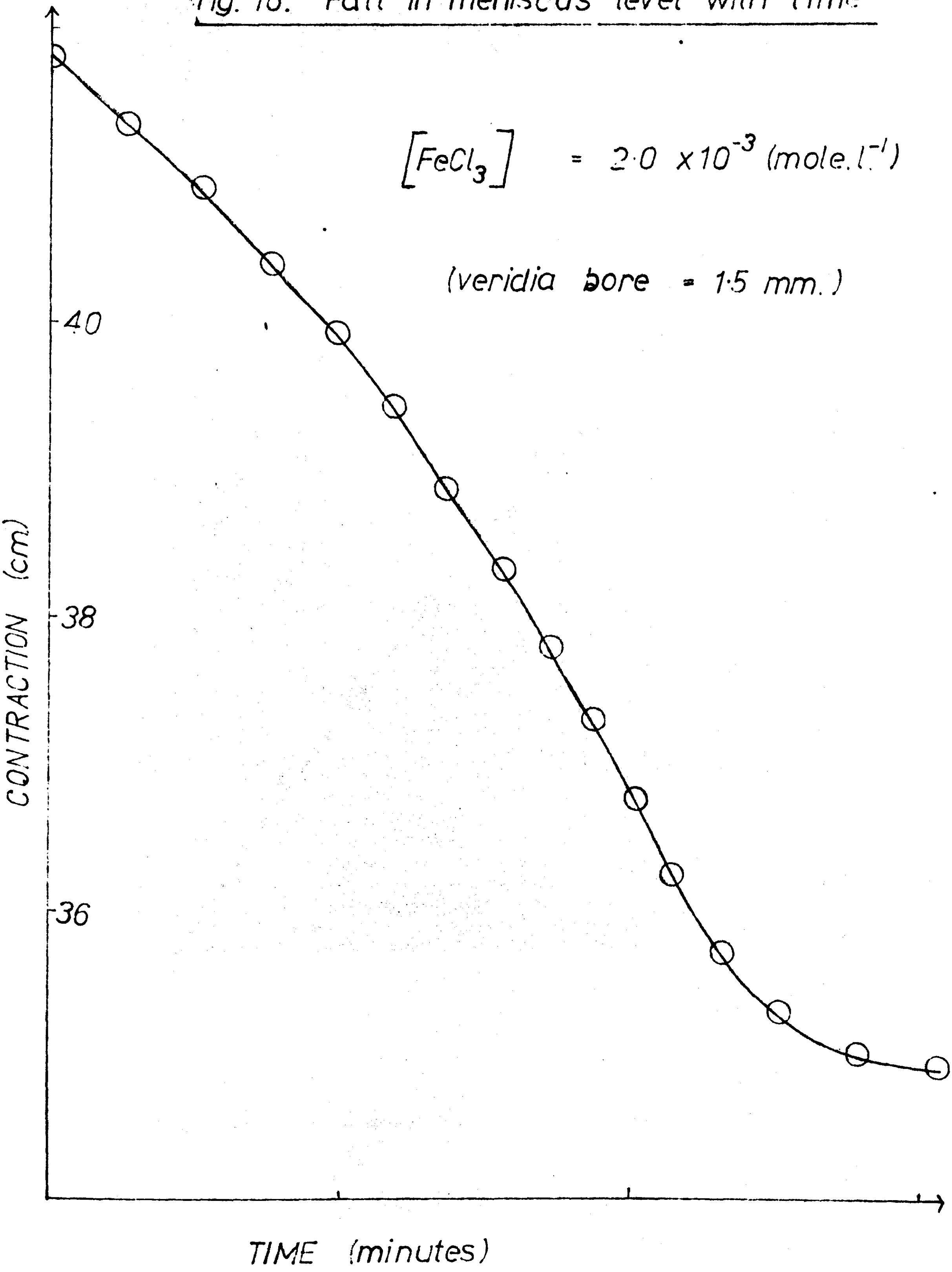


fig. 15. Fall in meniscus level with time

$[FeCl_3] = 5{\cdot}2 \times 10^{-3}$ (mole l^{-1})

fig. 16. Fall in meniscus level with time



$[FeCl_3] = 2{\cdot}0 \times 10^{-3}$ (mole.l^{-1})

(veridia bore = 1·5 mm.)

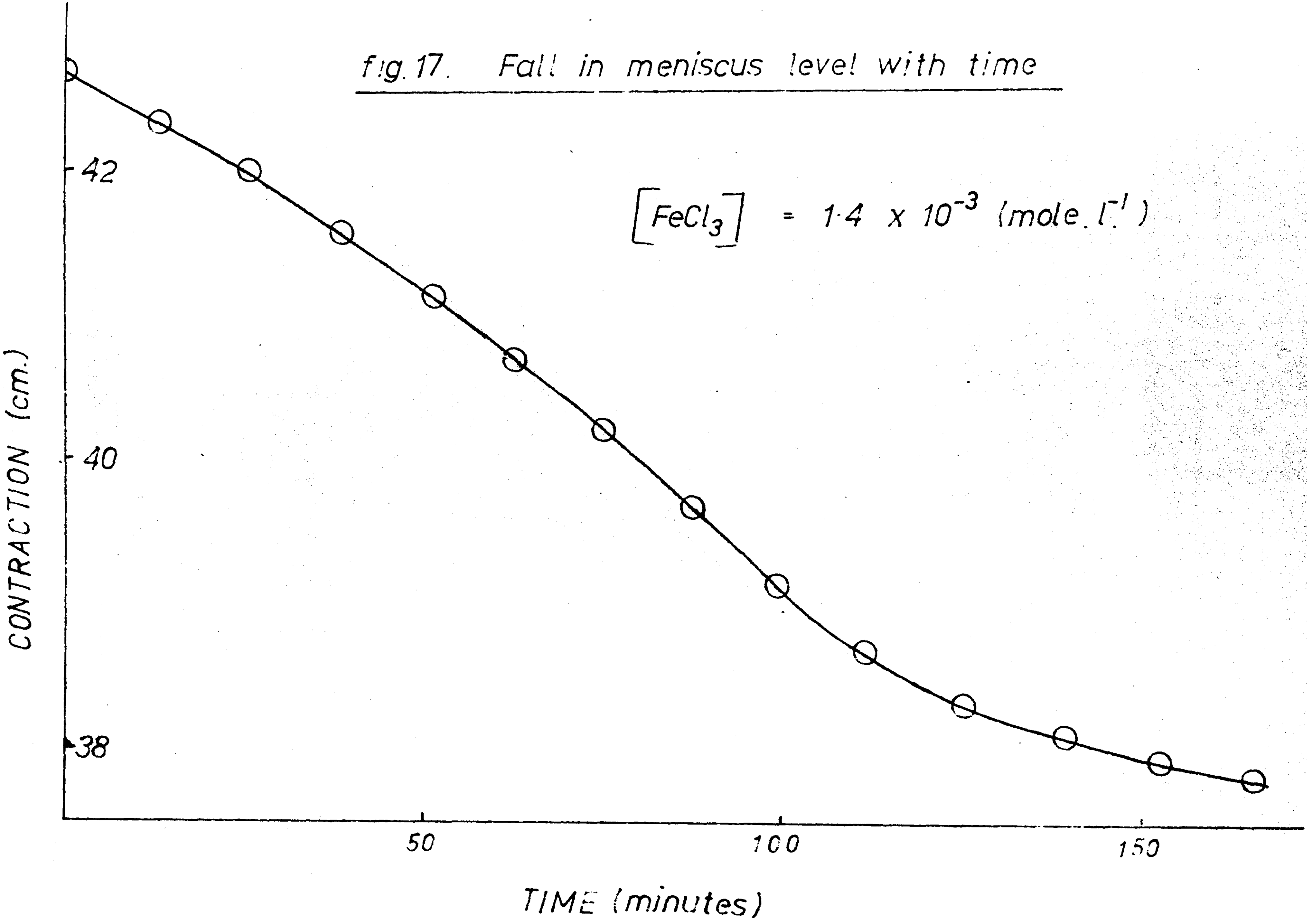
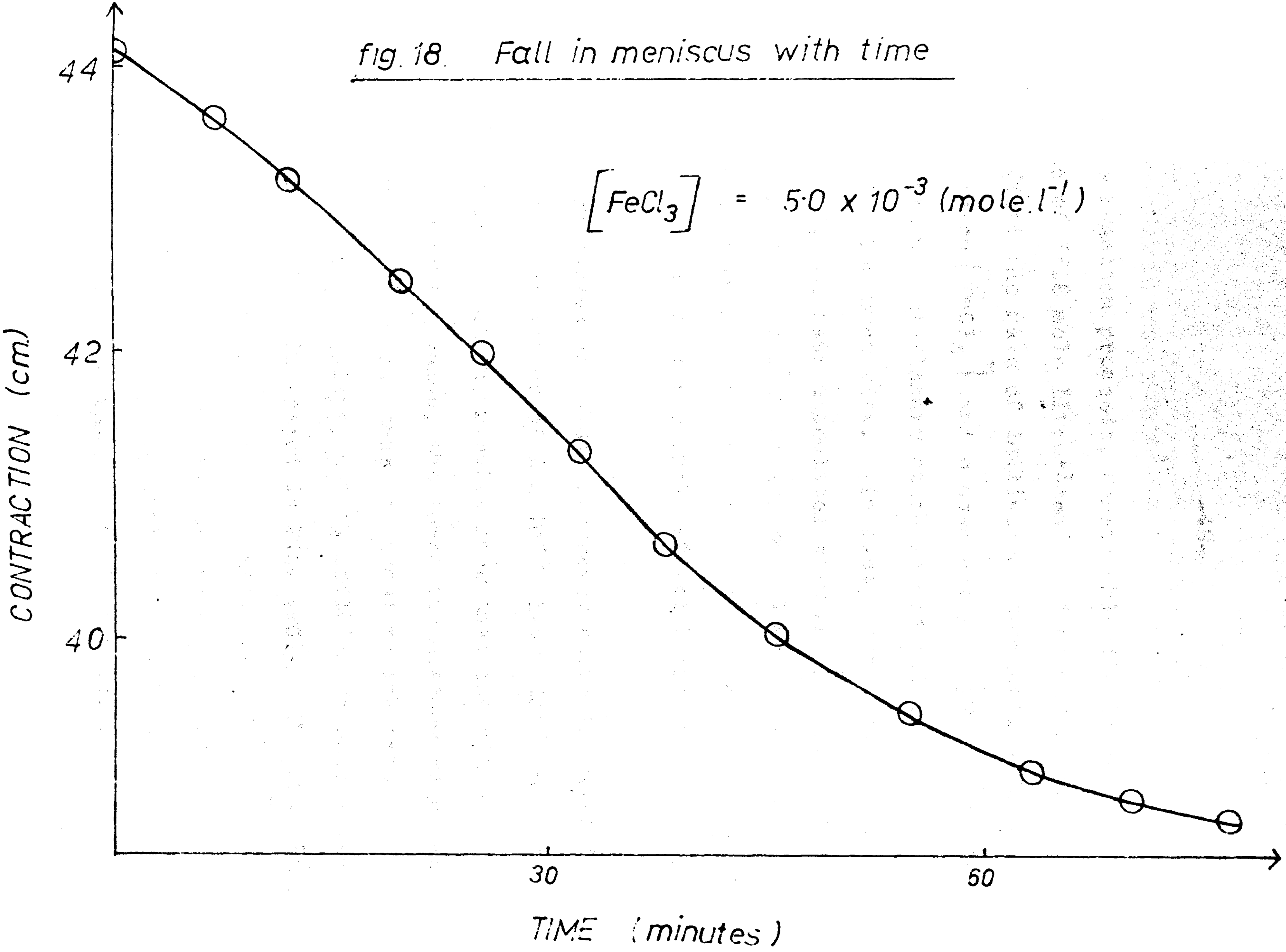


fig.17. Fall in meniscus level with time

$[FeCl_3] = 1 \cdot 4 \times 10^{-3}$ (mole. l^{-1})

fig. 18. Fall in meniscus with time


$[FeCl_3] = 5{\cdot}0 \times 10^{-3}$ (mole.l^{-1})

As the reaction proceeds, ferric chloride is used up at a rate of 3·28 mole litre^{-1}sec^{-1} and although this will not affect the rate of initiation, termination depends directly on $[FeCl_3]$ and consequently as $[FeCl_3]$ falls, to maintain a stationary state in radicals, the radical concentration must rise. In fact, from Fig. (9) in Chapter 5, the rate associated with any $[FeCl_3]$ value on the slope of -1 should follow this line as the reaction proceeds, then fall as the region of second order termination is reached, the overall effect being an S - shaped curve.

Such curves are shown for reactions with initial ferric concentrations of 2×10^{-3}, $1{\cdot}4 \times 10^{-3}$ and 5×10^{-4} mole litre^{-1}, but the results show that the higher the initial $[FeCl_3]$ value, the lower the maximum rate value reached. This means that the accelerating rate does not follow the -1 slope, but is modified to some extent. This effect is illustrated in Fig. (20). The full line shows a continuation of the log Rate against log $[FeCl_3]$ plot in Fig. (10). The dotted lines join points suggested from the data in table (VI.1.) Fig. (19). The ferric concentrations for maximum rates for runs at 8·3, 5·2 and 2×10^{-3} mole litre^{-1} are calculated from titrations made after the maximum rates shown in the fig 19 — Table VI 1

initial $[FeCl_3]$ (mole.l^{-1})	initial rate (mole.$l^{-1}s^{-1}$)	maximum rate (mole.$l^{-1}s^{-1}$)	titration at maximum rate. (ml. N/100 C.A.S. on 13 ml vessel)	estimated $[FeCl_3]$ at maximum rate (mole.l^{-1})
$8{\cdot}3 \times 10^{-3}$	$4{\cdot}48 \times 10^{-6}$	$7{\cdot}0 \times 10^{-6}$ *	7·6	$2{\cdot}0 \times 10^{-3}$
$5{\cdot}2 \times 10^{-3}$	$7{\cdot}06 \times 10^{-6}$	$1{\cdot}84 \times 10^{-5}$ *	5·9	$3{\cdot}0 \times 10^{-4}$
$2{\cdot}0 \times 10^{-3}$	$1{\cdot}78 \times 10^{-5}$	$3{\cdot}96 \times 10^{-5}$	2·3	$2{\cdot}0 \times 10^{-4}$
$1{\cdot}4 \times 10^{-3}$	$2{\cdot}58 \times 10^{-5}$	$4{\cdot}5 \times 10^{-5}$	–	–
$5{\cdot}0 \times 10^{-4}$	$4{\cdot}5 \times 10^{-5}$	$5{\cdot}0 \times 10^{-5}$	–	–

* rate still increasing

fig 20

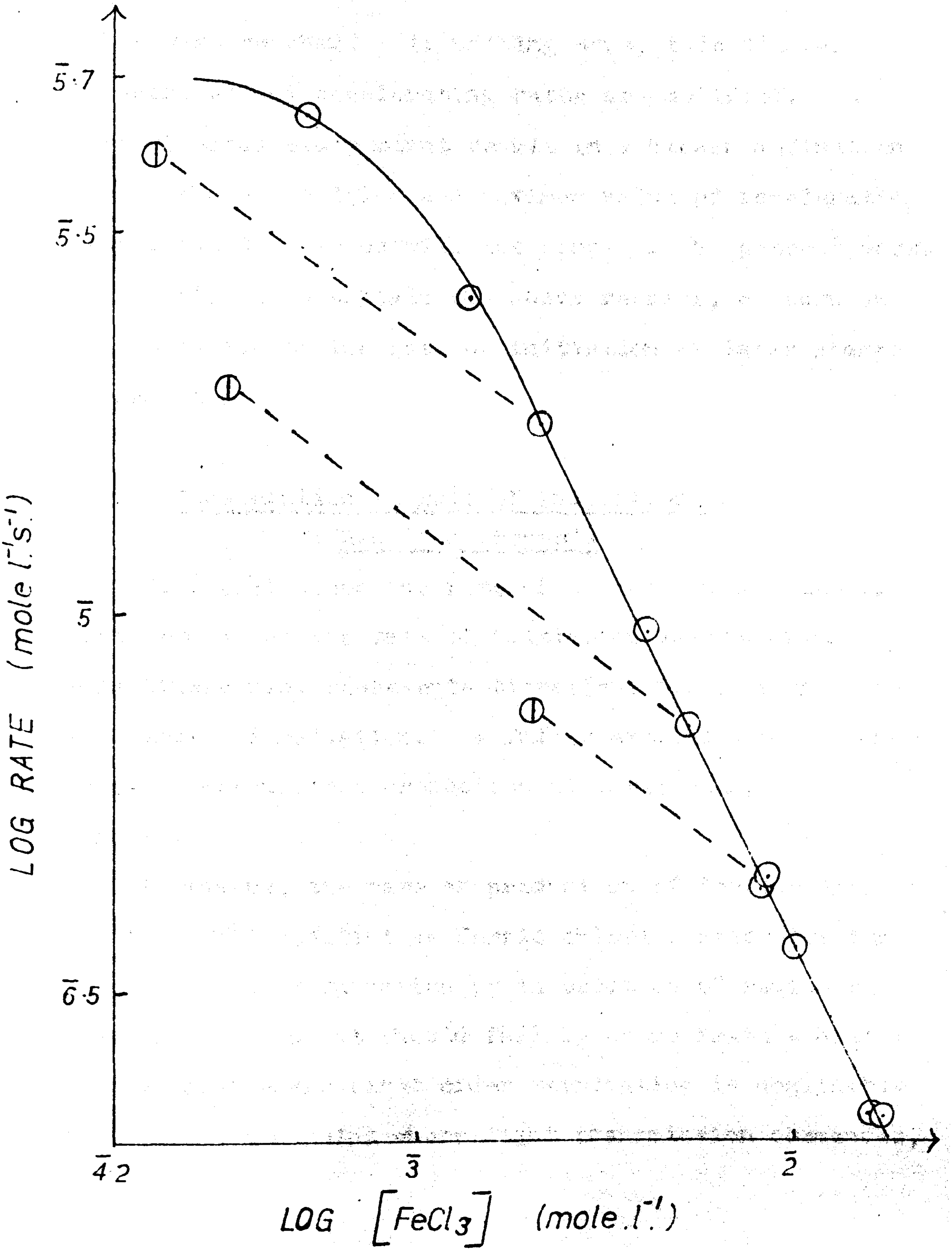


table were reached. If nothing more, this diagram illustrates how accelerating rates are modified. A more rigorous study might result in a closer definition of the shape, position and maximum value of accelerating rates, but this is outwith the scope of the present work. In an attempt to explain the above results, we turn our attention now to the rate of initiation at later stages in reaction.

6.2. Deceleration in Rate of Initiation as Reaction Proceeds

Fig. (12) shows the rate of production of ferrous iron from which the rate of initiation is obtained. This linear plot represents titrations taken only up to 100 minutes irradiation. A fuller examination is made here of ferrous iron production at later stages in reaction.

In theory, the rate of production of ferrous iron should remain constant as ferric chloride concentration decreases till termination by interaction of radicals commences, whence it should fall by approximately half at the point where first order termination is negligible. On reaching the point where light transmission commences, the expression

$$-\frac{dC}{dt} = \frac{d(C_0 - C)}{dt} = \frac{k_1 I_0}{\varepsilon}(1 - e^{-\varepsilon cd})$$

where $C = [FeCl_3]$ gives the rate of ferrous formation. Integration yields an expression of the form

$$\text{Constant} + e^{-\varepsilon cd} - \varepsilon cd = Kt$$

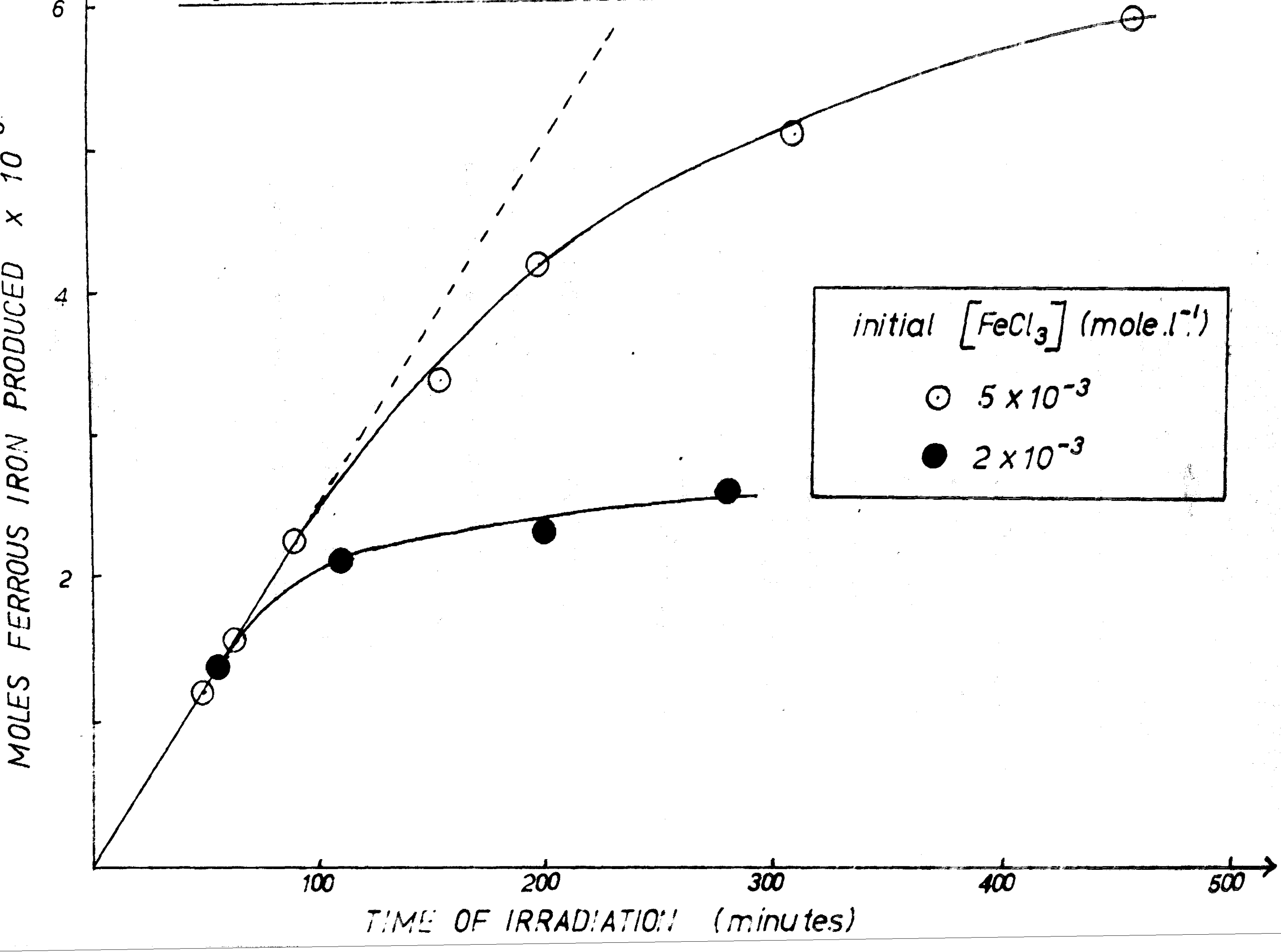
Thus the plot should fall by half then follow this modified exponential curve.

6.2.1. Results

Fig. (21) shows the results of titrations taken after long periods of irradiation. The curves are for initial ferric chloride concentrations of 5×10^{-3} and 2×10^{-3} mole litre^{-1}, with monomer concentration of 3·02 mole litre^{-1}. Each point represents titration of the contents of reaction vessels of 13 ml. volume, such that conversion to mole litre^{-1} reduced simply involves multiplication by $\frac{1}{13} \times 10^3$.

6.2.2. Discussion

The results agree fairly closely with the theory above. The rate of ferrous production for 5×10^{-3} mole litre^{-1} ferric chloride appears to decrease somewhat fig. 21. Ferrous iron produced at later stages in reaction



prematurely, but this is only really noticeable after about 150 minutes irradiation when the titration of $3{\cdot}6 \times 10^{-5}$ moles indicated shows that the ferric concentration has fallen to about $2{\cdot}2 \times 10^{-3}$ mole litre^{-1}. Nevertheless, the rate of ferrous production for 2×10^{-3} mole litre^{-1} ferric chloride is constant up to about 50 minutes when the ferric concentration is 1×10^{-3} mole litre^{-1}, so that runs at 5×10^{-3} mole litre^{-1} should not show a decrease in rate till the concentration has fallen to 1×10^{-3} mole litre^{-1} after approximately 200 minutes.

This slightly premature fall in I_n would not however have a very noticeable effect on the accelerating rate; the results above indicate that the rate of reaction for an initial ferric concentration of 5×10^{-3} mole litre^{-1} should at least follow the -1 slope in Fig. (20) till $[FeCl_3]$ falls to 2×10^{-3} mole litre^{-1}, and consequently we must look elsewhere for an explanation of this "modified acceleration" effect.

6.3. Effect of the Accumulation of Ferrous Chloride in Reaction Mixtures

It has been found, (i) that rates of reaction accelerate much less rapidly and reach lower maxima than expected; (ii) that the rate of production of ferrous chloride decreases slightly earlier than expected.

In a recent paper on the use of cupric chloride as an inhibitor in the polymerization of AN in DMF solution, Monteiro postulates that the cuprous chloride so formed can further retard the reaction (31). In an effort to explain effect (i) above, it was decided to check whether the ferrous chloride formed during polymerization of AN can act as a retarder by comparing the rate of polymerization with (a) no ferrous chloride initially present, and (b) an added quantity of ferrous chloride present.

Effect (ii) might be explained if it were found that ferrous chloride absorbs some irradiation at 3650Å, and consequently the extinction coefficient of this salt in DMF has been measured.

6.3.1. Experimental

(i) The rate of polymerization of 3·02 mole litre^{-1} of AN in DMF with an initial ferric chloride concentration of 5 x 10^{-3} mole litre^{-1} was measured before and after the addition of 5 x 10^{-3} mole litre^{-1} ferrous chloride under vacuum.

(ii) Ferrous iron in DMF oxidises rapidly in air to ferric and in Chapter 4 it was shown that the rate of conversion is linear, provided the amount of air is not limited. A measure of the extinction coefficient for ferrous chloride in DMF at 3650Å can be obtained by making up a solution under vacuum as described in Chapter 4, opening this to air, and taking O.D. readings, (at 3650Å in quartz cells in a Unicam S.P. 500 spectrophotometer), at noted time intervals; the value of ϵ ($FeCl_2$/DMF) is obtained by extrapolation to zero time.

Two runs were carried out:-

(a) $[FeCl_2] = 2 \times 10^{-3}$ mole litre^{-1} with oxidation linear

(b) $[FeCl_2] = 1{\cdot}36 \times 10^{-3}$ mole litre^{-1}. In this case the quartz cell was closed after 30 seconds with a close fitting lid thus limiting the quantity of air above solution. This latter procedure produces an exponential type of curve.

6.3.2. Results

(i) The addition of as much as 5×10^{-3} mole litre^{-1} ferrous chloride to a reaction mixture containing 5×10^{-3} mole litre ferric chloride was found to make virtually no difference to the rate of reaction.

(ii) Fig. (22) shows the rate of increase of O.D. of ferrous chloride in DMF in an open vessel. Extrapolation to zero time is linear and gives O.D. = 0·2.

From this:-

$$\varepsilon(\mathrm{FeCl_2/DMF}) = \frac{0{\cdot}2}{2 \times 10^{-3} \times 1} = 100 \text{ litre mole}^{-1}\text{cm}^{-1}.$$

Fig. (23) shows the rate of increase of O.D. of ferrous chloride in DMF in a vessel closed to air after 30 sec. This curve can be extrapolated to give an initial O.D. reading anywhere between zero and 0·05.

Thus the maximum value of $\varepsilon(\mathrm{FeCl_2/DMF})$ from this plot is

$$= \frac{0{\cdot}05}{1{\cdot}36 \times 10^{-3} \times 1} = 73{\cdot}5 \text{ litre mole}^{-1}\text{cm}^{-1}$$

From these results, $\varepsilon(\mathrm{FeCl_2/DMF})$ lies between limits of 0 and 100 litre mole^{-1}cm^{-1}.

6.3.3. Conclusions

(i) Ferrous chloride formed during reaction would not affect the rate of polymerization of AN in DMF.

(ii) It appears that absorption of light of wavelength 3650Å by ferrous chloride in DMF is very low compared to that by ferric chloride. (Even if the value of $\varepsilon(\mathrm{FeCl_2/DMF})$ is as high as 100 litre mole^{-1}cm^{-1}, this fig 22 Air oxidation of ferrous chloride in DMF

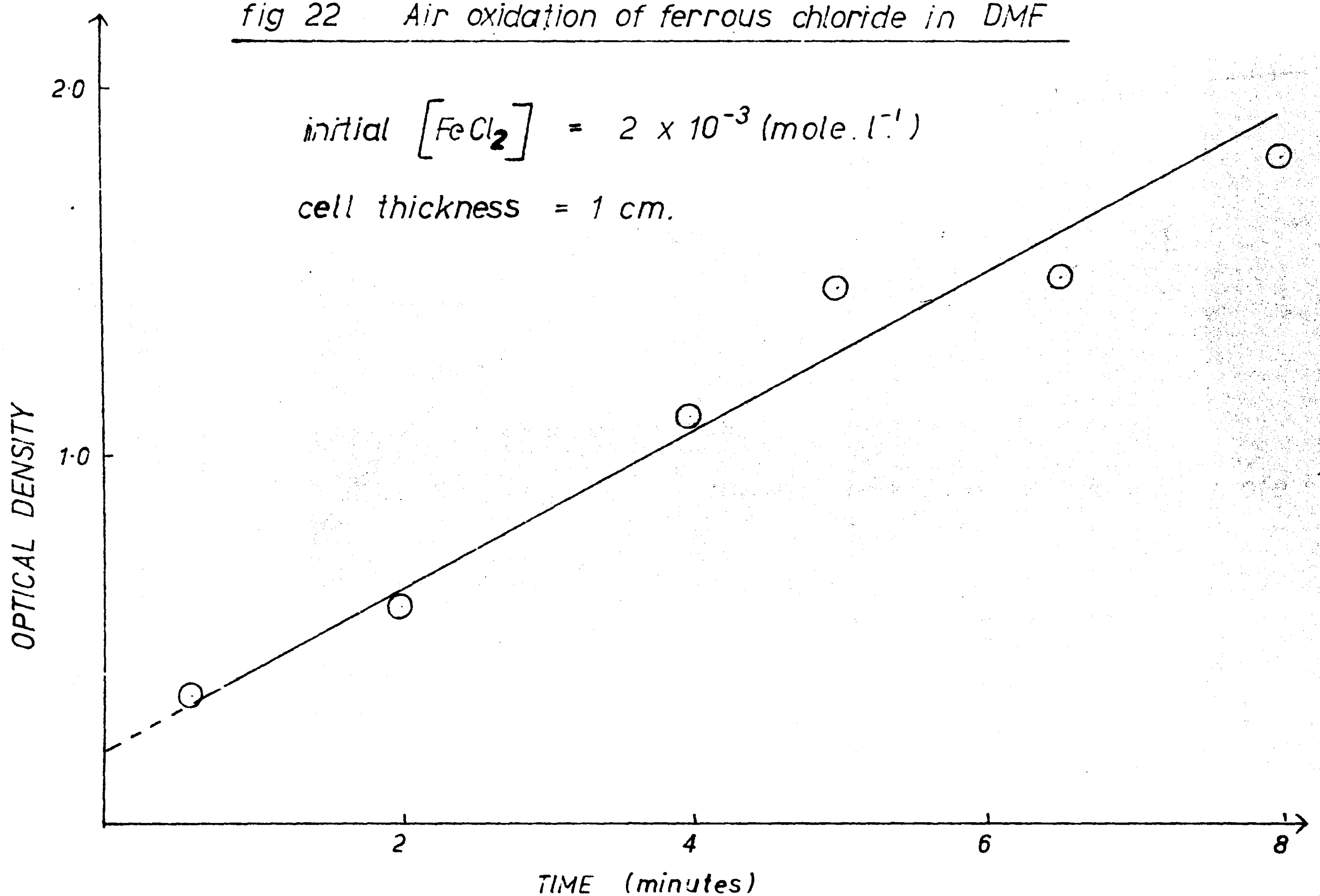
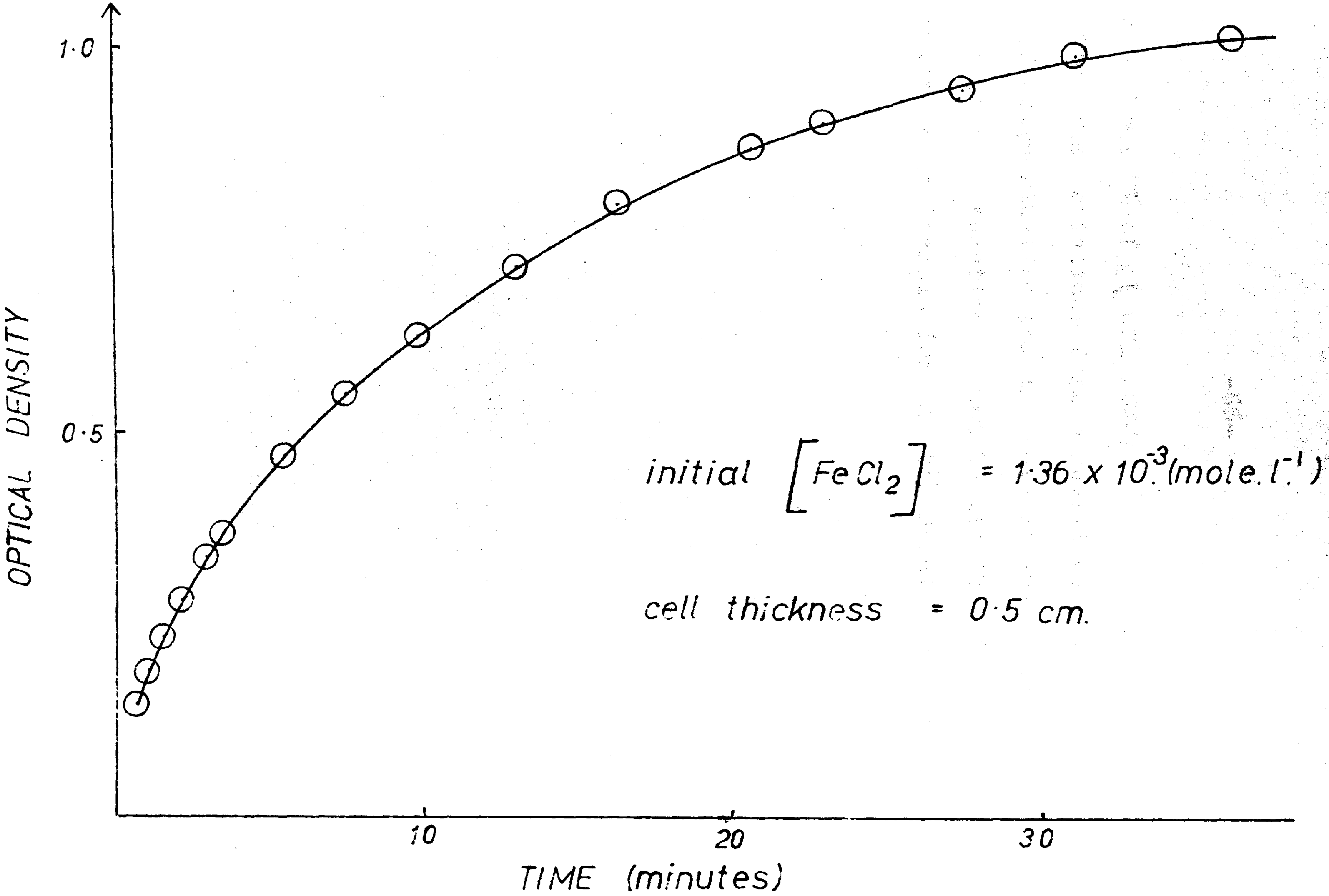


fig. 23. Air oxidation of ferrous chloride in DMF



is only about 2% of $\varepsilon(FeCl_3/DMF)$.

Thus the deviations from expected behaviour of the rate of polymerization and the rate of initiation at later stages in reaction cannot be attributed to the accumulation of ferrous iron in the reaction mixture.

CHAPTER 7.

Determination of Intensity Exponents

The intensity exponent for a reaction can be found by evaluating the rate dependence on the intensity of initiating irradiation.

$$\text{Rate} = \text{Intensity}^{x}$$

$$\text{Log } \frac{\text{Rate}(f)}{\text{Rate}_{(r)}} = x \log \frac{I(f)}{I_{(r)}}$$

where $\text{Rate}_{(f)}$ and $\text{Rate}_{(r)}$ refer to the rates at full and reduced intensity, I and I

$$x = \frac{\log \text{Rate}_{(f)} / \text{Rate}_{(r)}}{}$$

Thus $$x = \frac{\log \text{Rate}_{(f)} / \text{Rate}_{(r)}}{\log \quad I_{(f)} / \ I_{(r)}} \qquad \text{.....(VII.1.)}$$

The intensity exponent therefore may be obtained from equation (VII.1.) by measuring the rate of reaction at different intensities of irradiation.

7.1. Experimental

The exponent was measured at ferric chloride concentrations of 2×10^{-3}, $3{\cdot}2 \times 10^{-3}$, 5×10^{-3}, $8{\cdot}3 \times 10^{-3}$, 1×10^{-2} and $1{\cdot}6 \times 10^{-2}$ mole litre^{-1}. The procedure in each case was to measure the rate of reaction at full intensity, then insert between vessel and source of irradiation a screen of known transmission and measure the reduced rate. On removing the screen, the rate of full intensity was remeasured. An average value of the rates before and after the screen insertion was taken as the rate at full intensity.

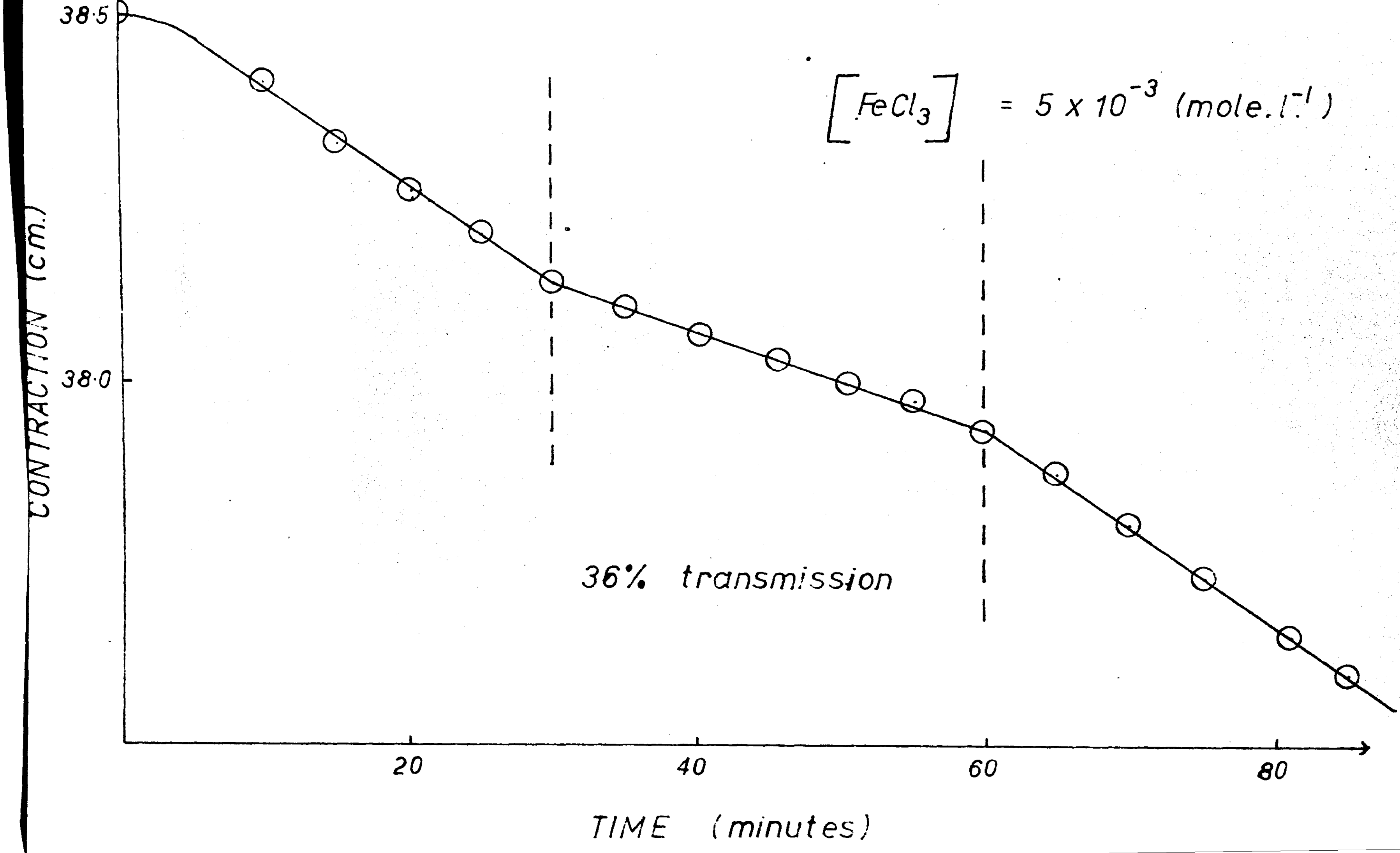
7.2. Results

Fig. (24) shows a typical determination for a run at $[FeCl_3] = 5 \times 10^{-3}$ mole litre^{-1} using a 36% transmission screen. This particular run gave $\chi = 0{\cdot}70$. The results are shown in Table (VII.1.)

TABLE (VII.1.)

Ferric Chloride Concentration	Outer Limits of Values of χ obtained	Mean Value χ
2×10^{-3}(Mole.l.$^{-1}$)	0·60 - 0·62	0·61
$3{\cdot}2 \times 10^{-3}$	0·59	0·59
$5{\cdot}0 \times 10^{-3}$	0·67 - 0·71	0·69
$8{\cdot}3 \times 10^{-3}$	0·61 - 0·65	0·63
1×10^{-2}	0·60 - 0·68	0·64
$1{\cdot}6 \times 10^{-2}$	0·72	0·72

Thus χ shows little variation throughout the region of first order termination and between 2×10^{-3} mole litre^{-1} and $1{\cdot}6 \times 10^{-2}$ mole litre^{-1} of ferric fig. 24. Typical determination of intensity exponent



chloride concentration has an overall mean value of 0·65.

7.3. Discussion

In Chapter 5 it was shown that

$$\text{Rate} = \frac{K[M]}{[FeCl_3]} \quad \text{for} \quad [FeCl_3] > 2 \times 10^{-3} \text{ mole litre}^{-1}$$

From the simple kinetic scheme postulated it was assumed that:-

$$K = \frac{k_p}{k_t} \times I_n$$

$$= \frac{k_p k_i}{k_t} \times I_o$$

where I_o = Intensity of Irradiation.

It has been shown that K is indeed a constant for constant I_o, but it appears from the work described here that $\text{Rate} \propto I_o^{0\cdot65}$

The value of x for a reaction involving termination first order with respect to radical concentration should of course be unity. (The value of 0·65 obtained here points to a predominance of 2nd order termination.)

Thus the sum total of our findings indicates that

$$\text{Rate} = \frac{K[M]\, I_n^{0\cdot65}}{[FeCl_3]}$$

and we must attempt now to construct a scheme to describe the kinetics of the system on the basis of the results at hand. To this end, a considerable number of theoretical schemes have been examined, and two of these are worth mention, if only to emphasise how incompatible are the relations

$$\text{Rate} \propto \left[\text{FeCl}_3\right]^{-1} \quad \text{and Rate} \propto I_n^{0 \cdot 65}$$

Scheme (i)

This is based on the assumption that the intensity exponent has been lowered from unity by the occurrence of some second order termination. The effect of this on the dependence of rate on ferric chloride concentration is desired.

	Rate
$FeCl_3 \xrightarrow{h\nu} Cl + FeCl_2$ $Cl + M \longrightarrow R_1$	I_n
$R_n + M \longrightarrow R_{n+1}$	$k_p [R][M]$
$R_n + R_m \longrightarrow \text{Polymer}$	$k_t [R]^2$
$R_n + FeCl_3 \longrightarrow \text{Polymer} + FeCl_2$	$k_t' [R][F]$

For stationary state in radicals,

$$I_n = k_t [R]^2 + k_t' [R][F]$$

$$\text{Thus } [R] = \frac{1}{2k_t}\left[\sqrt{(k_t'F)^2 + 4I_n k_t} - k_t'F\right]$$

A typical plot for the function $\log\left[\sqrt{(k_t'F)^2 + 4I_n k_t} - k_t'F\right]$ against $\log F$ is shown in Fig. (25). This is for

$$\begin{cases} k_t' = 10^4 \\ k_t = 10^8 \\ I_n = 10^{-7} \end{cases}$$

such that $\log f(\text{Rate}) = \log\left[\sqrt{10^8F^2 + 40} - 10^4F\right]$

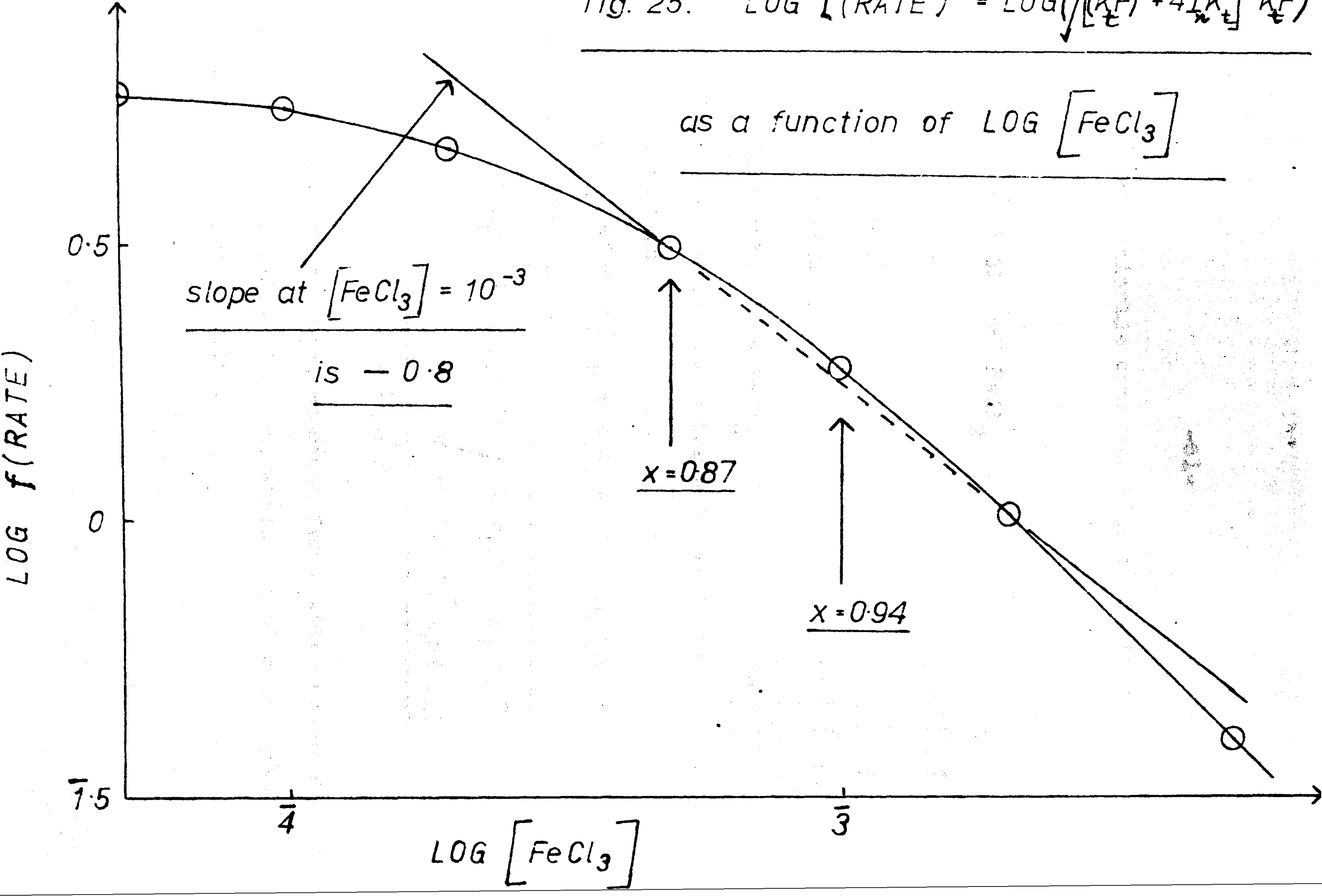
The rate dependence on rate of initiation has been calculated at various points on this line e.g. for $[FeCl_3] = 10^{-3}$ mole litre^{-1} from the form $f(\text{Rate}) = \left[\sqrt{100 + 4 \times 10^8 I_n} - 10\right]$

We see that, for this particular system of constants, at $[FeCl_3] = 10^{-3}$, x is found to be 0·94, yet the slope of $\log f(\text{Rate})/\log F$ is as low as - 0·8. A value of 0·65 would be accompanied by a slope less than 0·6 which is a far cry from the value of - 1·0 obtained. Other combinations of constants give similar results.

Scheme (ii).

This is based on the assumption that the intensity exponent has been lowered by some termination involving interaction of a radical and an initiator atom of chlorine, and again the effect on the dependence of fig. 25. $\mathrm{LOG}\ f(\mathrm{RATE}) = \mathrm{LOG}\left(\sqrt{[(k_t'F)^2 + 4Ik_x k_t]} - k_t'F\right)$

as a function of $\mathrm{LOG}\ [\mathrm{FeCl_3}]$



rate on ferric chloride concentration is desired.

	Rate
$FeCl_3 \xrightarrow{h\nu} Cl + FeCl_2$	I_n
$Cl + M \longrightarrow R_1$	$k_1 [Cl] [M]$
$R_n + M \longrightarrow R_n$	$k_p [R] [M]$
$R_n + Cl \longrightarrow R_n\,Cl$	$k_t [R] [Cl]$
$R_n + FeCl_3 \longrightarrow R_n\,Cl + FeCl_2$	$k_t' [R] [F]$

Assuming a stationary state for both chlorine and polymer radicals, we find

$$(k_t k_t' F)\, R^2 + (k_t' I_n + k_t k_1 MF)\, R - k_1 I_n M = 0$$

Thus $[R]$ is given by:-

$$\frac{-(k_1 k_t MF + k_t' I_n) + \sqrt{(k_1 k_t MF + k_t' I_n)^2 + 4(k_t k_t' k_1 MF\, I_n)}}{2\, k_t k_t' F}$$

This system has been examined for a wide number of combinations of values for constants, all of which gave basically the same results.

For example:-

$$\left\{\begin{array}{ll} k_i & 10 \\ k_t & 10^{3} \\ k_t & 10^{9} \\ I_n & 10^{-7} \\ M & 3 \end{array}\right.$$

In this system, for $[FeCl_3] > 10^{-1}$, $\chi = 1{\cdot}0$, and the slope of log f(Rate) against log F = - 1·0

TABLE (VII.2.)

$[FeCl_3]$	χ	$\frac{\log f(R)}{\log F}$ slope
10^{-1}	0·96	- 0·84
10^{-2}	0·77	- 0·50
10^{-3}	0·40	

From Table (VII.2.) it is seen that even with χ as high as 0·70, the slope would be between - 0·50 and - 0·8.

From another system giving a slope of - 0·95 between $[FeCl_3] = 10^{-3}$ and 10^{-2}, χ was measured at $[FeCl_3] = 10^{-3}$ and found to have fallen only to 0·98.

In both of the above schemes then, it is seen that lowering of χ to 0·6 - 0·7 would be accompanied by a very large deviation from minus unity in the slope of log Rate against log $[FeCl_3]$ and consequently schemes of this type must be rejected.

Further consideration of this problem is left till the general discussion in Chapter 12.

CHAPTER 8.

Determination of Overall Activation Energy

The velocity coefficient k of a reaction is related to the energy of activation by the expression

$$k = A e^{-E/RT}$$

where A = Frequency factor
E = Activation Energy
T = Temperature (degrees absolute)
R = Molar gas constant

As derived in Chapter 5, the Rate of Polymerization is given by the expression:-

$$\text{Rate} = \frac{k_p \, I_n [M]}{k_t [FeCl_3]}$$

thus $$\frac{k_p}{k_t} = \frac{A_p}{A_t} e^{-(E_p - E_t)/RT}$$

and $$\log_{10} \text{Rate} = \log_{10} \frac{A_p}{A_t} + \log_{10} \frac{I_n [M]}{[FeCl_3]} - \frac{(E_p - E_t)}{2{\cdot}3\, RT}$$

Since I_n, $[M]$ and $[FeCl_3]$ will remain sensibly constant over initial stages of reaction, and I_n is independent of temperature for the photosensitized reaction, the equation may be written

$$\log_{10} \text{Rate} = K - \frac{E_0}{2 \cdot 3\ RT}$$

where K is a constant and $E_0 = E_p - E_t$

A plot of $\log_{10}$ Rate against 1/T will have a slope of $-\frac{E_0}{2 \cdot 3\ R}$

8.1. Experimental

Rates of polymerization were measured at different temperatures between 25°C and 50°C for solutions containing 1×10^{-2}, $8 \cdot 2 \times 10^{-3}$, $5 \cdot 2 \times 10^{-3}$, and 2×10^{-3} mole litre^{-1} ferric chloride to examine the region of first order termination and at 2×10^{-4} mole litre^{-1} to obtain an estimate of $(E_p - \frac{1}{2}E_t^{\prime})$ in the region of second order termination. ($E_t^{\prime}$ refers to the activation energy for the interaction of two polymer radicals).

All reaction mixtures contained $3 \cdot 02$ mole litre^{-1} acrylonitrile.

8.2. Results

These are shown graphically in Figs. (26) to (28) and also in Table (VIII.1.)

fig 26 Typical determination of activation energy

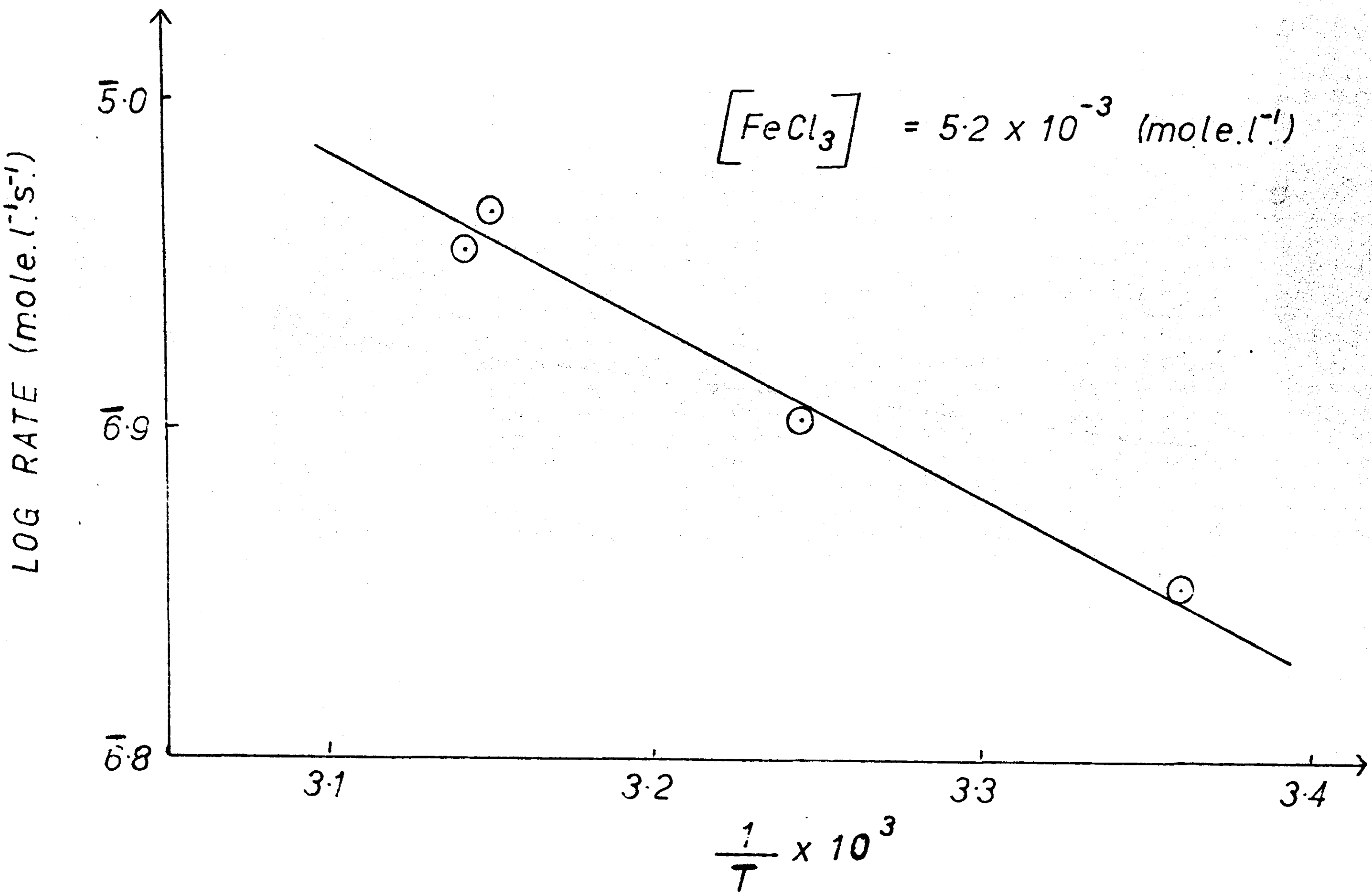


fig. 27. Determination of activation energy

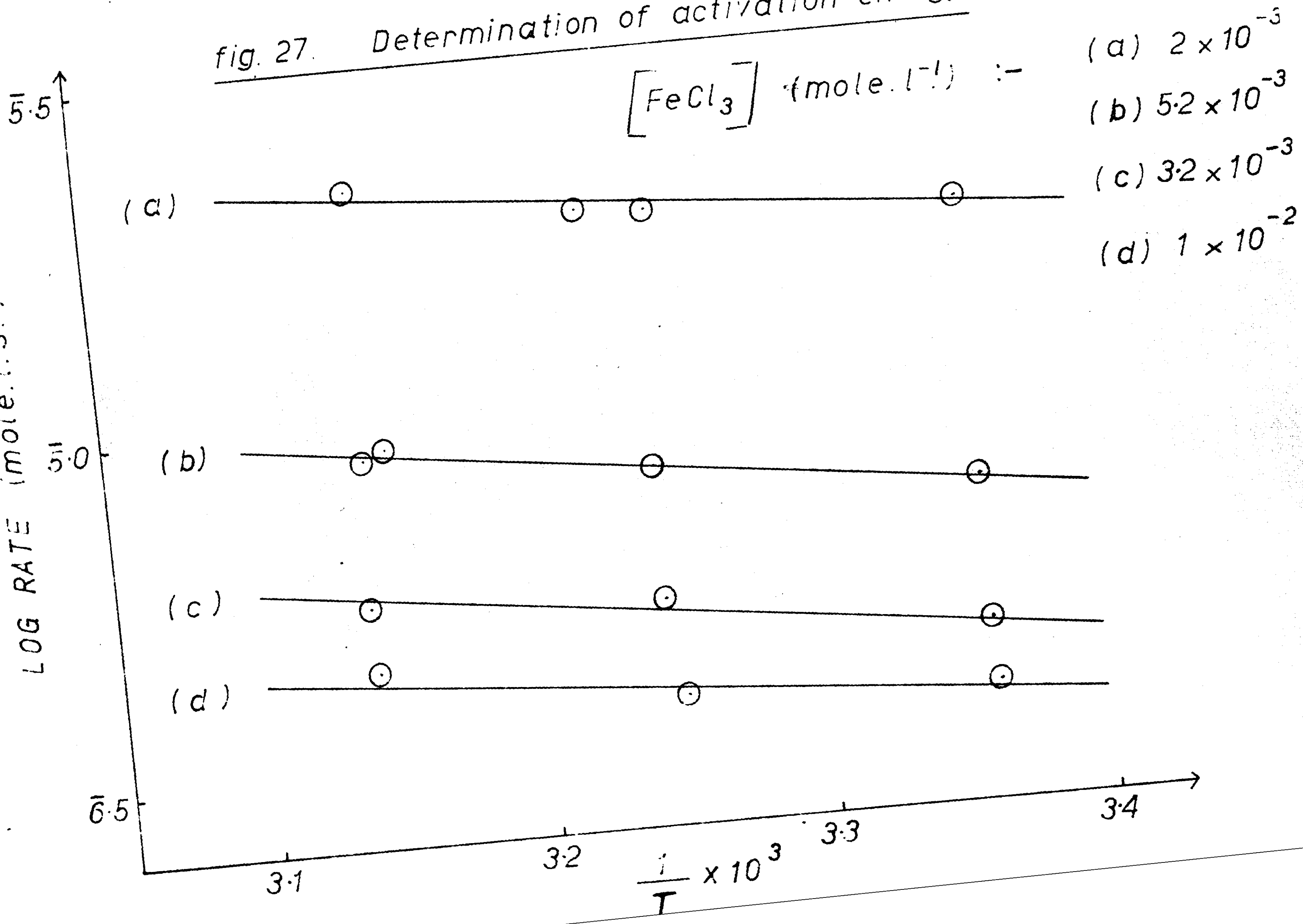


fig. 28. Determination of activation energy

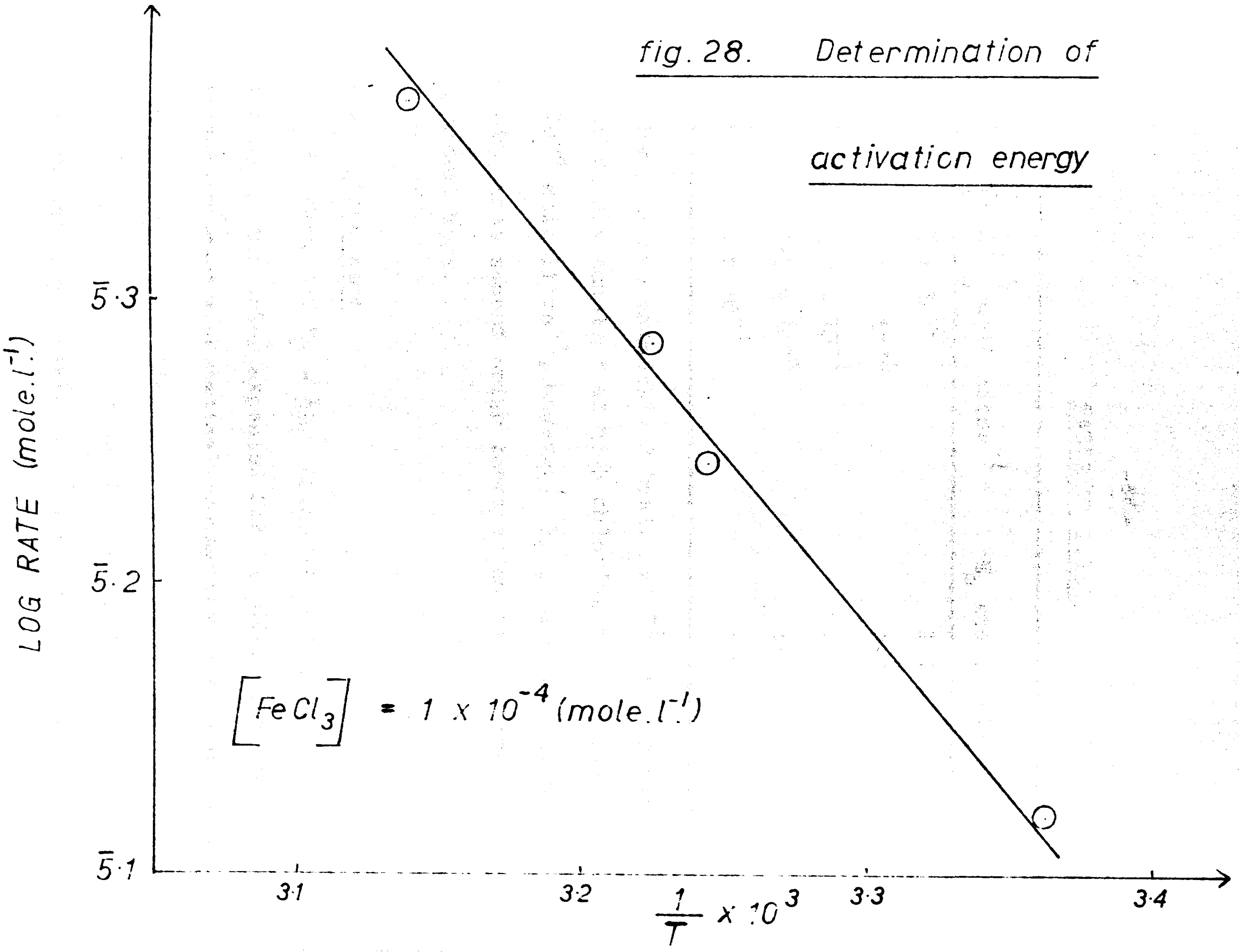


TABLE (VIII.1.)

$[FeCl_3]$ mole litre^{-1}	E_o kcal. mole^{-1}
1×10^{-2}	1·7
$8{\cdot}2 \times 10^{-3}$	2·2
$5{\cdot}2 \times 10^{-3}$	2·4
$2{\cdot}0 \times 10^{-3}$	1·7
1×10^{-4}	5·5

E_o then, is approximately 2 kcal. mole^{-1}, and appears to be fairly constant at high chloride concentrations. At 10^{-4} mole litre^{-1}, however, E_o is markedly higher showing that second order termination is much more important here.

8.3. Discussion

The value of $E_p - \frac{1}{2}E_t'$ obtained is 5·5 kcal. mole^{-1}. This is of the order expected for the difference in activation energy of radical propagation reaction and an interaction of radicals.

If E_t' is of the order of 1 kcal. mole^{-1}, then E_p is approximately 6 kcal. mole^{-1}, and E_t is approximately 4 kcal. mole^{-1}.

This is lower than would be expected for a reaction involving electron transfer. In a study of the decomposition of azobisisobutyronitrile in DMF between 60°C and 80°C using ferric chloride and styrene as scavengers, Betts, Dainton and Ivin quote the value of E_t for reaction between ferric chloride and primary radicals, (cyanoisopropyl or styryl radicals), as being slightly higher than 8 kcal. mole^{-1} (47). However, in the photosensitized polymerization of AN in DMF in presence of ferric chloride, the low intensity exponents obtained in the region of first order termination suggest that, although it has been found that rate of reaction is inversely proportional to ferric chloride concentration, the termination step may be somewhat more complex than that represented by the equation

$$R + FeCl_3 \longrightarrow \text{Polymer} + FeCl_2$$

such that the value of E_t obtained above may not be truly representative of the activation energy required for this reaction.

CHAPTER 9.

Measurement of the Rate of Photolysis of Ferric Chloride by Spectrophotometry

As observed in Chapter 3, the optical density of a solution which obeys Beer's law is given by the expression

$$\text{O.D.} = \log \frac{I_o}{I} = \varepsilon cd$$

where ε = extinction coefficient,

c = concentration of substrate,

d = path length of light through solution

such that any change in concentration of the substrate can be followed by measuring O.D. at a suitable wavelength. From a calibration plot of O.D. against c at this wavelength, the changes in O.D. can be converted to changes in c.

This procedure can be used for measurement of the rate of reduction of ferric chloride in AN - DMF mixtures, and from this, the rate of initiation of the polymerization of AN in DMF photosensitized by ferric chloride may be obtained.

Furthermore the rate of photolysis of ferric chloride in pure DMF and in various other solvents can be measured, and comparison of the rates obtained in different solvents may yield information on the nature of the reaction

$$FeCl_3/\text{solvent} \xrightarrow[3650\text{Å}]{h\nu} \text{radical} + FeCl_2$$

9.1. Experimental

9.1.1. Apparatus

A Unicam S.P. 1400 spectrophotometer was used so that O.D. measurements could be made directly on solutions under vacuum. Wide tubes were employed to allow stirring by magnetic follower. The tubes were matched and fitted exactly the space provided in the instrument (diameter approximately 2·5 cm.) Before each O.D. measurement was made, transmission was set at 100% with pure solvent as blank. The volume of solution used in all experiments was 16 ml.

9.1.2. Measurements

The rate of photolysis of ferric chloride has been measured in the following solvents.

(i) DMF - AN mixtures

With monomer concentration held constant at 3·02 mole litre^{-1}, runs were carried out with initial ferric concentrations of 5·2 x 10^{-3}, 8·1 x 10^{-3}, 1·2 x 10^{-2}

and $1{\cdot}6 \times 10^{-2}$ mole litre^{-1}.

With ferric chloride concentration held constant at 8×10^{-3} mole litre, runs were carried out at monomer concentrations of 0·75 and 4·53 mole litre^{-1}, (5% and 30% by volume).

(ii) Pure DMF

Runs were carried out in this solvent with initial ferric concentrations of $5{\cdot}2 \times 10^{-3}$, 8×10^{-3} and $1{\cdot}6 \times 10^{-2}$ mole litre^{-1}.

(iii) Other Solvents

Runs were carried out with initial ferric concentration of 1×10^{-2} mole litre^{-1} in ethanol, ethyl acetate, methyl cyanide, acetone and diethyl ether.

Titration Tests

In each of the above runs, after measurement of the photolysis rate, the reaction mixture was titrated for ferrous iron.

Reduced Intensity

The rate of photolysis of ferric chloride in 20% AN - 80% DMF solution at reduced intensity of irradiation has been measured.

9.2. Results

Fig. (29) shows absorption curves for each of the pure solvents studied. On the Unicam S.P. 1400 spectrophotometer it is generally accepted that beyond limits of 0•8 and 0•2 on the O.D. scale, accuracy of measurement diminishes rapidly; consequently, where possible, wavelengths have been chosen such that O.D. readings lie within these limits.

9.2.1. Rate of Photolysis of Ferric Chloride in systems containing DMF

Fig. (30) shows the fall in O.D. at a wavelength of 4800Å with time of irradiation for four different ferric chloride concentrations in AN - DMF mixtures containing 20% by volume of monomer.

This shows that, in the region of first order termination, the rate of reduction of ferric chloride is constant, being independent of initial chloride concentration. This verifies the constancy of I_n as found by titration.

Fig. (31) shows the fall in O.D. at 4800Å against time for three chloride concentrations in pure DMF, and here too, the rate is independent of initial chloride concentration.

fig. 29. Absorption curves for ferric chloride solutions

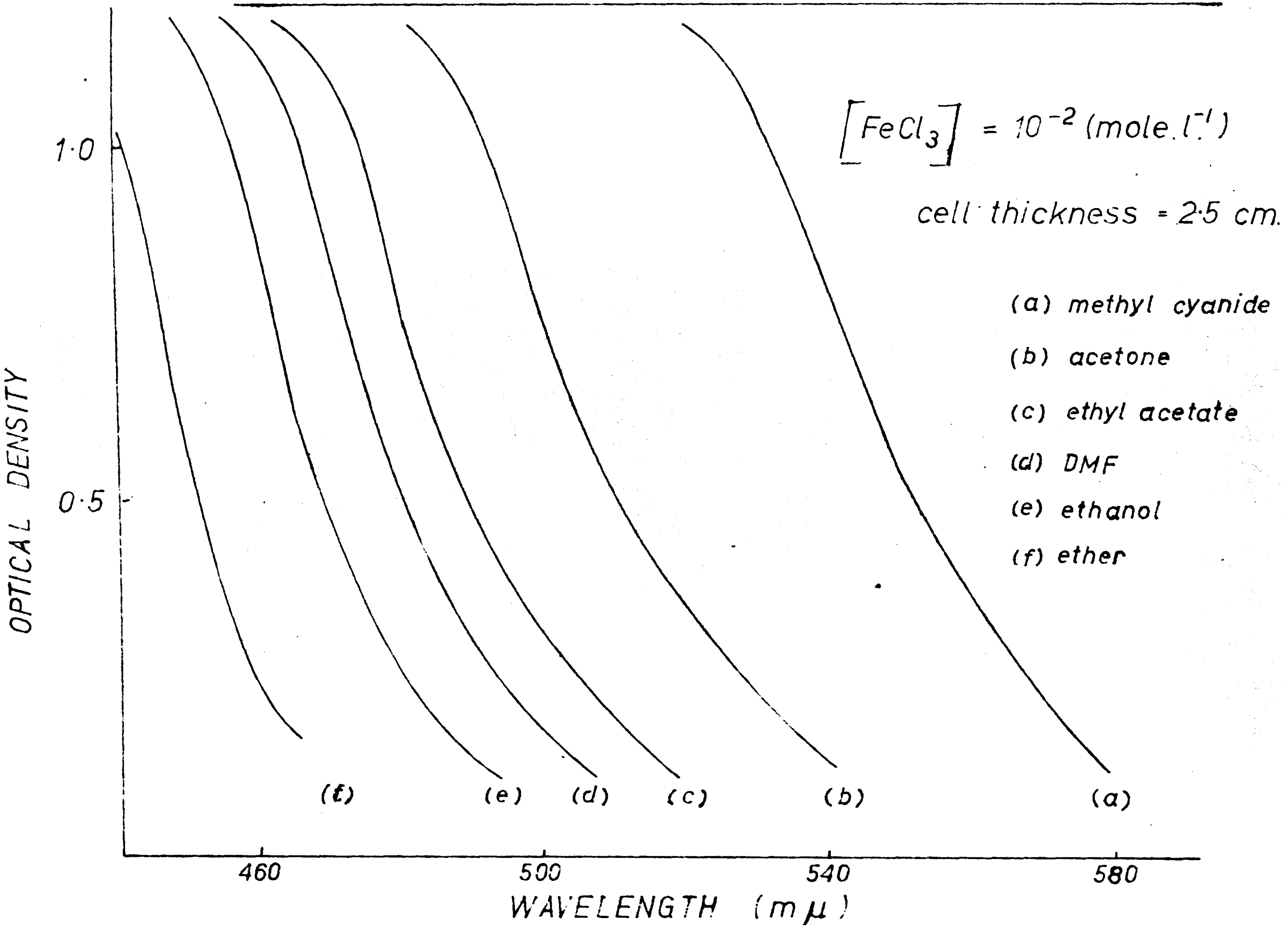


fig. 30. Photolysis of ferric chloride in AN-DMF mixture wavelength = 4800 Å

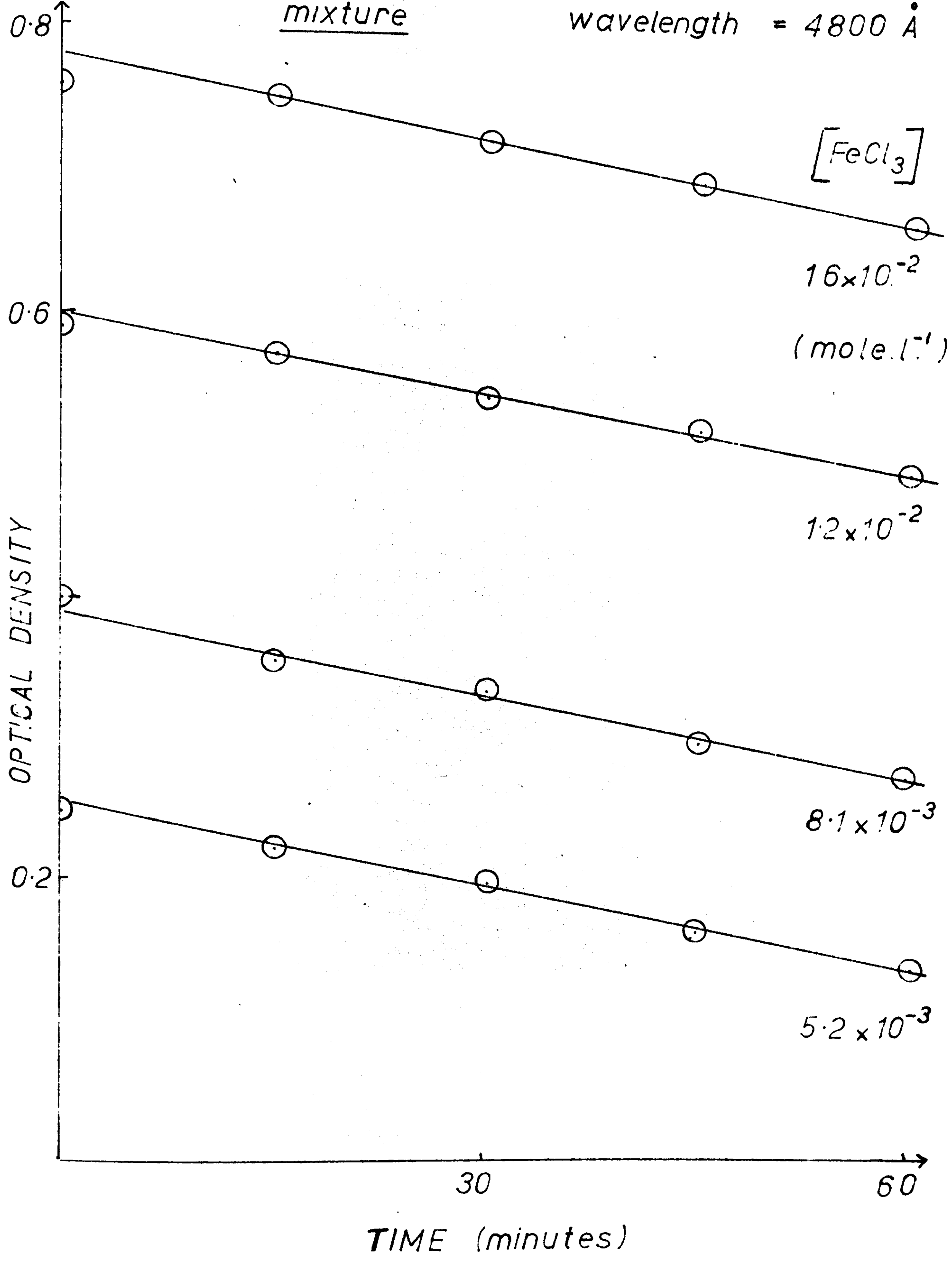


fig 31 Photolysis of ferric chloride in DMF

wavelength = 4800 Å

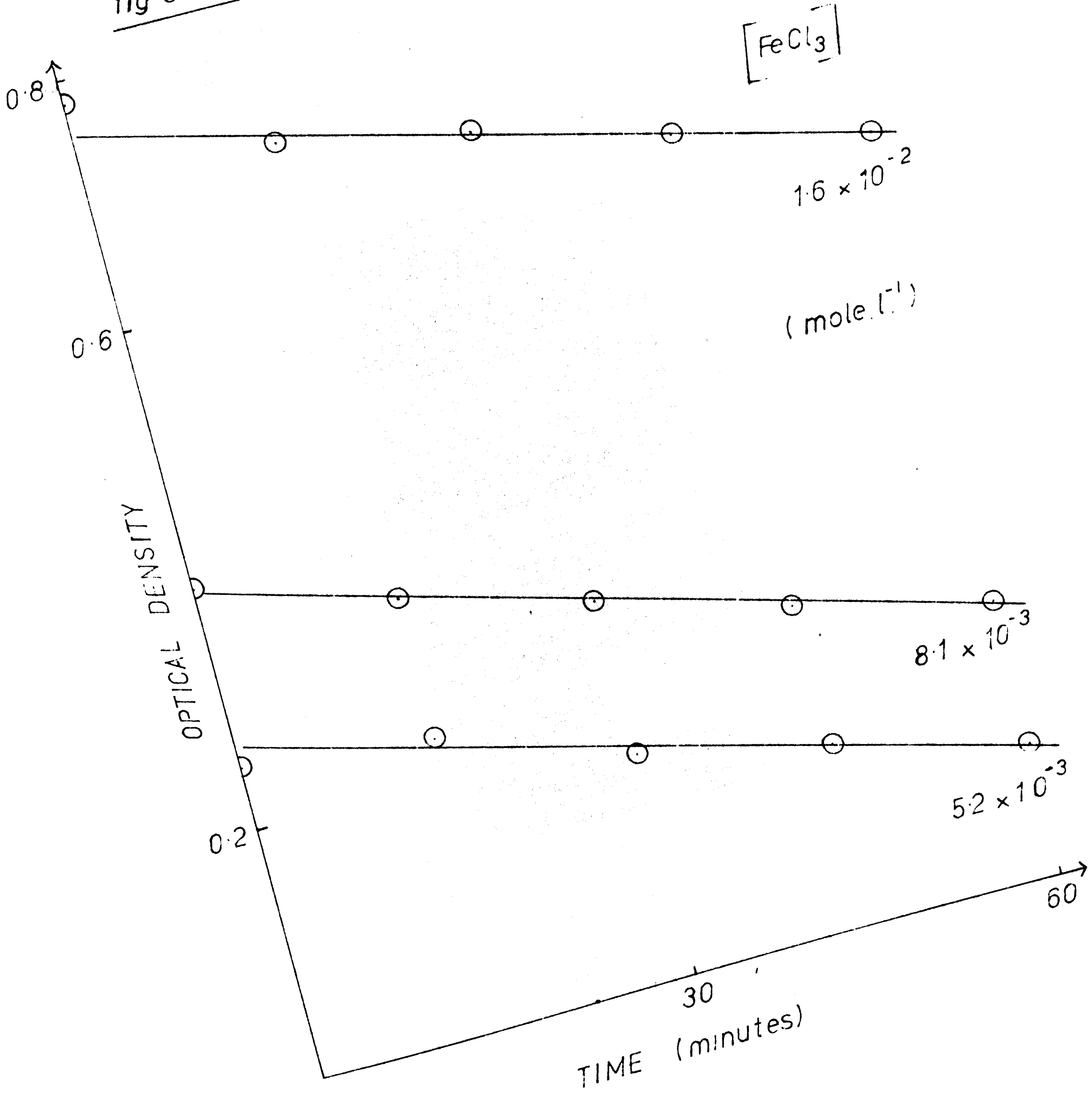
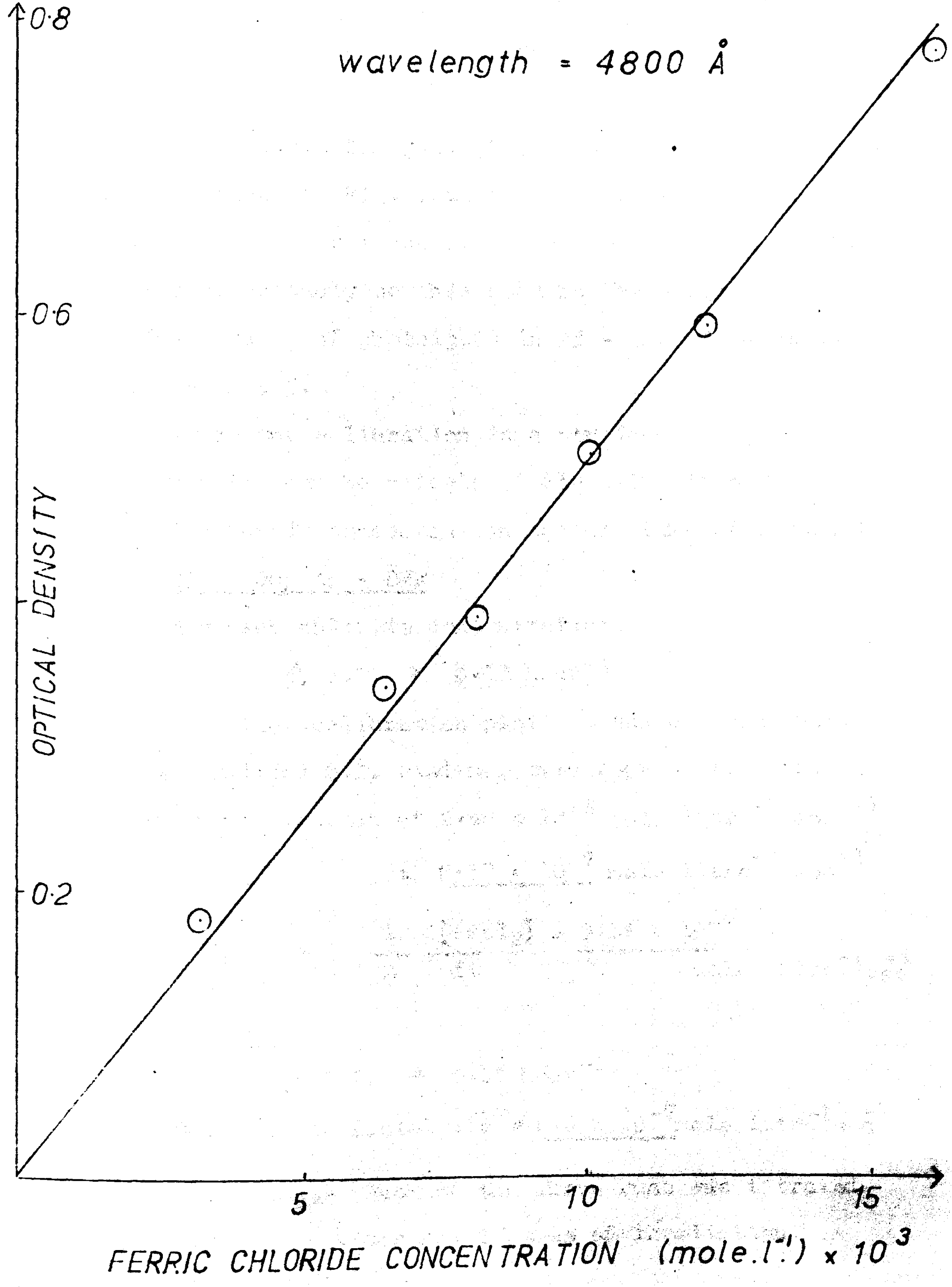


fig. 32. Calibration plot for DMF



The calibration plot of O.D. against ferric concentration shown in Fig. (32) is for pure DMF but it was found that the presence of 20% AN does not alter O.D. values measureably so this plot has been used to evaluate rates of photolysis in AN - DMF mixtures as well as in DMF.

Since the calibration is a straight line, the linear rates can be calculated directly without plotting ferric concentration against time of irradiation.

20% - 80% AN - DMF

For each chloride concentration,

$$\Delta \text{ O.D.} = 0{\cdot}12 \text{ hour}^{-1}$$

From the calibration plot, it can be seen that, for any initial O.D. reading, this represents a fall in ferric concentration of $2{\cdot}40 \times 10^{-3}$ mole litre^{-1} hour^{-1}

$$= \underline{6{\cdot}67 \times 10^{-7}} \text{ mole litre}^{-1} \text{ sec}^{-1}$$

and $$I_n = \frac{1}{2}\frac{d[FeCl_2]}{dt} = \frac{3.34 \times 10^{-7}}{} \text{ mole litre}^{-1} \text{ sec}^{-1}$$

Pure DMF

Here Δ O.D. $= 0{\cdot}16$ hour^{-1}

Thus Rate of Photolysis $= \underline{8{\cdot}9 \times 10^{-7}}$ mole litre^{-1}sec^{-1}

Titrations:- Each of the above runs was titrated for ferrous iron after noted times of irradiation

Example:- Run with $5 \cdot 2 \times 10^{-3}$ mole litre^{-1} ferric chloride in 20% - 80% AN - DMF by volume.

Time or irradiation = 60 minutes

Titration = $2 \cdot 10$ ml $\frac{N}{100}$ C.A.S.

$\equiv 2 \cdot 10 \times 10^{-5}$ moles iron

Initial O.D. = $0 \cdot 25$

Final O.D. = $0 \cdot 135$

Δ O.D. = $0 \cdot 115$

Thus percentage ferric reduced = $\frac{0 \cdot 115}{0 \cdot 25} \times 100 = 46\%$

Total ferric initially present

$= 5 \cdot 2 \times 10^{-3}$ mole litre^{-1}

$= 8 \cdot 32 \times 10^{-5}$ mole in 16 ml. reaction vessel.

Thus from O.D. readings, number of moles ferrous formed in 16 ml. vessel

$= 0 \cdot 46 \times 8 \cdot 32 \times 10^{-5}$

$= 3 \cdot 83 \times 10^{-5}$ moles

The titration actually obtained is about one half of this.

$$\text{Percentage} = \frac{2 \cdot 10 \times 10^{-5}}{3 \cdot 83 \times 10^{-5}} \times 100$$

$$= 55\%$$

Similar results were obtained for the other runs carried out in this series as shown in Table(IX.1.)

TABLE (IX.1.)

$[FeCl_3]_0$ mole litre^{-1}		$\frac{\text{Moles Fe}^{++}\text{ by Titration}}{\text{Moles Fe}^{++}\text{ from O.D.}} \times 100\%$
$5{\cdot}2 \times 10^{-3}$	AN : DMF	55%
$8{\cdot}1 \times 10^{-3}$		49•5%
$1{\cdot}2 \times 10^{-2}$		57%
$1{\cdot}6 \times 10^{-2}$		-
$5{\cdot}2 \times 10^{-3}$	DMF	51%
$8{\cdot}0 \times 10^{-3}$		52%
$1{\cdot}6 \times 10^{-2}$		56%

In view of the above results, two special runs were carried out at $5{\cdot}2 \times 10^{-3}$ mole litre^{-1} ferric chloride in pure DMF.

(i) Solution was irradiated till colourless (approximately 8 hours) and titrated.

Total Iron present $= 5{\cdot}2 \times 10^{-3}$ mole litre^{-1}

In 16 ml. volume $= 5{\cdot}2 \times 10^{-3} \times \frac{16}{1000}$

$= 8{\cdot}32 \times 10^{-5}$ moles

and since solution is colourless, this is the quantity of ferrous iron indicated by O.D. measurements.

Actual titration = 8·5 mls N/100 C.A.S.

≡ 8·5 x 10^{-5} moles ferrous iron

Thus O.D. and titration are in agreement when conversion is complete.

(ii) Solution was irradiated for 105 minutes such that O.D. fell quite close to zero

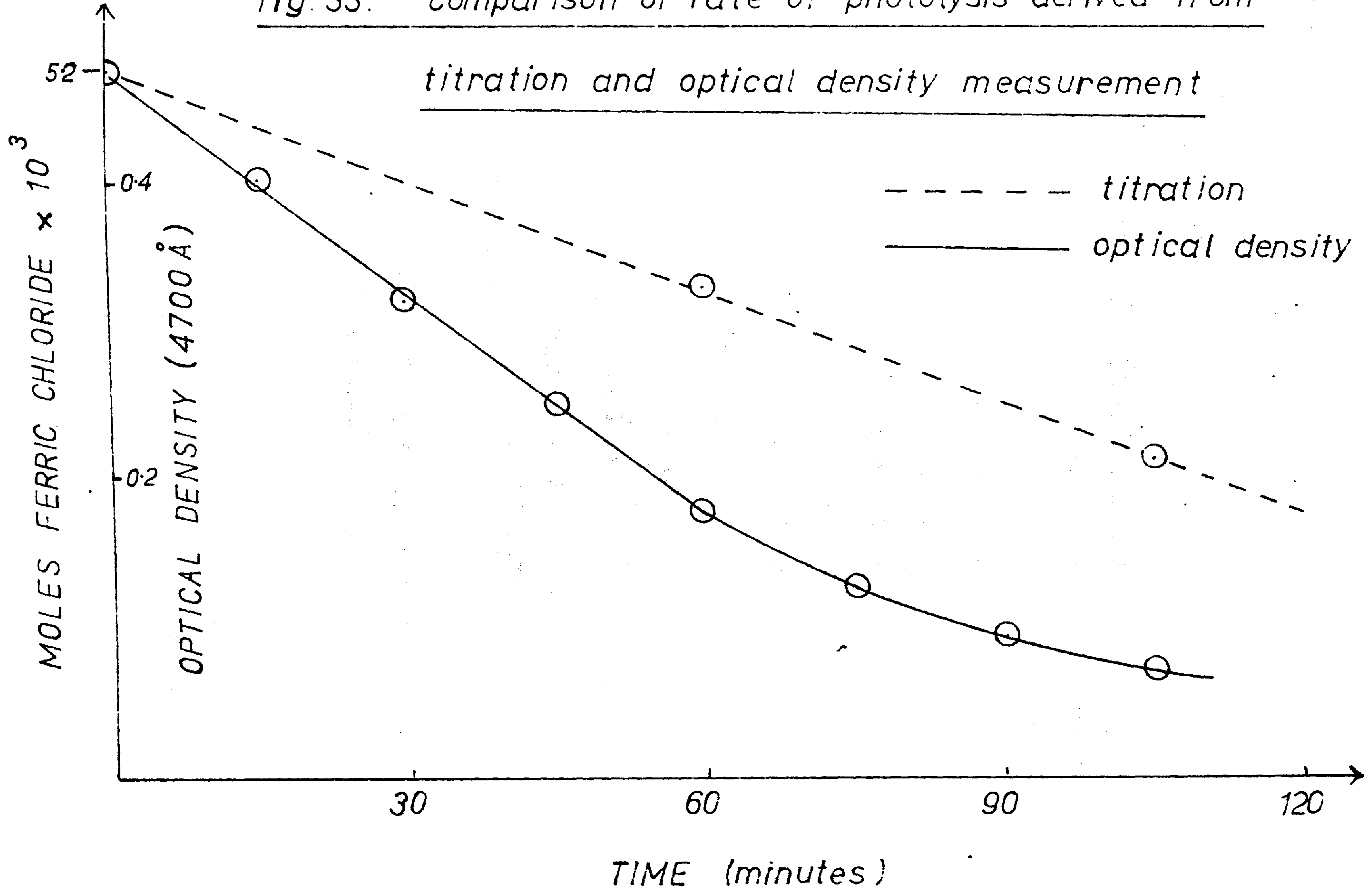
Initial O.D. at 4700Å = 0·47

O.D. after 105 minutes = 0·07

Titration = 4·6 mls.

Thus, whereas O.D. measurements indicate that 85% of the ferric has reacted, the titration indicates only about 55% of the total iron present has been reduced.

The situation is illustrated in Fig. (33) which is a plot of results obtained for solutions of 5·2 x 10^{-3} mole $litre^{-1}$ of ferric chloride in pure DMF. This shows that the rate of photolysis as measured by titration is about half that from O.D. measurements where these are both linear, and that, while the titration line is linear after as much as 105 minutes in agreement with results obtained previously, the rate of fall of O.D. with time decreases rapidly after about 60 minutes. At 105 minutes the actual titration is about 65% of that indicated by O.D. and as shown above these lines must fig. 33. Comparison of rate of photolysis derived from titration and optical density measurement



eventually meet.

Effect of altering Monomer Concentration

From results above, it can be seen that the rate of reduction of ferric chloride in pure DMF is about 4/3 times that in DMF containing 20% monomer. Thus inclusion of monomer in reaction mixtures causes a lowering of rate. To examine this effect more closely, two runs have been carried out at 8 x 10^{-3} mole litre^{-1} ferric chloride in mixtures containing 5% and 30% by volume of monomer. See Fig. (34).

Rate for 5:95 by volume AN - DMF system

= $\underline{8{\cdot}45 \times 10^{-7}}$ mole $\text{litre}^{-1}\text{sec}^{-1}$

Rate for 30:70 by volume AN - DMF system

= $\underline{6{\cdot}67 \times 10^{-7}}$ mole $\text{litre}^{-1}\text{sec}^{-1}$

9.2.2. Rate of Photolysis of Ferric Chloride in other Solvents

(a) Ethanol

Spectroscopically pure ethanol was used, and results are shown in Fig. (35). In conjunction with calibration plot, Fig. (36) this gives a rate of photolysis at 1 x 10^{-2} mole litre^{-1} ferric chloride of

$\underline{8{\cdot}55 \times 10^{-7}}$ mole $\text{litre}^{-1}\text{sec}^{-1}$

fig. 34. Effect of varying AN concentration on rate of photolysis in AN-DMF mixture

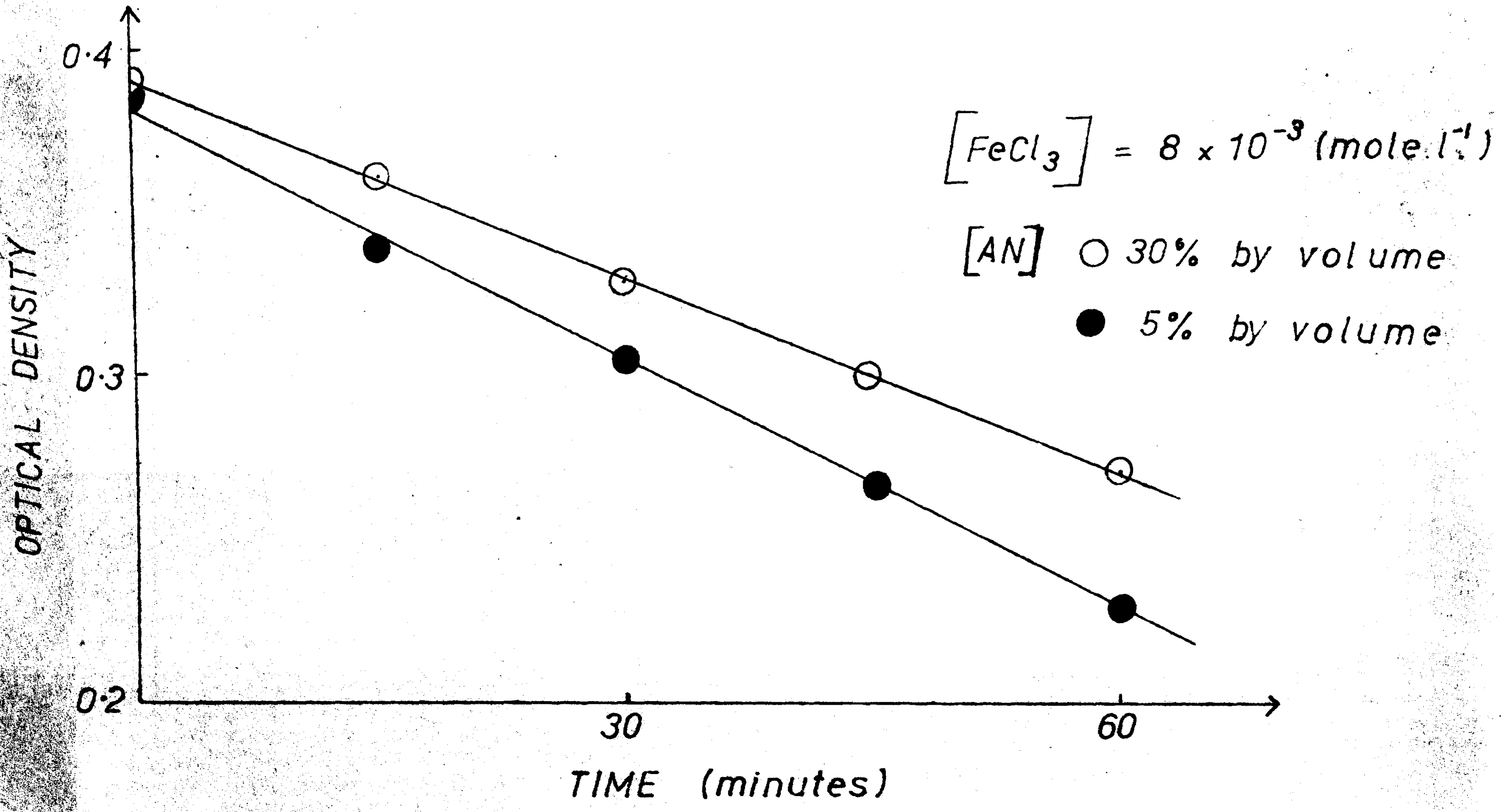


fig. 35. Photolysis of ferric chloride in ethanol

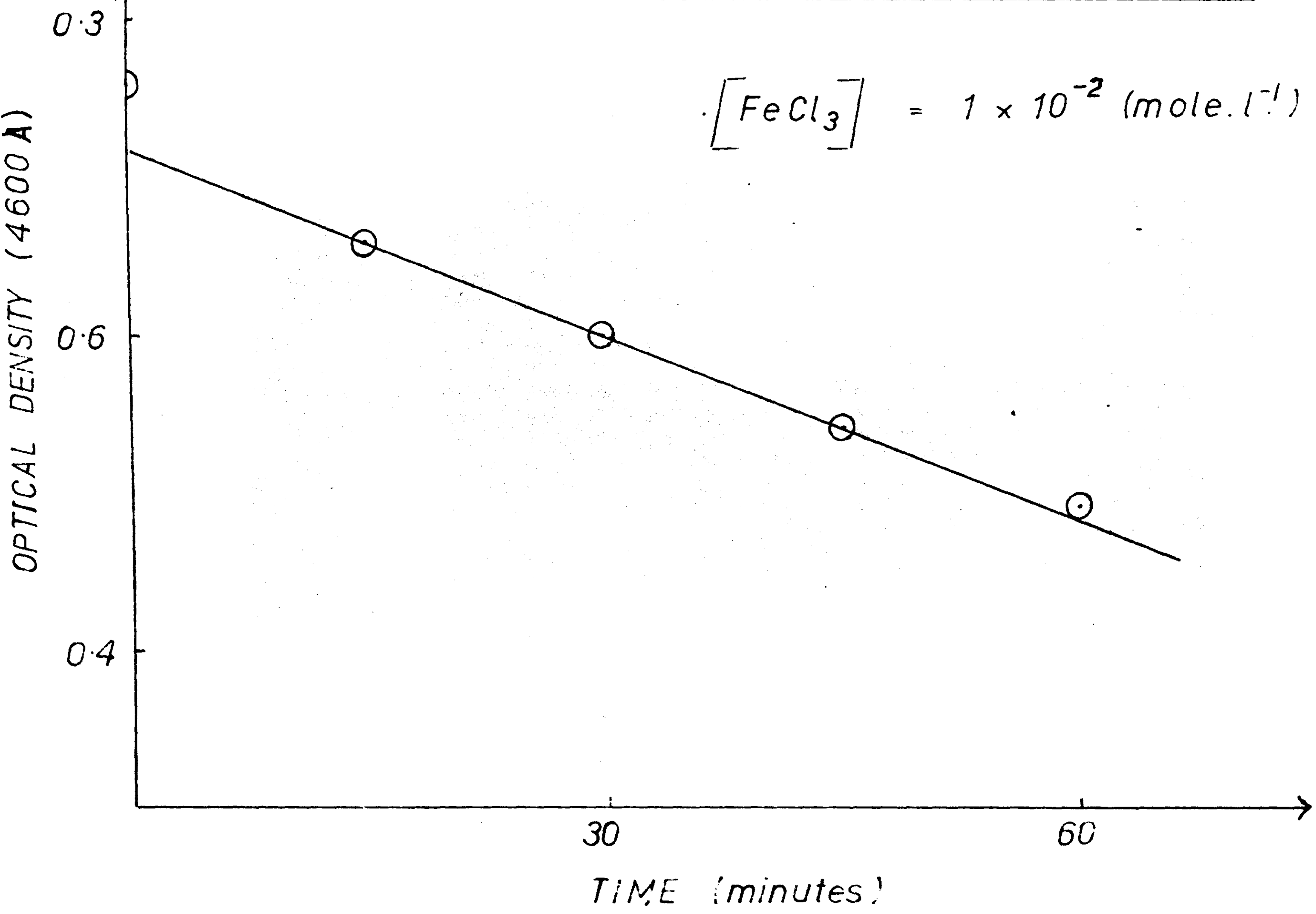
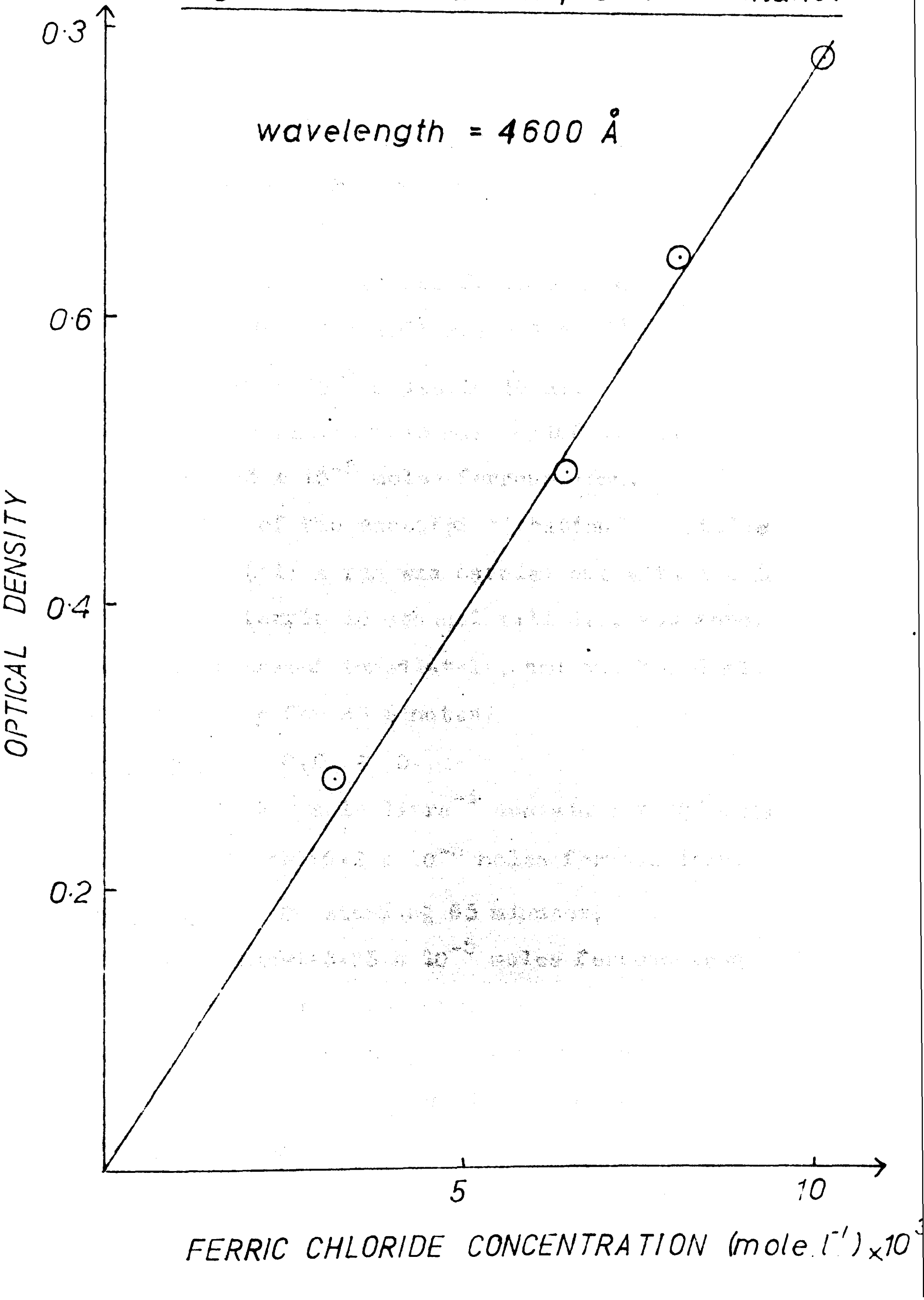


fig. 36. Calibration plot for ethanol



Titrations: (i) The fall in O.D. at 4600Å after 60 minutes indicates that 35% of ferric present has been reduced.

Thus expected titration for ferrous iron

$$= 0{\cdot}35 \times 1 \times 10^{-2} \text{ moles litre}^{-1}$$

$$= 5{\cdot}6 \times 10^{-5} \text{ moles in 16 ml.}$$

Actual titration = 3·3 mls N/100 C.A.S.

$$\equiv 3{\cdot}3 \times 10^{-5} \text{ moles ferrous iron.}$$

Thus only 59% of the expected titration is obtained.

(ii) A run was carried out with 1×10^{-2} mole litre^{-1} ferric in ethanol till O.D. was zero.

6 ml. were titrated immediately, and another 6 ml. after standing in air for 65 minutes.

First 6 ml. O.D. = 0.

6 ml. at 1×10^{-2} mole litre^{-1} contain 6×10^{-5} moles iron.

Titration obtained = $6{\cdot}2 \times 10^{-5}$ moles ferrous iron.

Second 6 ml. On standing 65 minutes,

Titration obtained = $3{\cdot}05 \times 10^{-5}$ moles ferrous iron

Thus the titration - O.D. situation is the same in ethanol as in DMF systems, and ferrous ions in ethanol oxidise rapidly in air as in DMF systems.

(b) Ethyl Acetate

Spectroscopically pure Ethyl Acetate was used and the results are shown in Figs. (37) and (38).

fig. 37. Photolysis of ferric chloride in ethyl acetate

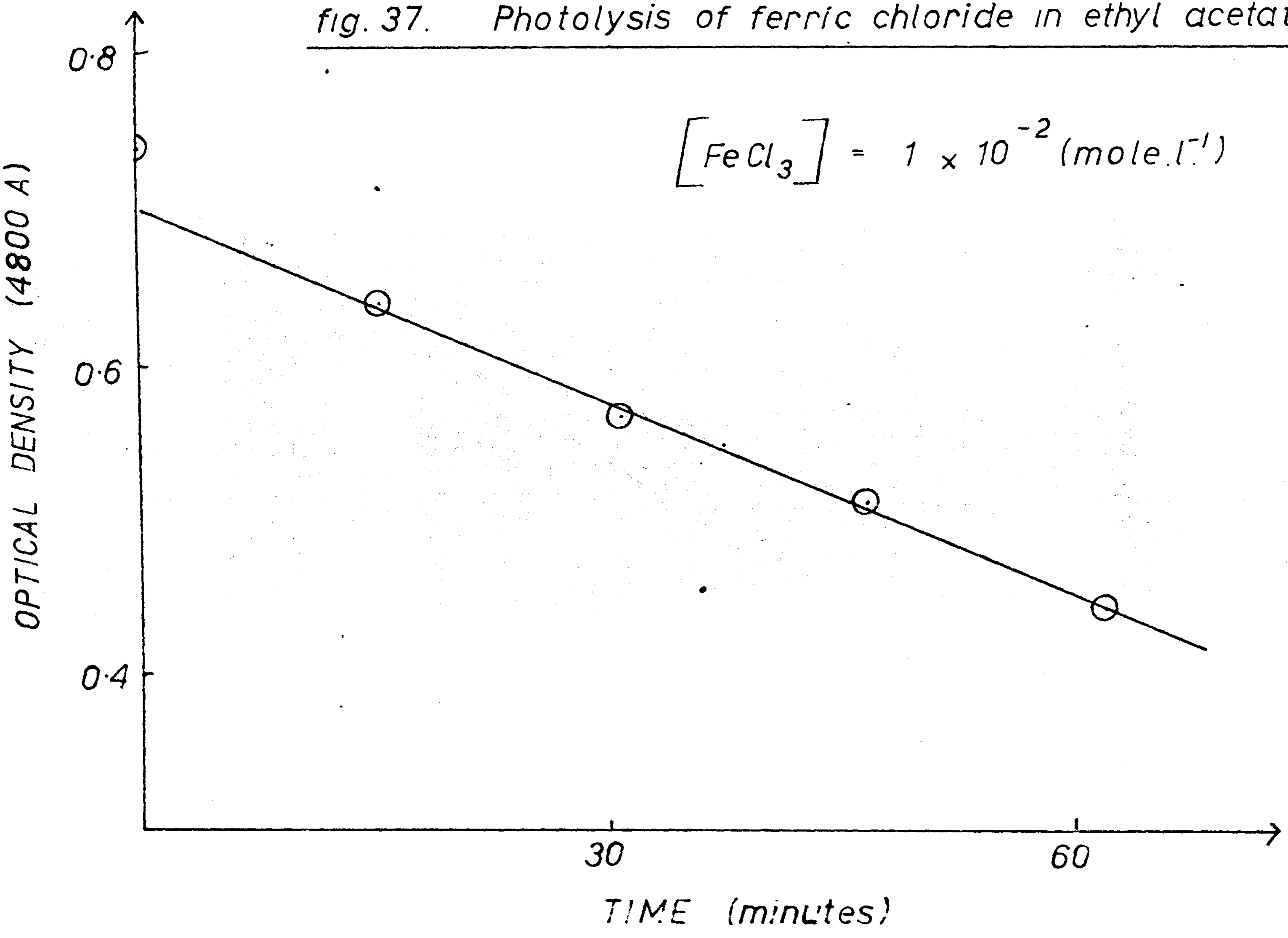
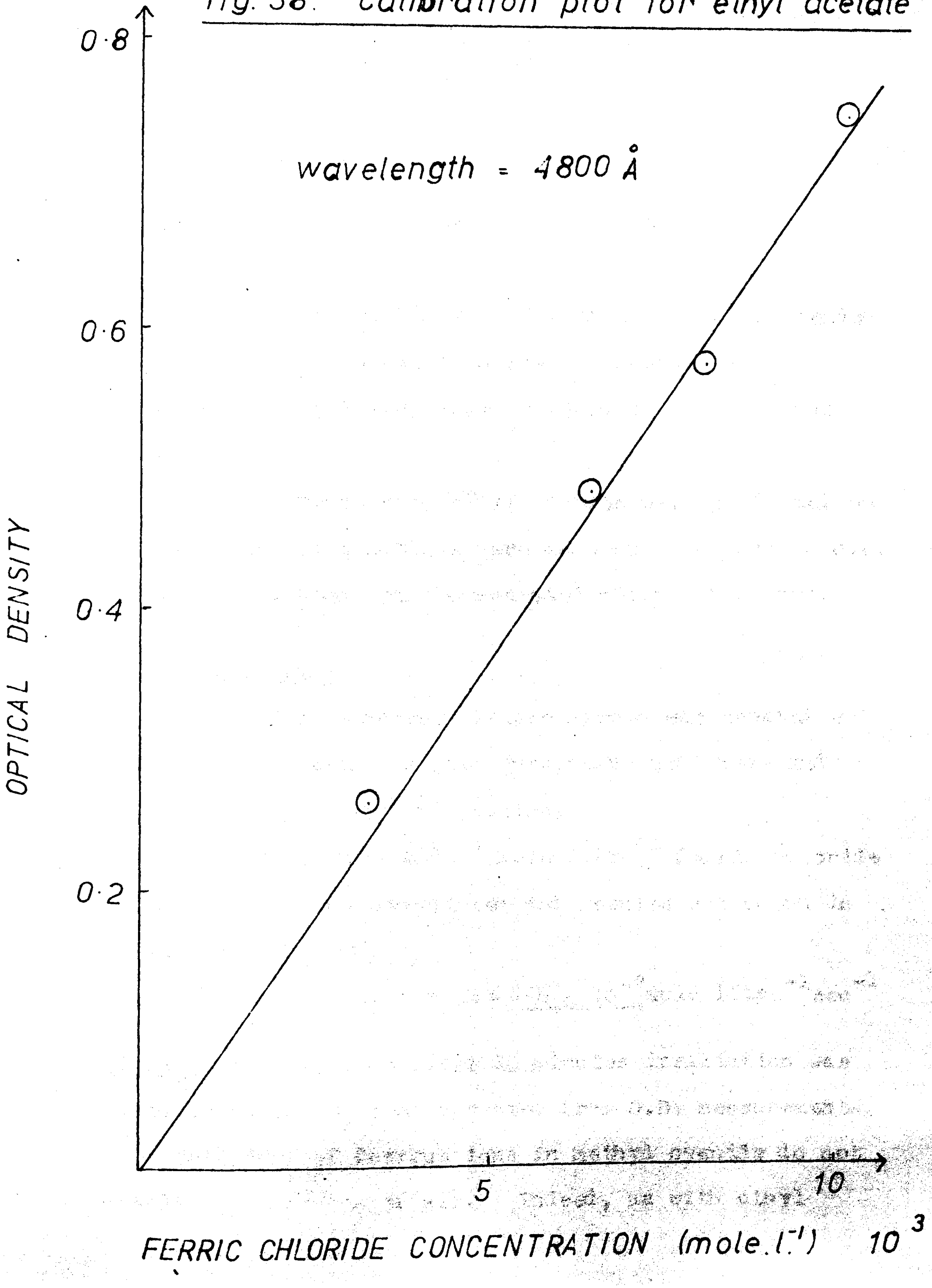


fig. 38. Calibration plot for ethyl acetate



Rate of reduction of ferric = $\underline{9{\cdot}34 \times 10^{-7}}$ mole litre^{-1}sec^{-1}

Titration: Ethyl Acetate is immiscible with the aqueous titration media of dilute sulphuric acid and it was found that, even on vigorous shaking, the colour tended to remain in the organic layer. Consequently no titrations with C.A.S. could be carried out for this solvent.

Note:- Experiments with ethyl acetate were performed on the same day as solutions were made up as a fall in O.D. of stock solutions can be detected after a few days.

(c) Methyl Cyanide

The B.D.H. laboratory reagent grade was treated with four one hour shakings with phosphorus pentoxide and distilled under reduced pressure.

A solution of 1×10^{-2} mole litre^{-1} ferric chloride in the cyanide was irradiated and results are shown in Figs. (39) and (40).

Rate of reduction of ferric = $\underline{6{\cdot}8 \times 10^{-7}}$ mole litre^{-1}sec^{-1}

Titration: Titration after 60 minutes irradiation was found to be 48% of that expected from O.D. measurements.

Solutions of ferrous ions in methyl cyanide do not oxidise in presence of air. Indeed, as with ethyl fig. 39. Photolysis of ferric chloride in methyl cyanide

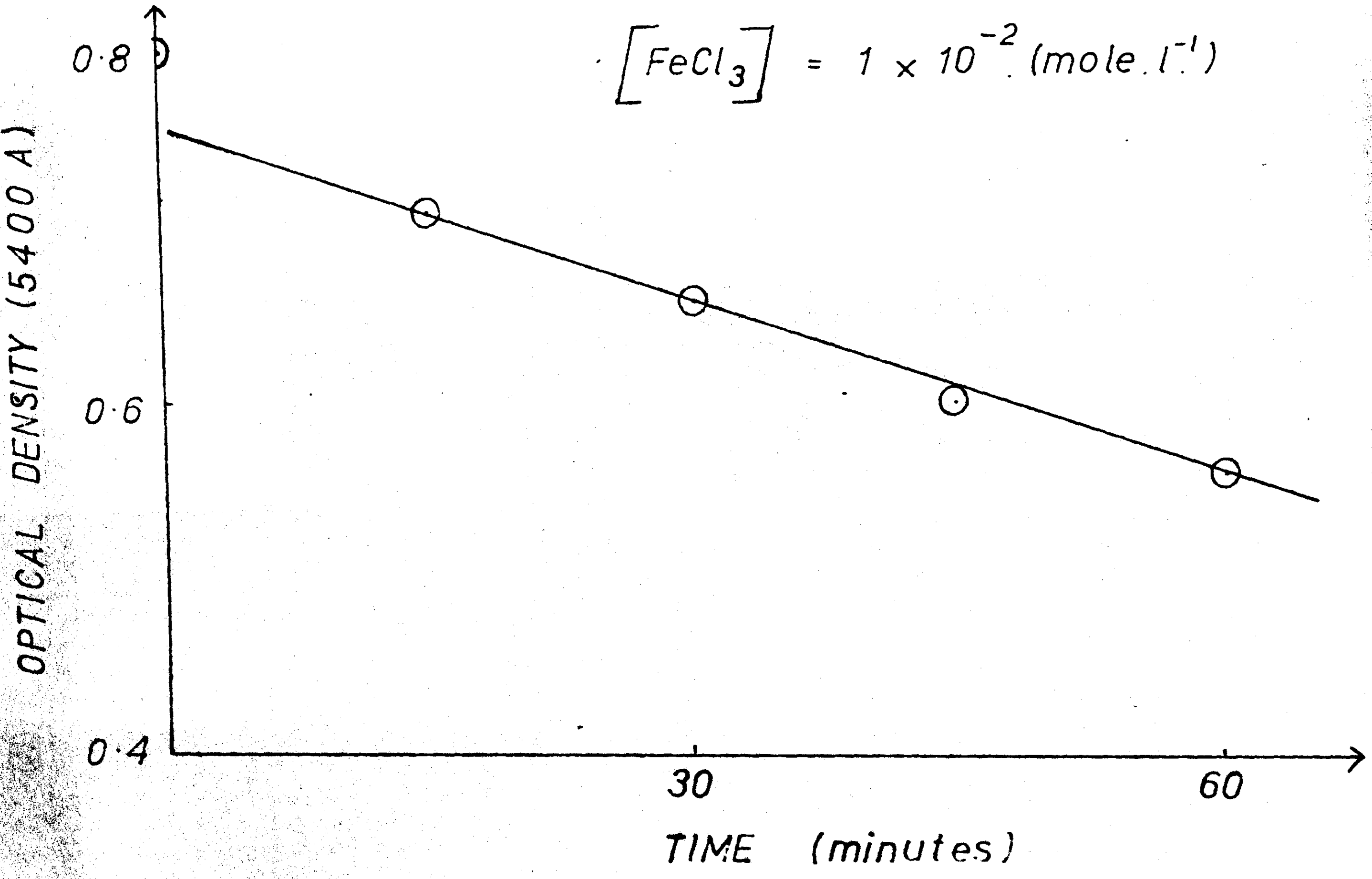
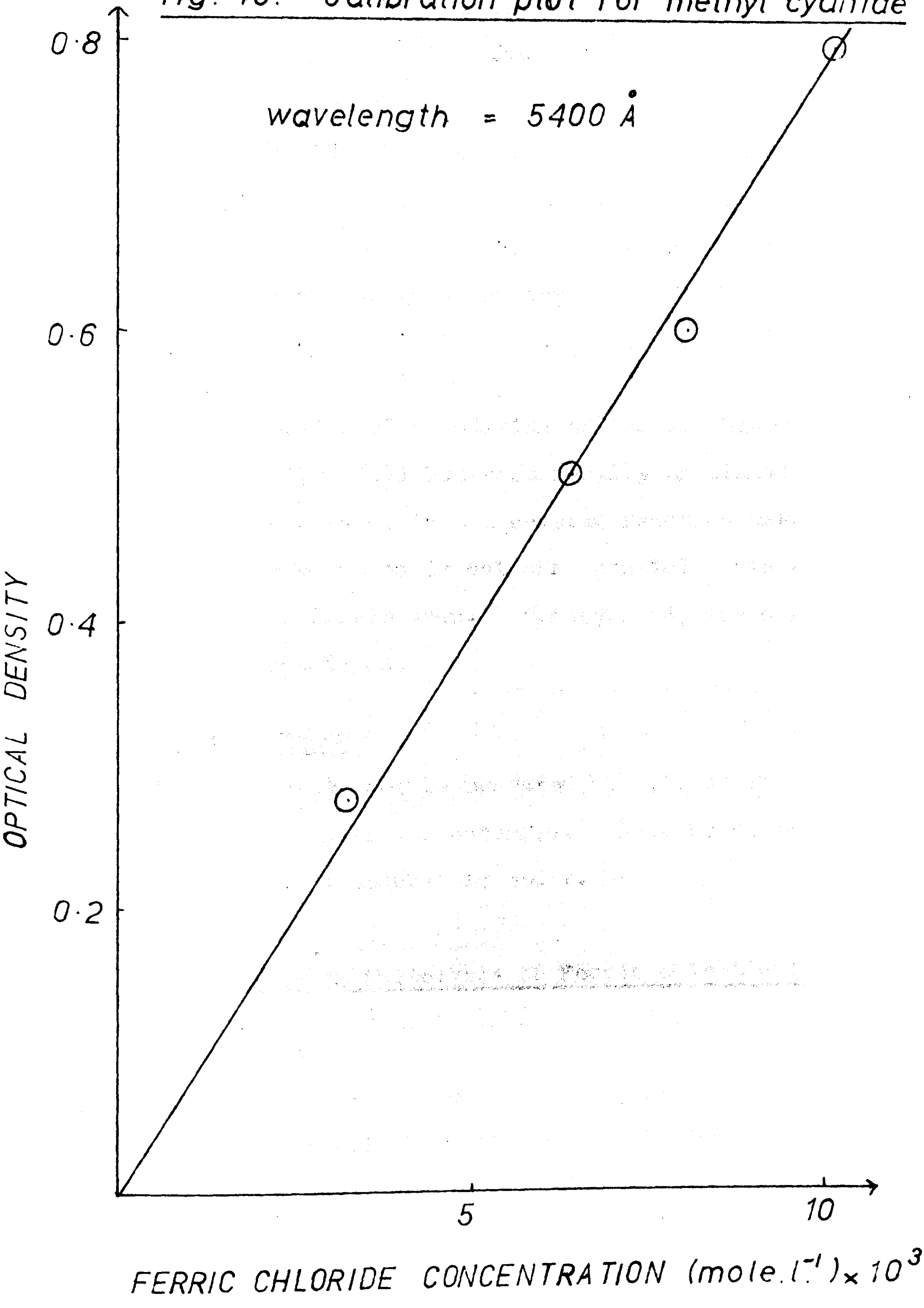


fig. 40. Calibration plot for methyl cyanide



acetate, runs with the cyanide had to be carried out as soon as possible after solutions were made up, as these tend to deteriorate to ferrous. This is detectable by O.D. measurements after a few days.

(d) Acetone

On irradiation of a solution of ferric chloride in acetone, the O.D. fell but rose rapidly on standing. It would appear then, that a reverse reaction takes place when irradiation is cut off, possibly involving reformation of ferric iron. Consequently the use of acetone was abandoned.

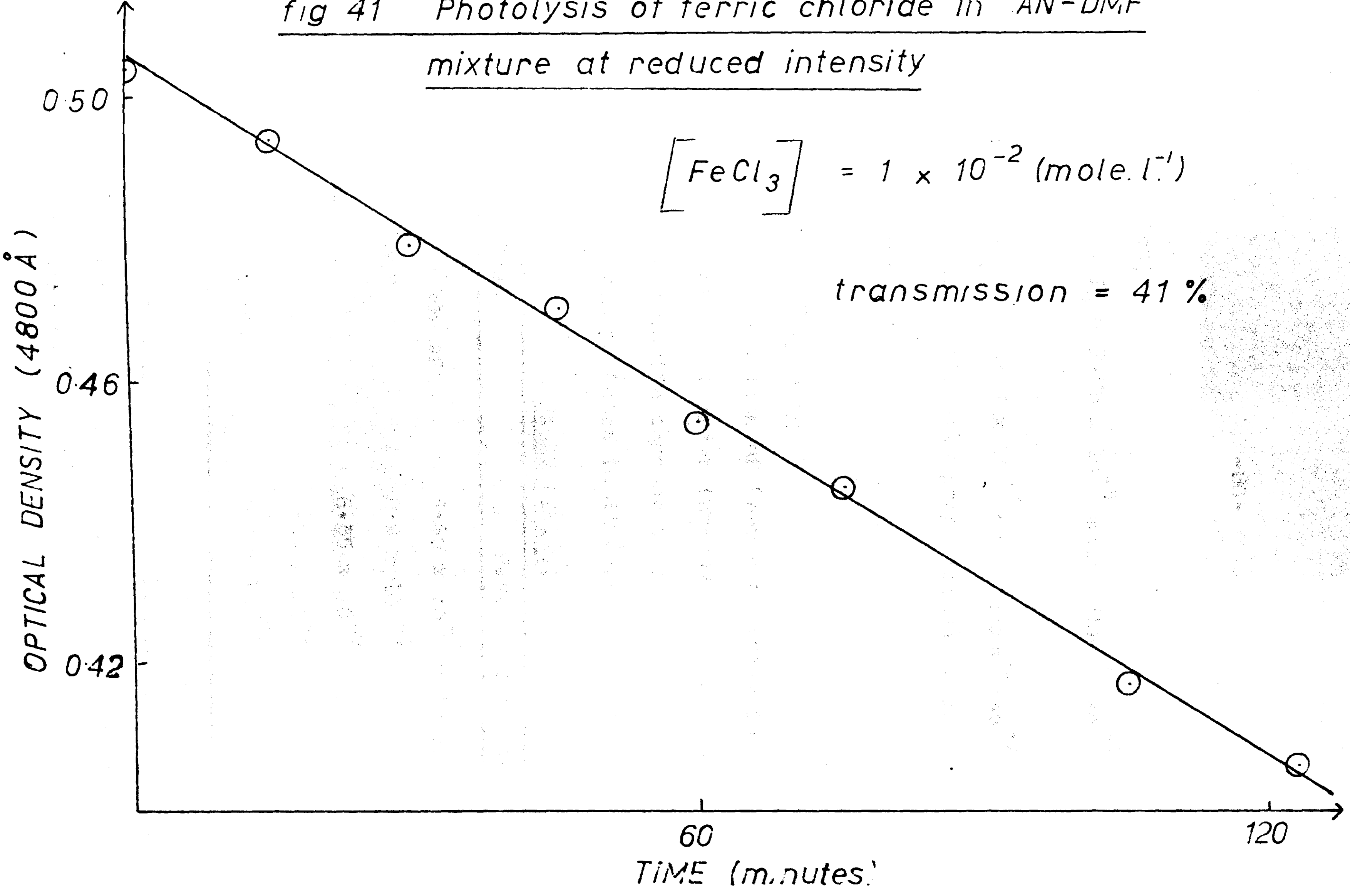
(e) Di-ethyl Ether

The rate could not be measured by O.D. in this solvent as precipitation occurred. Ferrous chloride was found to be insoluble in ether.

9.2.3. Rate of Photolysis of Ferric Chloride in AN:DMF Mixture at Reduced Intensity of Irradiation.

Fig. (41) shows a plot of O.D. v time for irradiation at 41% of full intensity of a solution containing 1 x 10^{-2} mole $litre^{-1}$ ferric chloride and 3·02 mole $litre^{-1}$ (20% by volume) of AN in DMF.

fig 41 Photolysis of ferric chloride in AN-DMF mixture at reduced intensity



From this plot,

Rate at $0{\cdot}41 \times I_o = 2{\cdot}78 \times 10^{-7}$ mole litre^{-1}sec^{-1}

from above,

Rate at $1{\cdot}0 \times I_o = 6{\cdot}67 \times 10^{-7}$ mole litre^{-1}sec^{-1}

Thus $\frac{d[FeCl_2]}{dt}$ is directly proportional to Intensity of irradiation.

9.2.4. Summary of Results

1. Rates of reduction of ferric chloride in the region of first order termination are independent of chloride concentration.
2. Comparison of Rates in different solvents.

TABLE (IX.2.)

Solvent	Rate of Reduction
80% DMF - 20% AN	$6{\cdot}67 \times 10^{-7}$ mole litre^{-1} sec^{-1}
DMF	$8{\cdot}9 \times 10^{-7}$
Ethanol	$8{\cdot}55 \times 10^{-7}$
Ethyl Acetate	$9{\cdot}34 \times 10^{-7}$
Methyl Cyanide	$6{\cdot}8 \times 10^{-7}$

3. The rate of reduction of ferric chloride as estimated by titration is between 50 -60% of that indicated by O.D. measurements.

4. For the expression

$$\frac{1}{2}\frac{d\left[FeCl_2\right]}{dt} = I_n \propto (\text{Intensity})^{x}$$

the value of $x = 1{\cdot}0$

9.3. Discussion

In Chapter 5, it was shown from titrations that the rate of production of ferrous iron was independent of initial ferric chloride concentration, and a rate of initiation was derived from the titrations ($1{\cdot}64 \times 10^{-7}$ mole litre^{-1}sec^{-1}). From the O.D. measurements described in this Chapter, we see that the independence of rate of reduction of ferric chloride on chloride concentration is verified but that the value for I_n derived is just over twice that from titrations ($3{\cdot}34 \times 10^{-7}$mole litre^{-1}sec^{-1}).

This effect is verified by titrations on the actual solutions whose rate of photolysis is being measured by changes in O.D. and the effect is also observed in ethanol and methyl cyanide. In all cases, where the fall in O.D. is linear, the amount of ferrous iron indicated by titration is about 50 - 60% of that by O.D.

Fig. (33) shows that the fall in O.D. decreases almost abruptly long before the rate of production of ferrous iron by titration, which is still linear after 100 minutes.

To find an explanation for this phenomenon is not easy. We know that the titration measurements are reliable since total conversion of ferric to ferrous results in titrations representing the total quantities of iron present. Thus it would not be unreasonable to suppose that the removal of colour represents the reduction of only half the ferric chloride present. This can only be explained by postulating that ferric chloride in non-aqueous media can exist in two forms, one of which is coloured and the other either very faintly coloured or colourless. For example, suppose that on solution of ferric chloride in DMF the complex

$$\left\{\mathrm{Fe}\left[\mathrm{HCON}\ (\mathrm{CH}_3)_2\right]_6\right\}\mathrm{Cl}_3$$

is formed, and that this can react further with DMF according to the reversible reaction:-

$$\left[\mathrm{Fe(DMF)}_6\right]\mathrm{Cl}_3 + \mathrm{DMF} \rightleftharpoons \left[\mathrm{Fe(DMF}_6)\right]\begin{matrix}\mathrm{Cl}_2\\ \mathrm{DMF(-H)}\end{matrix} + \mathrm{HCl}$$

Let us also suppose that

(i) the equilibrium is such that approximately 50% of the chloride is in each form

(ii) the equilibrium is a very slow one

(iii) one form is coloured, the other colourless

(iv) finally, one form is preferentially reduced.

Such a system would explain the results as shown in Fig. (33). Where the linear fall in O.D. ceases would mark roughly the growing importance of photolysis of the colourless species.

As an alternative to the above, the forms might be $\left[Fe(DMF)_6\right]Cl_3$ in conjunction with ferric chloride unassociated with solvent. Again, $FeCl_3$ might be the coloured form in conjunction with a colourless dimer Fe_2Cl_6.

It has been found that the rate of photolysis of ferric chloride in pure DMF is 30% greater than in solutions containing 20% AN. The effect of altering the monomer concentration was examined to see whether a ferric - AN complex is the controlling influence here or whether reduction of ferric chloride involves contributions from ferric - AN and ferric - DMF complexes such that lowering of AN concentration, in lowering the proportion of ferric - AN complex reacting, would raise the rate of photolysis towards the value in pure DMF. The results are mixed. The rate with only 5% AN is much nearer the value in pure DMF than in 20% AN solutions, yet there appears to be a point where increasing the AN concentration does not alter the rate since this is the same in 30% AN solution as in 20%.

In plotting the fall in O.D. with time of irradiation for solutions of ferric chloride in ethanol, ethyl acetate and methyl cyanide, it is observed that between 0 and 15 minutes a large drop occurs in O.D. followed by a linear fall. In each case the rate taken is the linear one, and no attempt is made to explain the high initial O.D. reading. This effect was generally not observed with solutions in DMF.

From Table (IX.2.) it can be seen that the rate of reduction for all solutions of ferric chloride examined lies between

$$6{\cdot}67 \times 10^{-7} \text{ and } 9{\cdot}34 \times 10^{-7} \text{ mole litre}^{-1}\text{sec}^{-1}.$$

Thus rates in different solvents are very much of the same order which suggests strongly that the initial reaction involves simply the fracture of an iron-chlorine bond, the process being represented by the simple equation:-

$$FeCl_3 \xrightarrow{h\nu} Cl + FeCl_2$$

The energy associated with irradiation of wavelength 3650Å is about 78 kcal mole^{-1} which compares favourably with published estimates of the Fe-Cl bond strength in ferric chloride (48).

Slight differences in rate, as are obtained, may be due to the effects of different ligands in complexes. Some of these will be more ready to donate electrons than others. The ligands will form co-ordinate bonds of varying strengths and will occupy different volumes around the iron nucleus and the ease with which charge transfer occurs might well be influenced by such factors.

On the other hand, these small differences may be bound up in rates of reactions subsequent to the primary photolysis. In the photolysis of ferric chloride in AN - DMF mixtures, half the chloride reduced is from reaction with a polymer radical, and, since the rate of reduction in other solvents is approximately the same as in the polymerization reaction, it is not unreasonable to assume that a similar system will exist in absence of monomer. For example in pure solvents, the system may be represented by the following scheme:-

$$FeCl_3 \xrightarrow{h\nu} Cl + FeCl_2$$

$$Cl + Solvent \longrightarrow S + HCl \qquad \ldots.(IX.1.)$$

$$S + FeCl_3 \longrightarrow S\,Cl + FeCl_2 \qquad \ldots.(IX.2.)$$

where S represents a radical derived from the solvent. (The chlorine atoms formed could combine but they are more likely to attack the solvent provided the activation energy for this process is not too high). The rate of reaction (IX.1.) will depend on the reactivity of the solvent to chlorine atoms, while the termination step (IX.2.) will depend on the reactivity of the solvent radical and also on the reactivity of ferric chloride as the ferric chloride - solvent complex. Either of these reactions may be rate determining.

A considerable number of factors then, may be responsible for the slight differences in the total rate of reduction of ferric chloride found in different solvents.

With regard to the nature of ferric chloride in AN - DMF mixtures, Bamford et. al. (29) have shown that the reactivity of the salt to polyacrylonitrile radicals produced in the thermosensitized bulk polymerization of AN is greatly reduced on the addition of a trace of DMF, and the same effect has been observed in this laboratory for the ferric chloride photosensitized reaction. It would appear that the effect is due to very strong complexing between ferric chloride and DMF such that, in solutions containing 20% AN in DMF all the chloride will exist as the DMF complex. Thus the primary photolysis of ferric chloride in 20% AN - 80% DMF mixtures (and in pure DMF) will be identical, yet the rate of reduction of the chloride in the former solution is lower than in the latter. This difference in rate must be associated then, with a reaction subsequent to the initial photolysis, and the difference in reactivity of the macromolecular polyacrylonitrile radicals and those derived directly from DMF may well be responsible.

Finally, as expected, the rate of formation of ferrous iron in AN - DMF mixture was found to be directly proportional to the intensity of irradiation.

CHAPTER 10.

Ultra-Violet Spectra of Ferric Chloride Solutions

With a view to obtaining information on the nature of ferric chloride in non aqueous solutions, and on the process whereby irradiation of these solutions yields free radicals, the ultra-violet spectra of the chloride in a range of solvents have been examined, and, where possible, compared with the spectra of solutions after irradiation.

10.1. Experimental

10.1.1. Apparatus

All u.v. spectra were obtained on a Unicam "Optica" spectrophotometer. Matched cells of 1 cm. thickness were used, and in each case the blank cell contained the solvent being examined.

10.1.2. Measurements

The spectra of ferric chloride between 2000Å and 4000Å were measured in the following solvents:-

AN, DMF, Methyl Cyanide, Ethanol, Ethyl Acetate, Diethyl Ether, Acetone and Water.

The spectra of ferric chloride between 2000Å and

4000Å after irradiation at 3650Å for periods of approximately 30 minutes - sufficient to convert most of the ferric to ferrous - were measured in the following solvents:-

DMF, Methyl Cyanide, Ethanol and Ethyl Acetate. Since solutions of ferrous iron in DMF and ethanol are oxidised by air, these spectra were measured immediately on opening reaction vessels. Solutions of ferric chloride in ethyl acetate and methyl cyanide have a slow tendency to go to ferrous even in air, so these are much less likely to be oxidised on opening vessels.

This experiment could not be carried out for solutions of ferric chloride in water, (difficulty in degassing), acetone, (unreliable O.D. readings), ether, (ferrous chloride precipitation), or AN, (heterogeneous polymerization).

Because of the high extinction of ferric chloride, low concentrations must be used. Generally solutions contained about 10^{-4} mole litre^{-1}.

10.2. Results

The spectra are shown in Figs. (42) to (49) and Fig. (50) is a comprehensive diagram illustrating the

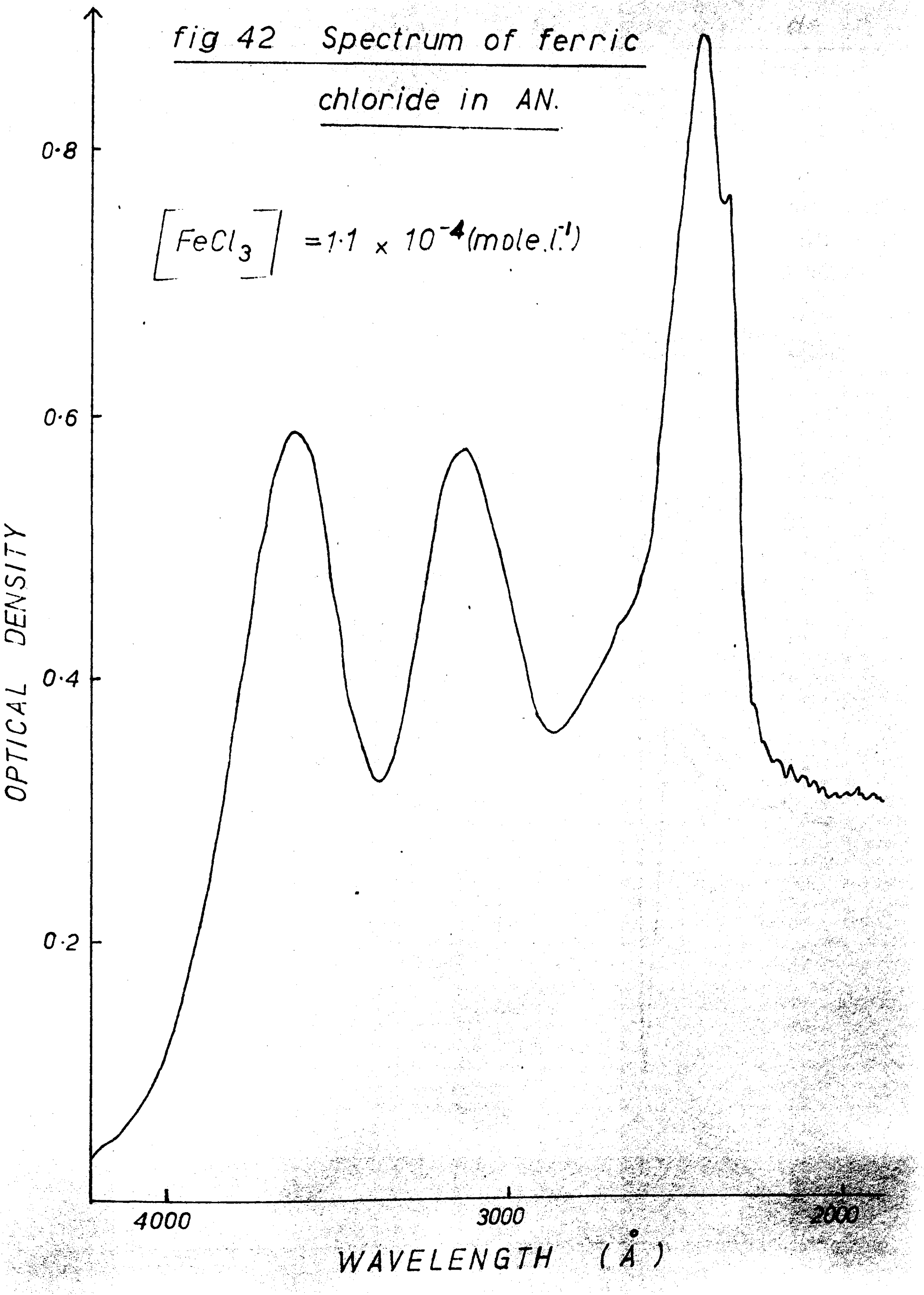
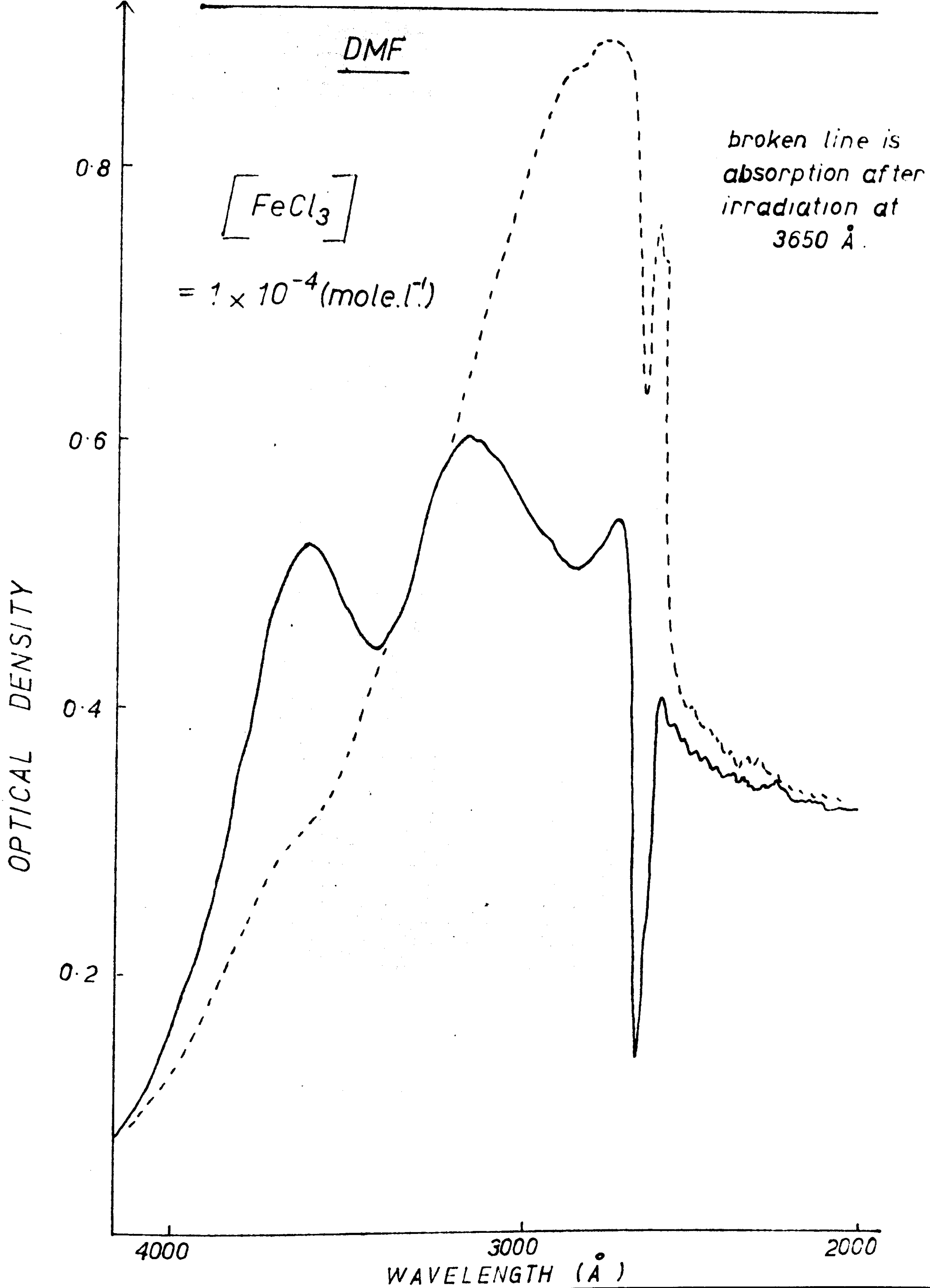


fig 42 Spectrum of ferric chloride in AN.

$[FeCl_3] = 1{\cdot}1 \times 10^{-4}$ (mole.l^{-1})

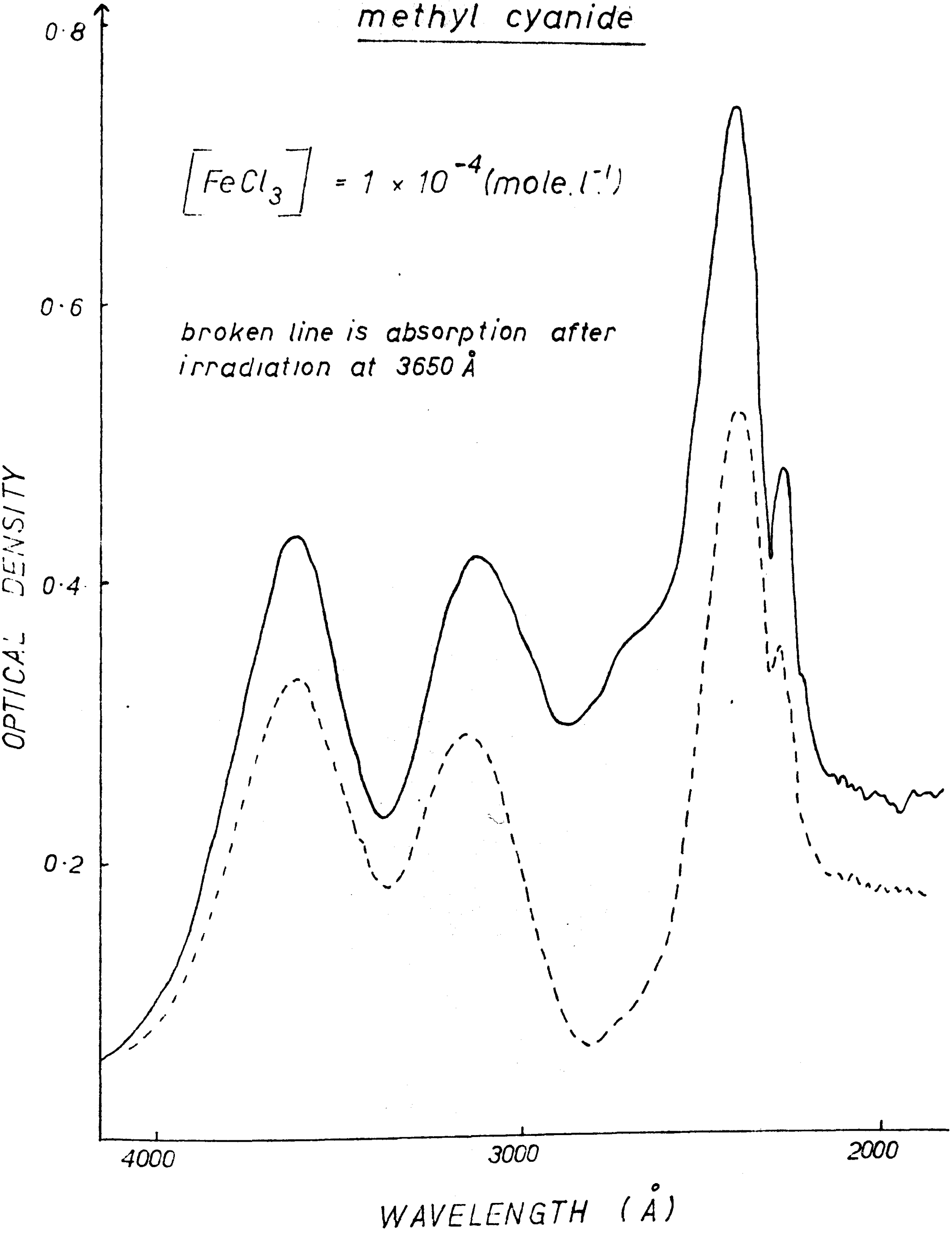
fig. 43. Spectrum of ferric chloride in DMF



$[FeCl_3] = 1 \times 10^{-4} (mole.l^{-1})$

broken line is absorption after irradiation at 3650 Å.

fig. 44. Spectrum of ferric chloride in methyl cyanide



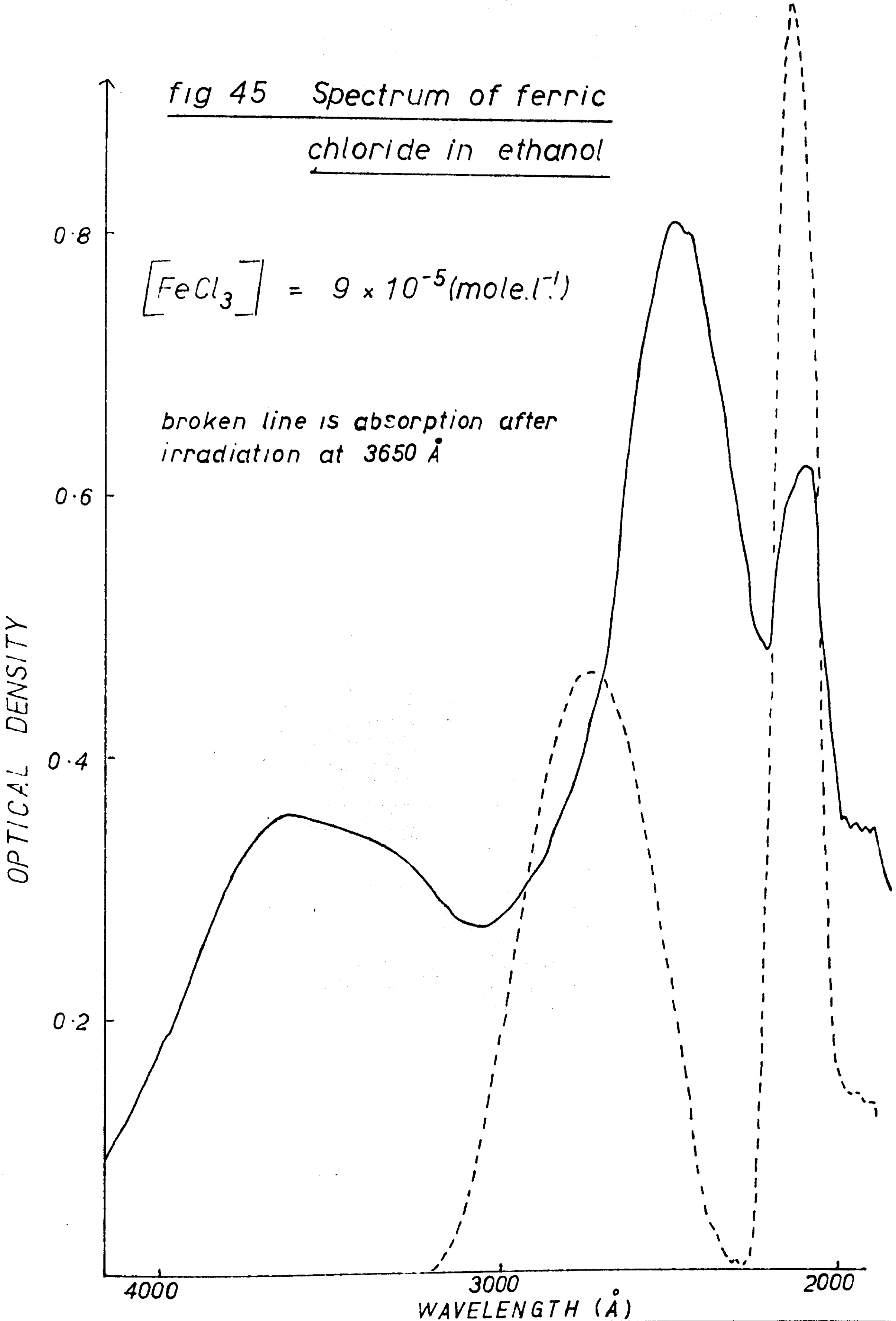


fig 45 Spectrum of ferric chloride in ethanol

$[FeCl_3] = 9 \times 10^{-5} (mole.l^{-1})$

broken line is absorption after irradiation at 3650 Å fig 46 Spectrum of ferric chloride in ethyl acetate

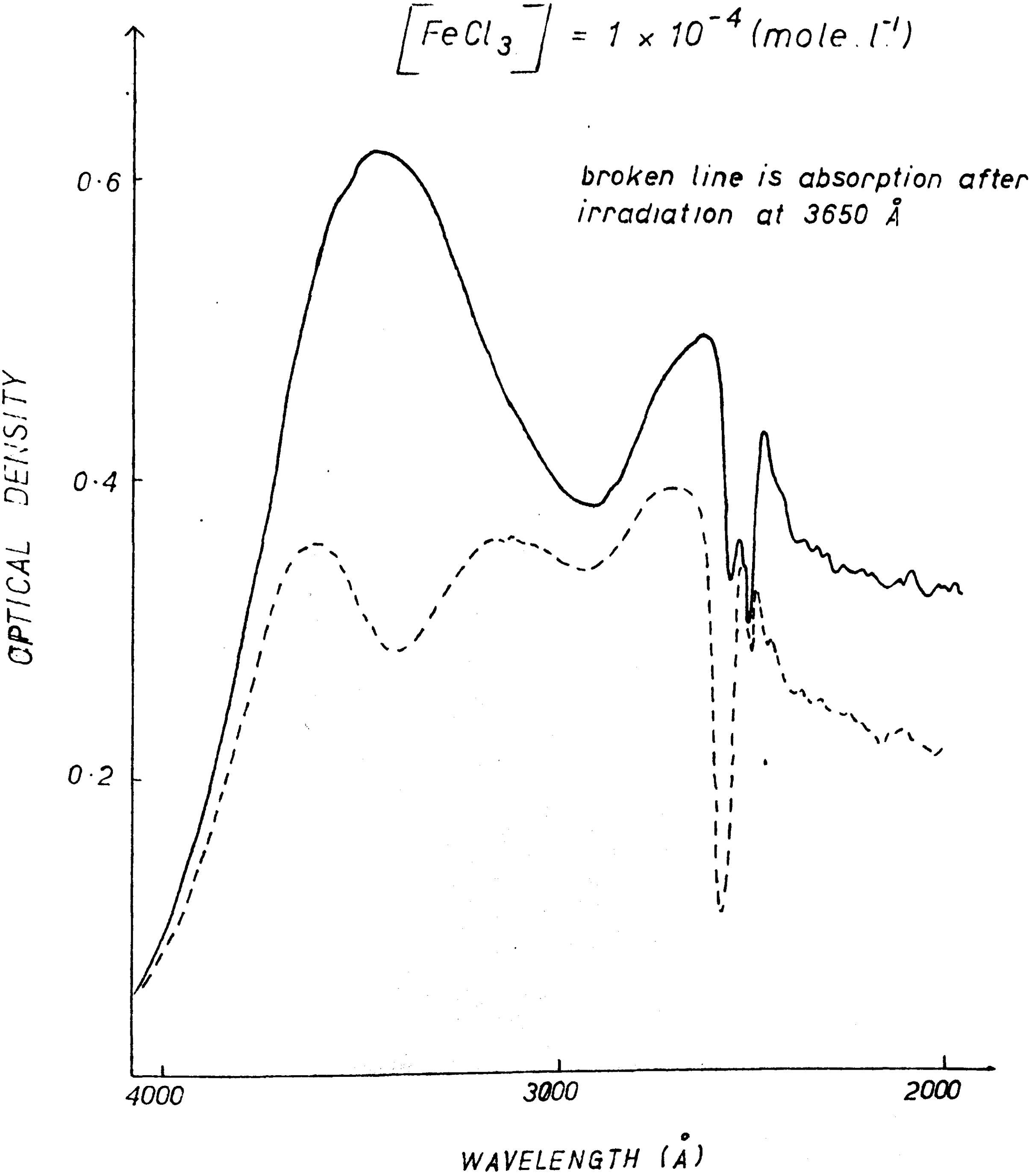


fig. 47. Spectrum of ferric chloride in di-ethyl ether

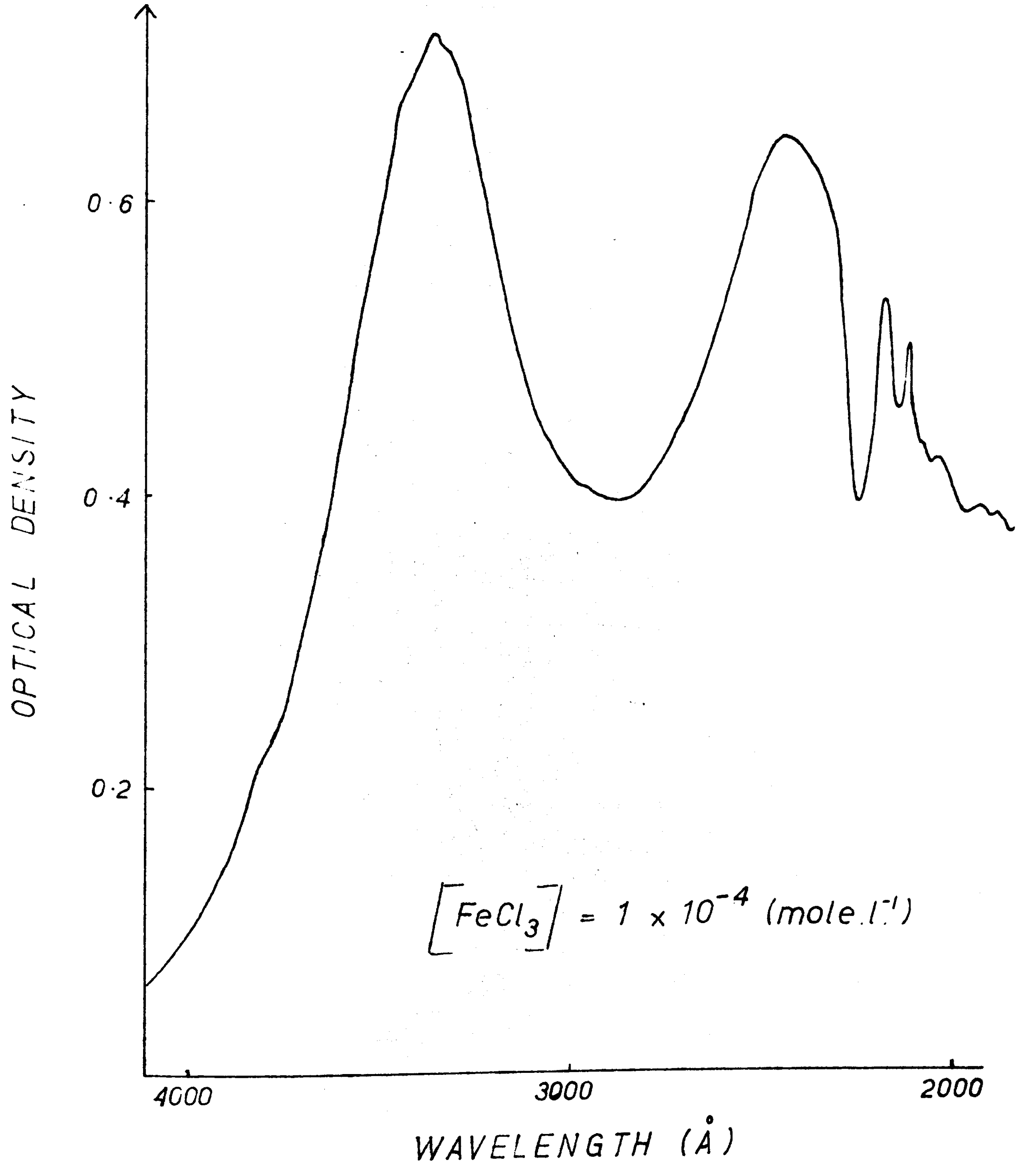


fig. 48. Spectrum of ferric chloride in acetone

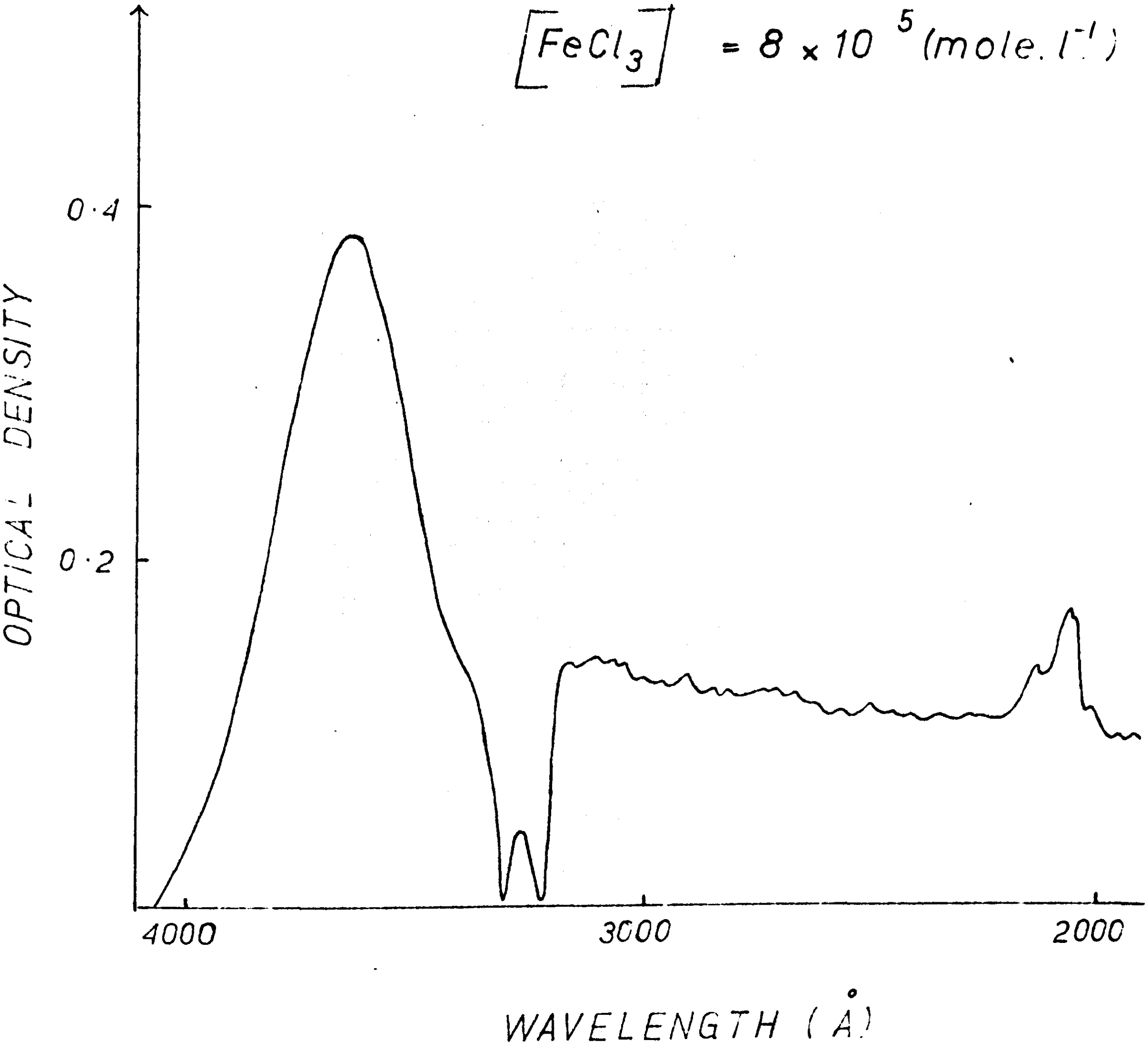


fig. 49. Spectrum of ferric chloride in water

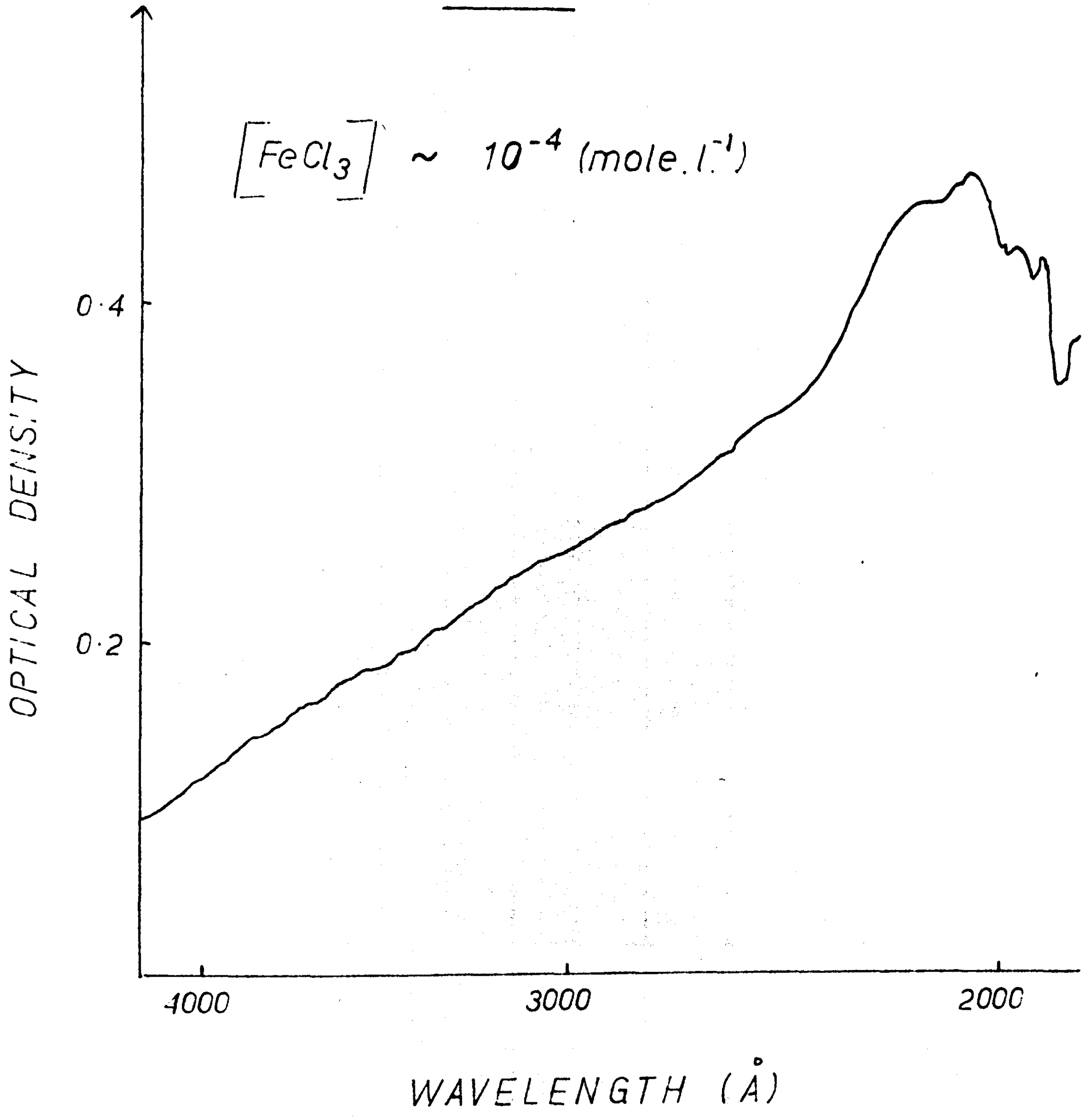
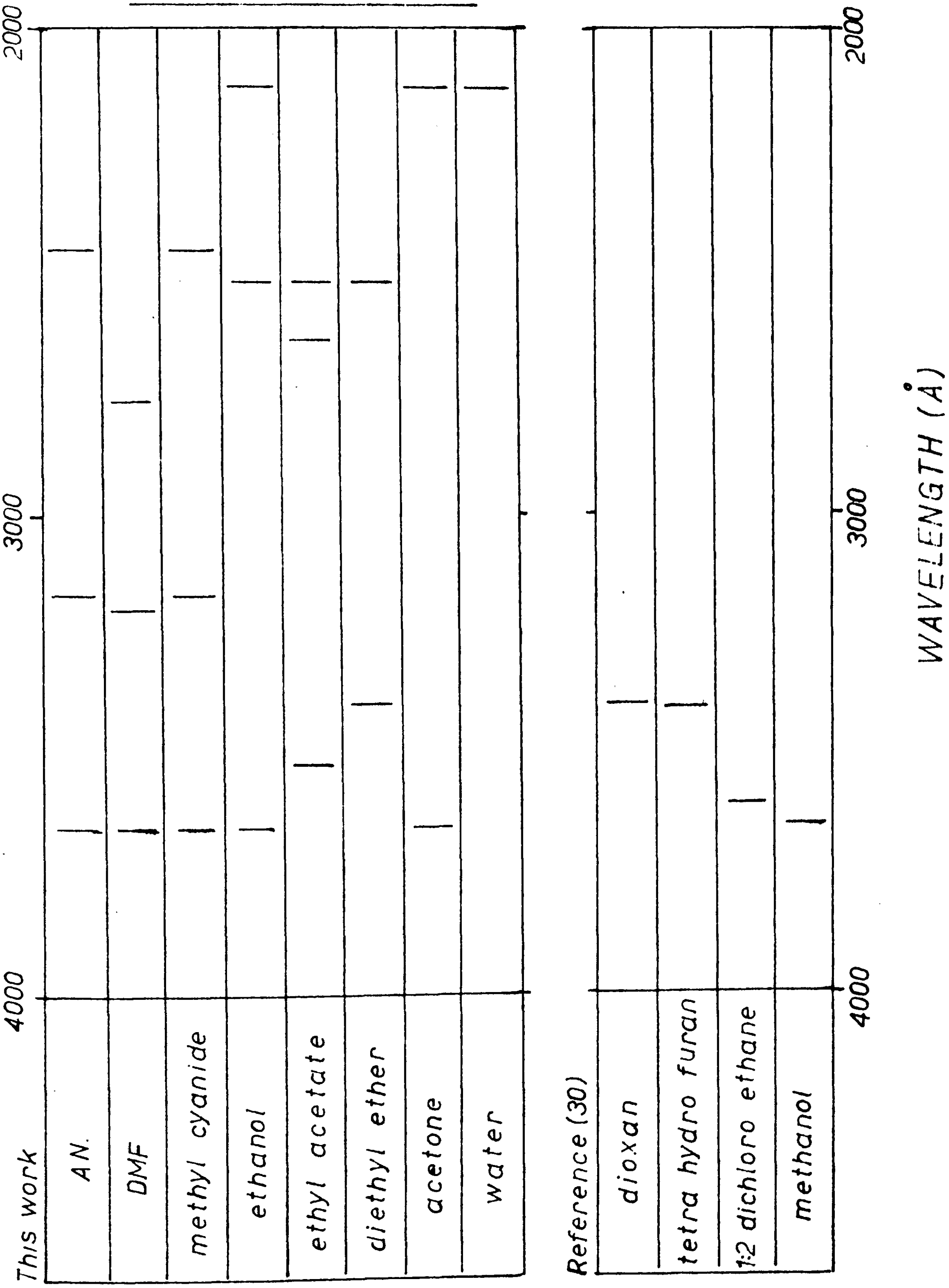


fig. 50. Location of peaks for main bands of absorption in u.v. specra of ferric chloride solutions



positions of the peaks of the main bands of absorption for the solutions examined together with those for four solutions examined by Cherniak et. al. (30).

10.3. Discussion

The fact that the u.v. spectra of ferric chloride in different solvents shows considerable differences is strong evidence for complex formation between the chloride and at least some of the solvents examined. Fig. (50) shows the position of the peaks for the main bands of absorption of 12 ferric solutions. The most striking feature of the region of absorption between 3000 to 4000Å is that solutions of ferric chloride in ether, dioxan, and tetrahydro furan have one band of absorption at approximately 3400Å while all other solutions except ethyl acetate have a band at approximately 3650Å, and in the case of AN, the methyl cyanide and DMF an additional band at about 3150Å. Solvents such as ether, dioxan, and tetrohydro furan are not usually electron donors and consequently it seems fairly safe to postulate that solutions in these solvents are not complexes, and that a peak at 3400Å indicates absorption by uncomplexed ferric chloride. If this is so, then complex formation in other solvents is accompanied by a shift to about 3650Å in the case of ethanol, methanol, acetone and 1:2 dichloro ethane, and by separation into two peaks at about 3650Å and 3150Å in the case of AN, methyl cyanide, and DMF. Thus all solvents suspected of forming complexes with the chloride have a common peak at about 3650Å.

Observation of the spectra of ferric chloride in DMF and ethanol after irradiation show that this common peak is removed while that in methyl cyanide, (shorter period of irradiation) diminishes. Irradiation of complex solutions of ferric iron results in reduction to ferrous, so it would appear that the absorption at 3650Å is due to charge transfer presumably from chlorine to iron.

These observations would appear to indicate that complexing is accompanied by a shift of the iron-chlorine bond absorption to <u>higher</u> wavelengths, such that charge transfer would occur more readily in the presence of complex bonding. This might be explained in terms of steric effects; the Fe-Cl distance is presumably greater where the iron has a co-ordination sphere such that the potential energy associated with the bond radius is raised.

These reflections are contrary to the now accepted view that complex formation stabilises a molecule to processes involving charge transfer. In Chapter 9. it was seen that ferric chloride in complexing solvents probably exists in two forms and apart from this, it must be admitted in all fairness that little is known of the spectra of complex molecules in the charge transfer region. Workers in this field maintain that any conclusions from such spectra must be drawn with great reservation, and consequently, no attempt is made here to elaborate on the interpretation of this apparent shift to higher wavelength, beyond stating that the value of the quantum necessary for reduction of ferric chloride appears to be very similar in all complexes indicating that production of free radicals primarily involves cleavage of the iron-chlorine bonds common to all solutions.

Commenting on individual spectra, those of ferric chloride in AN and methyl cyanide are almost identical. The narrow bands of high absorption at 2450Å are not shared by any other solution, and must be due to absorption by complex bonding between the iron and cyanide nitrogen atoms. The spectrum in DMF is similar to that in solutions containing the CN group, and very different from that in ethyl acetate. This might be taken as evidence that DMF complexes via the amide nitrogen atom, but the spectrum in ethyl acetate is unique in that the main peak is at approximately 3500Å. After irradiation of ferric chloride in the acetate, a spectrum is obtained very similar indeed to that in DMF, and this spectrum is probably characteristic of complexing via the carbonyl oxygen atoms which exist in both DMF and the ester. To explain why the acetate solution only shows this spectrum after a period of irradiation, we must invoke the theory that two species of ferric chloride exist in this solution, one of which is not complexed, and that this form is preferentially reduced. (This would in fact mean that complexing stabilises the ferric chloride molecule). Thus DMF probably does donate via the oxygen atom as postulated by Nortia (42) and Muetterties (49).

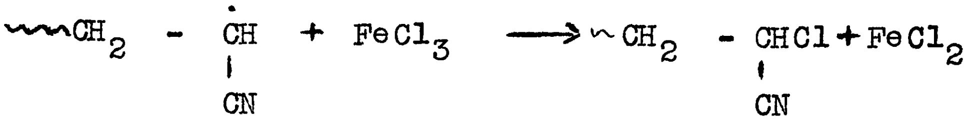
CHAPTER 11.

Radioactive Tracer Studies; (^{36}Cl) - Labeled Ferric Chloride as Photoinitiator.

By the use of radioactive isotopes as tracers a great deal of interesting information can be obtained relating to the mechanisms and extents of chemical reactions. The method is particularly advantageous because amounts of isotopes can be detected and estimated which are so small as to be beyond the limits of chemical analysis.

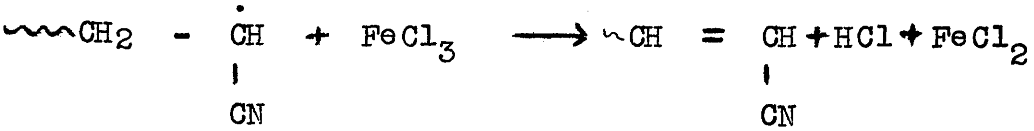
In polymerization reactions, work in this field has generally been confined to ^{14}C studies. For example, (^{14}C) - labeled azobisisobutyronitrile catalyst has been used by Arnett and Peterson in the determination of efficiencies of initiation (50), and by Bevington, Bradbury and Burnett (51) in the measurement of kinetic chain lengths.

With regard to the present work, it was reckoned that if ferric chloride could be prepared from pure iron and the readily available ^{36}Cl radioactive isotope of chlorine, this could be used as the photoinitiator in the polymerization of AN in DMF, and, provided the activity could be easily detected and measured, information relating to the mechanisms of the initiation and termination reactions might be obtained. It might, for example, be possible to establish whether the initiation step involves attack of monomer units by chlorine atoms on measurement of the activity in the polymer formed in the region of ferric concentration where termination is second order with respect to radical concentration. In the region of first order termination, it should be possible to establish whether termination involves addition of chlorine atoms (XI.1.) or abstraction of hydrogen atoms (XI.2.).



$$\sim\!\sim CH_2 - \underset{\displaystyle CN}{\underset{|}{\overset{\bullet}{C}H}} + FeCl_3 \longrightarrow \sim CH_2 - \underset{\displaystyle CN}{\underset{|}{CHCl}} + FeCl_2$$

....(XI.1.)



$$\sim\!\sim CH_2 - \underset{\displaystyle CN}{\underset{|}{\overset{\bullet}{C}H}} + FeCl_3 \longrightarrow \sim CH = \underset{\displaystyle CN}{\underset{|}{CH}} + HCl + FeCl_2$$

....(XI.2.)

If both occur, the relative rates of these reactions might be determined.

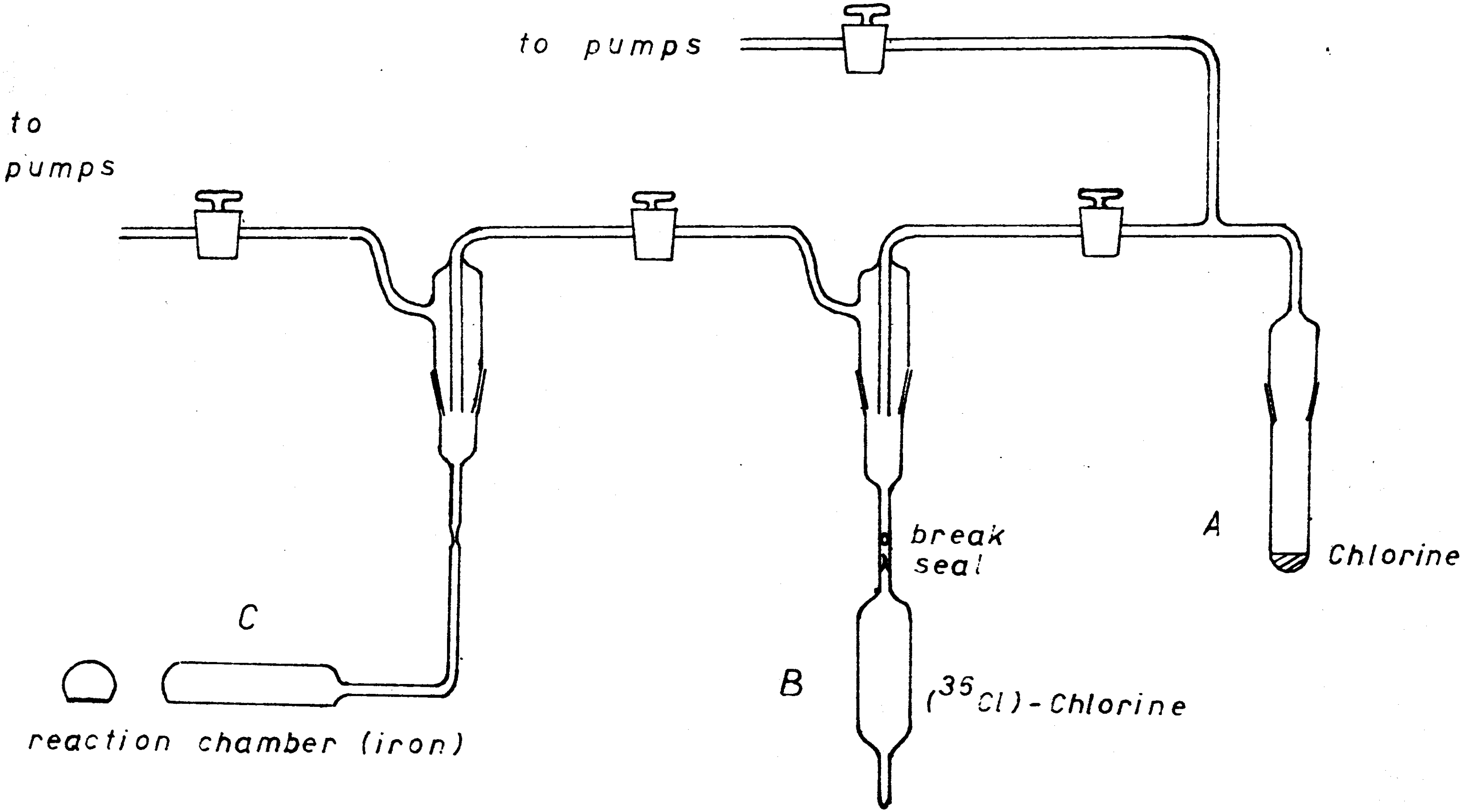
Unfortunately lack of time has decreed that the present study be confined to qualitative work though it is hoped that tentative quantitive statements might be made from the results obtained.

11.1. (^{36}Cl) - Chlorine

The isotope is supplied in 50 ml. samples containing - c.a. 50 μ.c. of activity. Samples generally contain c.a. 40 μ.c. per mM. such that at N.T.P. the volume is c.a. 25 ml. and the pressure in the sample vessel c.a. $\frac{1}{2}$ atmospheric. The isotope emits β particles of energy 0·71 Mev.

11.2. Preparation of Radioactive Ferric Chloride

The following procedure was found to produce lustrous deep purple crystals of anhydrous radioactive ferric chloride without the occurrence of side reactions encountered in Chapter 2. Ordinary chlorine was twice distilled under vacuum from -78°C, (Drikold-acetone), to -200°C, (liquid nitrogen), and allowed to stand overnight over calcium chloride in a 1 litre round bottomed flask at about $\frac{3}{4}$ of an atmosphere pressure, then distilled into vessel A shown in Fig. (51). The 50 ml. sample of (^{36}Cl) - chlorine, (vessel B), and the reaction vessel containing an even layer of A.R. iron filings, (dried overnight at 40°C), were attached to the vacuum line. Chlorine was allowed to diffuse into B and C by keeping A at -38°C for about 15 minutes, and A shut off thus incorporating chlorine at almost fig 51 Vacuum apparatus for preparation of radioactive ferric chloride



atmospheric pressure into C and the space above B. B was now broken open and all the chlorine in B and C frozen and thawed twice in B to ensure complete mixing of the radioactive chlorine with the ordinary chlorine. The iron was now heated very gently and crystals of ferric chloride containing (Cl^{36}) - chlorine were formed. The vessel was sealed off and small amounts of unreacted iron were carefully drawn from the reaction chamber with a very strong magnet. The crystals were stored in a dry vessel with a tight fitting lid.

Note:- Heating must be very gentle as overheating can cause the formation of ferrous chloride particularly when the chlorine pressure is becoming low.

The (^{36}Cl) - chlorine is diluted with ordinary chlorine to provide a sufficient quantity of chlorine at a sufficiently high pressure to provide a good yield of ferric chloride.

In the foregoing sections, the crystals obtained by the above procedure, which will contain ordinary ferric chloride as well as radioactive, will be referred to as "active ferric chloride".

11.3. Experimental

11.3.1. Apparatus

For activity measurements a scintillation counter, with a linear pulse amplifier and a pulse height selector, (all supplied by Nuclear Enterprises Ltd.), were used in conjunction with a Dynatron scaler.

The conditions used for counting were as follows:-

Gain = 1250 times
Pulse height = 30 volts
Gate width = 20 volts
E.H.T. = 1·35 K volts

The scintillator consisted of a mixture of 3 gm. litre^{-1} of 2:5 diphenyl oxazole, (P.P.O.) and 0·1 gm. litre^{-1} of 1:4 bis (2 -(5 phenyl oxazole)) - benzene, (P.O.P.O.P), in toluene.

11.3.2. Measurements

Polymerizations of 3·02 mole litre^{-1} (20% by volume) of AN in DMF at concentrations of 2 x 10^{-4} mole litre^{-1} and 5 x 10^{-3} mole litre^{-1} of the radioactive ferric chloride were carried out, and these were repeated for the same concentrations of ordinary ferric chloride. The runs at 2 x 10^{-4} mole litre^{-1} ferric were taken to completion while those at 5 x 10^{-3} mole litre^{-1} were stopped after 180 minutes irradiation.

Polymers were precipitated in methanol, filtered through sintered glass crucibles, (porosity 4), washed with methanol and dried at 80°C. Solution in DMF followed by reprecipitation was carried out twice to ensure removal of all active ferrous chloride and any unreacted active ferric chloride.

In each case, the entire sample of polymer obtained was dissolved in DMF and added to the toluene solution containing the scintillator, (precipitation of the polymer does not occur), and the resultant solutions were used for counting.

The activity of the polymers obtained from active catalyst were measured and compared with that from ordinary catalyst for each of the ferric concentrations used and the activity of a solution of active ferric chloride was measured and compared with that of ordinary ferric chloride.

11.4. Results

Experiment A. $\left[FeCl_3\right] = 2 \times 10^{-4}$ mole litre^{-1}

Volume of reaction vessels = 15 ml. and reaction was taken to completion. Therefore total ferric chloride converted to ferrous = 3×10^{-6} moles

Activity found in polymer (counts per sec.)

Solution	-	3·66	± 3%
Blank	-	0·46	± 10%

Experiment B. $\left[FeCl_3\right] = 5 \times 10^{-3}$ mole litre^{-1}

Volume of reaction vessel = 15 ml. Reaction was stopped after 180 minutes, and from the titration-time data for vessels of volume 13 ml. shown in Fig. (21) it is seen that this is equivalent to a conversion of $4{\cdot}5 \times 10^{-5}$ moles of ferric chloride in a 15 ml. vessel.

Activity found in Polymer (counts per sec.)

Solution	-	344·0	± 1%
Blank	-	0·59	± 10%

Experiment C.

For comparison with Experiment A above, the activity of a solution containing 1×10^{-6} moles of active ferric chloride was measured. This would have the same activity as the polymer from conversion of 3×10^{-6} moles of ferric chloride if it is assumed (a) that each truly active ferric chloride molecule contains one active chlorine atom - a very reasonable assumption under the conditions of preparation of the chloride, and (b) that one chlorine atom is incorporated in the polymer from the initiation process for each molecule of ferric chloride reduced, i.e. ignoring termination by the chloride at this low concentration.

Activity from 1 x 10^{-6} moles active ferric chloride

Solution	-	124	± 1%
Blank	-	0·41	± 10%

11.5. Conclusions

(i) Chlorine from Initiation step; comparing results from Experiment A with those from Experiment C, it is seen that the ratio

$$\frac{\text{Activity in polymer from conversion of } 3 \times 10^{-6} \text{ moles active ferric chloride}}{\text{Activity from } 1 \times 10^{-6} \text{ moles active ferric chloride}}$$

$$= \frac{3{\cdot}66}{124}$$

$$= 2{\cdot}95\%$$

Thus little or no chlorine is incorporated in the polymer in polymerizations initiated with 2 x 10^{-4} mole litre^{-1} ferric chloride.

(ii) Chlorine from termination; from Experiment B the total ferric chloride converted is 4·5 x 10^{-5} moles.

Starting with the assumptions

(a) that half the active chlorine from the reduction of this number of moles of the active ferric chloride is lost in the initiation step, (conclusion (i),)

(b) that, as before, only one third of the active chlorine atoms available react in the termination step, and (c) that one chlorine atom is incorporated in the polymer for each molecule of ferric chloride reduced due to the reaction (XI.1.),

the activity which should be present in polymer B is that equivalent to $\frac{4\cdot5 \times 10^{-5}}{6} = 7\cdot5 \times 10^{-6}$ moles of active ferric chloride.

From Experiment C,

Activity $\equiv$ 1×10^{-6} moles active ferric chloride
$=$ 124 counts per second.

Therefore Activity $\equiv$ $7\cdot5 \times 10^{-6}$ moles active ferric chloride $=$ 930 counts per sec.

Activity found in Experiment B $=$ 344 counts per sec.

$$\text{Percentage} = \frac{344}{930} \times 100 = 37\%$$

Thus it might be concluded that termination by (XI.2.) is of greater importance than that by (XI.1.).

11.6. Discussion

It must be emphasised that the conclusions outlined above are put forward very tentatively in view of the few experiments carried out. Nevertheless it does seem safe to say (i) that no chlorine atoms react directly with monomer units in the initiation process, (the small amount of chlorine, c.a. 3% of expected, indicated in the polymer might well be the result of first order termination at 2 x 10^{-4} mole $litre^{-1}$ ferric), and (ii) that at least some termination by reaction (XI.1.) occurs.

That chlorine atoms do not react directly with monomer is at first sight surprising, but at the high concentrations of DMF present the atom might well react preferentially with solvent such that a solvent radical is the effective polymerization initiator. Certainly abstraction of hydrogen by chlorine from the monomer is possible but hardly likely in the absence of any addition to the monomer. Evans and Uri claimed that chlorine analysis and molecular weight determination on polymethylmethacrylate produced photochemically with the aqueous $Fe^{3+}Cl^{-}$ ion pair indicated that each polymer chain was initiated directly by chlorine radicals, (16). The system, of course, for methylmethacrylate in aqueous solution might be very different from that of AN in DMF solution, but as Dainton and Tordoff (26) have pointed out, the ferric concentrations used by Evans would almost certainly result in a considerable proportion of first order termination. Apart from this, chlorine analyses, especially in the small proportions found in high polymers should be interpreted with reservation.

A more rigorous study of the region of ferric concentration where termination is effected by the salt might show that, in fact, all termination involves transfer of a chlorine atom to the polymer radical. Entwhistle maintains that this is the case, (again from chlorine analysis and molecular weight determination), but it is considered that tracer experiments of the type outlined above might provide more conclusive evidence for the mechanism of this reaction. Certainly the (^{36}Cl) - isotope of chlorine is very easily detected even at low concentrations, and, with the high counts obtained, background counts are negligible, and it should not be too difficult to obtain sound quantitative estimations of chlorine in products of reaction with ferric chloride.

CHAPTER 12.

General Discussion

The previous chapters contain discussions of the individual experimental results obtained. In this chapter the significance of these results in relation to each other and to a general kinetic scheme for the polymerization of AN in DMF solution photoinitiated and terminated by ferric chloride is considered.

Considerable information relating to the nature of ferric chloride in non aqueous media has been amassed. Bamford et. al. (29) and McIntosh (41), postulated that the chloride complexes strongly with DMF and Nortia (42) has recently described complexes of the type $\left[M(DMF)_6\right](ClO_4)_3$ for other transition metals in the iron series. It has been observed in the present work that the strong red-yellow colour of ferric - DMF solutions is discharged on addition of acid, which is strongly indicative of the existance of a complex between iron and DMF, but the most conclusive evidence for complexing is obtained from a study of the u.v. spectrum of ferric chloride in a series of non aqueous solvents. The spectra in solvents which are not usually electron donors are very similar but show considerable differences from those in solvents containing nitrogen atoms or carbonyl oxygen atoms. Further small differences are observed in the latter spectra, although those in AN and methyl cyanide are almost identical, indicating that these spectra are characteristic of co-ordination between iron and cyanide nitrogen atoms.

It is not known whether DMF complexes via the nitrogen or carbonyl oxygen atom but the u.v. spectrum of ferric chloride in this solvent is almost identical with that in ethyl acetate after the latter solution has been subjected to a short period of irradiation at 3650Å. This is discussed fully in Chapter 10, and may be taken as evidence for complexing via the oxygen atom. This is in agreement with prevailing opinion; Nortia (42) and Muetterties (49), now seem convinced, from steric and other considerations, that the probability of complexing by DMF via the amide nitrogen atom is low.

The nature of ferric chloride in non aqueous media is further complicated by the apparent existance of two species one of which is more highly coloured and preferentially reduced than the other. Only by such a postulate can it be explained that estimations of ferrous iron by spectrophotometry yield results approximately twice those from titrations. It is odd admittedly that both species should be present in approximately equal proportions not only in DMF and AN - DMF mixtures but also in ethanol and methyl cyanide. Uncomplexed ferric chloride or the dimer may be involved here.

With regard to the mechanism of the primary process whereby free radicals are obtained on photolysis of non aqueous solutions of ferric chloride, it appears that, notwithstanding the complex nature of these solutions, the reaction can be represented by the equation

$$FeCl_3 \xrightarrow{h\nu} FeCl_2 + Cl$$

This conclusion is drawn from the following observations:-

(a) The rate of photolysis of ferric chloride in several non aqueous solvents is very similar varying only between c.a. 7×10^{-7} and c.a. 9×10^{-7} mole $\text{litre}^{-1}\ \text{sec}^{-1}$.

(b) The u.v. spectra of ferric chloride in different solvents involving suspected complexes have in common a band of absorption with a peak at c.a. 3650Å which disappears on irradiation. This band is associated then with absorption by the iron chlorine bonds common to all of these solutions.

(c) The energy of light of wavelength 3650Å is 78 kcal. mole^{-1} which compares favourably with estimates of the iron - chlorine bond strength (47).

Thus it is considered that cleavage of an iron - chlorine bond is responsible for the production of primary radicals and that ligands are not involved as, for example, in the photolysis of oxalate complexes to produce $C_2O_4^-$ radical ions shown to initiate the polymerization of AN (19, 20).

In Chapter 5, it is shown that, for the polymerization of AN in DMF solution in presence of ferric chloride at concentrations greater than c.a. 2×10^{-3} mole litre^{-1}, the rate of reaction should be given by the expression

$$\text{Rate}_p = \frac{k_p I_n [M]}{k_t [FeCl_3]}$$

and that use of ferric chloride as photoinitiator gives rise to the relation

$$I_n = k_1 I_o$$

whence $$\text{Rate}_p = \frac{k_p k_1 I_o [M]}{k_t [FeCl_3]}$$

The following observations have been made.

(a) The rate of reaction is proportional to the reciprocal of the ferric chloride concentration.

(b) The rate of reaction is proportional to the monomer concentration.

(c) The rate of initiation, both from spectrophotometry and titrations, is independent of the ferric chloride concentration, and is proportional to the intensity of irradiation.

(d) The overall energy of activation is independent of the ferric chloride concentration.

(e) The rate of reaction is dependent on intensity of irradiation to the power 0·65.

Observations (a) to (d) are in full agreement with the above expression, but (e) is totally incompatible. This last observation would, in fact, appear to indicate the participation of a considerable proportion of second order termination. This possibility, and the possibility of interaction between polymer radicals and initiator radicals, have been examined in Chapter 7 and the conclusion is that any termination other than that by interaction of polymer radicals with ferric chloride would cause largo deviations from relation (a) above.

The only way in which the simultaneous application of the relationships

$$\text{Rate}_p \propto \frac{1}{[\text{FeCl}_3]} \quad \text{and} \quad \text{Rate}_p \propto I_n^{0\cdot65}$$

can be visualized is by postulating that the termination reaction is in some manner dependent on the intensity of irradiation. Let us suppose, for example, that there are two species of ferric chloride present in the polymerization mixture of AN in DMF and that one of these can only act as a terminator by absorption of a quantity of light energy, - the classical "hot molecule" theory.

Let the species be represented by F_a and F_b such that termination is effected by F_a and F_b^* (where F_b^* represents a "hot molecule").

The rates of initiation and termination will be given by the equations

$$I_n = k_{ia}[F_a]\, I_{abs.} + k_{ib}[F_b]\, I_{abs.}$$

$$\text{Rate}_t = k_{ta}[F_a][R] + k_{tb}^*[F_b^*]\, I_{abs.}$$

(where k_{ia}, k_{ib}, k_{ta}, k_{tb}^* are constants and $I_{abs.}$ is the actual intensity of irradiation absorbed)

Let $[F_b^*] = k_e \quad [F_b]\, I_{abs.}$

where k_e is a constant.

Then, for a stationary state in radicals the rate of reaction will be given by the expression

$$\text{Rate}_p = \frac{k_p [M] (k_{ia} [F_a] I_{abs.} + k_{ib} [F_b] I_{abs.})}{k_{ta} [F_a] + k_{tb}^{*} k_o [F_b] I_{abs.}}$$

Now it has been shown that, at relatively high ferric chloride concentrations, the rate of initiation is independent of ferric concentration and depends only on I_o. If the energy absorbed by the terminating species is of similar order to that involved in initiation process, the rate of production of F_b^{*} (and consequently the F_b^{*} concentration), will also depend only on I_o.

$$\text{i.e.} \quad I_n = k_i I_o$$

$$\text{and} \quad [F_b^{*}] = k_I I_o$$

where k_i and k_I are constants.

$$\text{Thus Rate}_p = \frac{k_p [M] k_i I_o}{k_{ta} [F_a] + k_{tb}^{*} k_I I_o}$$

Let us suppose, for the moment however, that $[F_b^{*}]$ does depend on the concentration of species F_b

$$\text{i.e.} \quad [F_b^{*}] = k_I' [F_b] I_o$$

and that a fraction α of the total ferric present exists as species F_a

$$\text{i.e.} \quad [F_a] = \alpha [F_o] \quad \text{and} \quad [F_b] = (1 - \alpha) [F_o]$$

$$\text{Then Rate}_p = \frac{k_p [M] k_i I_o}{[F_o] \{ k_{ta} \alpha + k_{tb}^{*} k'_I (1 - \alpha) I_o \}} \qquad \text{....(XII.1.)}$$

By arrangement of the constants in this equation it can be shown that Rate $_p$ can depend on $^1/[F_o]$ and $I_o^{0{\cdot}65}$ simultaneously.

The success of this explanation hinges on the direct dependence of the concentration of "hot molecules" on the concentration of the species from which they are formed as well as on the intensity of irradiation. Unfortunately, as explained above, this should not be the case. (Even if the energy involved in termination is very much less than that in initiation, direct dependence of $[F_b^{*}]$ on $[F_b]$ could not be expected as non uniformity of irradiation results from absorption in the initiation process). Consequently it is only very tentatively that the above theory can be postulated, yet only by an expression of the type (XII.1.) can these incongruous dependences on ferric concentration and intensity of irradiation be reconciled.

The theory makes use of the conclusion from Chapter 9 that two species of ferric chloride exist in AN - DMF solution. Other kinetic observations can be related to the involvement of light absorption in the termination reaction. For example, we could expect the activation energy E_t, for the termination reaction to be low if part of this energy was provided by irradiation, and the value obtained (ca. 4 kcal. mole^{-1}), does seem low for reaction between a polymer radical and an inorganic salt. The overall effect of lowering of E_t is to raise $E_o = E_p - E_t$ and the fact that E_o is positive accounts for part of the difference between the value of $k_p/k_t = 0{\cdot}078$ obtained in this work at 25°C and that of 0·33 obtained at 60°C by Bamford et.al. (29). E_o in fact was found to be c.a. 2 kcal. mole^{-1} so that k_p/k_t would rise from 0·078 at 25°C to 0·11 at 60°C. As observed in Chapter 5, the remaining discrepancy could be ascribed to a low efficiency of initiation though it would have to be postulated that as much as two thirds of the radicals formed combine to form inert products.

With regard to the radicals which actually react with monomer units to initiate chains, the radioactive tracer studies described in Chapter 11 indicate that in 20% AN - 80% DMF reaction mixtures, chlorine atoms are not involved. This, in turn, indicates that the primary photolysis

$$FeCl_3 \xrightarrow{h\nu} FeCl_2 + Cl$$

is followed by the reaction,

$$Cl + DMF \longrightarrow R_d + HCl$$

such that solvent radicals are the effective initiating species.

The retarding effect of ferric chloride in DMF on the polymerization of AN is considerably less than that of aqueous solutions of ferric ions on the polymerization of acrylamide. For example, Dainton and Tordoff, in their study of the latter system, (26), maintain that termination is first order with respect to radical concentration when the ferric concentration is greater than c.a. 4×10^{-4} mole litre^{-1}, while dependence of rate of reaction on the reciprocal of the ferric chloride concentration was not observed in the present work at less than c.a. 2×10^{-3} mole litre^{-1}. It is interesting to note that in this work with aqueous ferric solutions, initiation and termination are reckoned to involve two species of ferric ion, though this apparently causes no complications in the kinetics of the reaction.

There is plenty of scope for future work both on the present polymerization system, and on other systems containing inorganic salts and vinyl monomers.

As observed in Chapter 5, kinetic chain lifetimes in the polymerization of AN in presence of ferric chloride are very short - too short, in fact, to measure by the usual non-stationary techniques. Consequently molecular weights are very low. As estimated from the expression

$$\text{M.W.} = \frac{\text{Rate of Polymerization}}{\text{Rate of Termination}} \times (\text{M.W. of monomer})$$

the molecular weight is c.a. 6000 when the ferric chloride concentration used is 2×10^{-3} mole litre^{-1}, and of course is even lower at higher chloride concentrations. Light scattering methods could be employed in the measurement of molecular weights of this order. If however, the mechanism of termination by ferric chloride in DMF can be firmly established by the tracer atom studies described in Chapter 11, those studies should provide an even more accurate estimate of molecular weights by comparison of weights of polymers with the number of chlorine atoms incorporated in these.

The extension of the study of non aqueous ferric chloride solutions by u.v. spectroscopy to a wider range of solvents might allow more definite conclusions to be derived concerning the nature of these solutions. Certainly it should be possible to obtain spectra characteristic of complexes between iron and selected donor atoms. Spectrum changes during irradiation could be examined by the use of quartz cells connected by graduated seals to pyrex tubing such that these could be sealed off under vacuum, though some alteration of the u.v. spectrophotometer might be necessary to accomodate these vessels.

Finally, the study of the photolysis of other transition metal salts, e.g. cupric chloride, in presence of AN in DMF and the comparison of results with those obtained for ferric chloride, with particular regard to intensity exponents in regions of first order termination, would be most interesting; extension of the work to other monomer-solvent systems might also provide some interesting comparisons.

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SUMMARY.

A detailed kinetic study has been made of the photosensitized polymerization of acrylonitrile in dimethyl formamide solution with ferric chloride as both catalyst and terminating agent.

It has been shown that ferric chloride readily forms complexes with solvents containing atoms which act as electron donors, and that a complex exists between ferric chloride and dimethyl formamide which probably involves co-ordination via carbonyl oxygen atoms.

There is evidence also that two species of ferric chloride exist in dimethyl formamide, and that one of these is more readily reduced by absorption of light or reaction with free radicals than the other.

Notwithstanding the complex nature of these solutions, it appears that the process whereby free radicals are obtained on photolysis with u.v. light primarily involves a relatively simple reaction, namely electron transfer from chlorine to iron to form chlorine atoms. These atoms, however, do not initiate polymerization directly; it is probable that the solvent is attacked to produce further radicals which react with monomer to initiate chains.

The extinction coefficient of ferric chloride in dimethyl formamide at 3650Å is 5×10^{3} litre mole^{-1} cm.$^{-1}$, such that absorption of irradiation at this wavelength in reaction vessels of 2 cm. diameter containing chloride concentrations greater than ca. 3×10^{-4} mole litre^{-1} is virtually complete. It is shown that under these conditions the rate of production of ferrous iron, and consequently the rate of initiation, is independent of ferric chloride concentration. At concentration greater than ca. 2×10^{-3} mole litre^{-1}, termination occurs by reaction of growing radicals with ferric chloride. To describe this system, a simple kinetic scheme is postulated which indicates that, under stationary state conditions, rates of polymerization and initiation should be given by the expressions

$$\text{Rate}_p = \frac{k_p k_1 I_o [M]}{k_t [FeCl_3]} \qquad \text{.....(1)}$$

and

$$I_n = k_1 I_o \qquad \text{.....(2)}$$

where k_p and k_t are the velocity coefficients of propagation and termination, k_1 is the constant relating the rate of initiation, I_n, to the intensity of irradiation, I_o, and $[M]$ and $[FeCl_3]$ represent the monomer and ferric chloride concentrations.

I_n, as measured by titration for ferrous iron with ceric ammonium sulphate, is $1{\cdot}64 \times 10^{-7}$ mole litre^{-1} sec^{-1}, and by substitution of this value for k_1I_0 in equation (1), a value of 0·078 is obtained for k_p/k_t at 25°C. This is somewhat smaller than that obtained by Bamford and co-workers, namely 0·33 at 60°C (29). The difference is due in part to the difference in temperature; the overall activation energy is ca. 2 kcal mole^{-1}. It may also however, be due to a lower efficiency of initiation for the radicals derived from ferric chloride than for cyanoisopropyl radicals.

Kinetic observations, in general, are in agreement with the scheme postulated, though the intensity exponent is lower than expected. A tentative theory has been put forward to explain this.