

INTERACTION OF POLYMER RADICALS WITH COMPLEX IONS

by

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ABSTRACT

The ionic species produced on dissolving small quantities of ferric compounds either alone, or in the presence of additives, in solvents N,N-dimethyl formamide, (DMF), or dimethyl sulphoxide, (DMSO), and in solvent/styrene mixtures at 20°C and 60°C have been studied spectroscopically. The nature of the iron(III) chloro-complexes has been established by studying the ultraviolet spectra of solutions containing model compounds such as hexakis(N,N-dimethyl formamide) iron(III) tetrafluoroborate, $[\text{Fe}(\text{DMF})_6](\text{BF}_4)_3$, A, hexakis(dimethyl sulphoxide) iron(III) tetrafluoroborate, $[\text{Fe}(\text{DMSO})_6](\text{BF}_4)_3$, D, and tetraethyl ammonium tetrachloroferrate(III), $(\text{C}_2\text{H}_5)_4\text{NFeCl}_4$, B, in the presence of varying amounts of lithium chloride. The tetrafluoroborate salts were chosen for study since BF_4^- ions show little tendency to complex.

The solution polymerization of styrene at 60°C, in DMF and in particular DMSO, initiated by α, α' -azobisisobutyronitrile (AIBN), has been studied kinetically. Molecular weight measurements have enabled the transfer constant, C_s , for DMSO at 60°C to be evaluated. Further kinetic studies of polymerizing systems with added ferric compounds, both in the absence and presence of lithium chloride, lithium bromide, sulphuric acid or phenanthroline have been made.

The presence of $\text{Fe}(\text{DMF})_6^{3+}$ or $\text{Fe}(\text{DMSO})_6^{3+}$ ions in the polymerizing systems caused retardation, but iron chloro-complexes

produced well-defined induction periods. Mean velocity constants at 60°C, for polystyryl radicals towards $\text{Fe}(\text{DMF})_6^{3+}$, $\text{Fe}(\text{DMSO})_6^{3+}$, $\text{Fe}(\text{DMF})_5\text{Cl}^{2+}$, $\text{Fe}(\text{DMF})_4\text{Cl}_2^+$, FeCl_4^- and $\text{Fe}(\text{DMSO})_5\text{Cl}^{2+}$ were 847, 229, 4.53×10^4 , 6.40×10^4 , 2.96×10^4 and 7.18×10^4 $\text{l.mole}^{-1}\text{sec}^{-1}$, respectively. Iron(III) bromo and phenanthroline complexes also produced well-defined induction periods. Values of the initiator efficiency, f , for most systems investigated, ranged from 0.59 to 0.62.

The transfer constant for DMSO was found to be 2.42×10^{-5} in the DMSO/styrene system at 60°C. The decomposition of AIBN in DMSO was followed spectroscopically at 60°C and the first order decomposition rate constant, k_d for AIBN was found to be $0.94 \times 10^{-5} \text{sec}^{-1}$, at 60°C.

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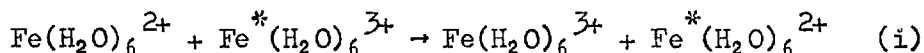
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I. INTRODUCTION

Interest in the mechanisms of reactions involving inorganic ions in solution has been marked in recent years and much of the growing literature has been periodically reviewed.¹⁻⁵ Many of these reactions may be classified as (a) Oxidation-reduction processes in which an electron or an atom is transferred, (b) substitution reactions in which one ligand is substituted by another and (c) acid-base reactions. Usually, studies of oxidation-reduction reactions have been confined to aqueous systems although more recently other solvents have been used.

Possibly the simplest type of electron transfer reaction involves two ions of the same metal in different valency states such as Fe(II) and Fe(III) and reactions,



may be studied by isotopic labelling, although NMR and ESR techniques are suitable for studying faster reactions. Perchlorate salts of metals are usually employed since the perchlorate ion shows little tendency to complex.

The electron exchange reaction (i) proceeds at greater velocities in the presence of added anions, X^- , such as, OH^- , F^- , Cl^- , Br^- and N_3^- . The kinetic data have usually been interpreted in terms of an equilibrium involving formation of the complex ions $[\text{Fe}^*(\text{III})(\text{H}_2\text{O})_5\text{X}^-]^{2+}$ followed by their subsequent reaction with $\text{Fe}(\text{H}_2\text{O})_6^{2+}$ ions.

The precise mechanism for electron transfer still remains obscure, however. One suggestion is that an inner-sphere transition complex of the type, $[(\text{H}_2\text{O})_5\text{Fe(III)} \dots \text{X}^- \dots \text{Fe(III)(H}_2\text{O)}_5]^{4+}$ is formed in which the negative ion, X^- , acts as a bridge for electron transfer. This suggestion was primarily due to Taube.^{6,7} When the Fe(III) and Fe(II) ions are inert to substitution by X^- , however, the co-ordination spheres of exchanging partners are not altered during the exchange process and then electron transfer proceeds by a so-called outer sphere mechanism. This mechanism would be involved for example in the $\text{Fe(CN)}_6^{4-} - \text{Fe(CN)}_6^{3-}$ exchange reaction. The process probably involves electron tunnelling,^{8,9} although it is possible that an electron is transferred from the outside of one co-ordination sphere to another if the ligand is suitably conjugated. The ligand then acts as an electron-conduction medium. A hydrogen atom transfer mechanism for electron transfer between two cations has also been suggested for aqueous solutions containing Fe(II) ions and various complex Fe(III) ions.⁸

The theoretical treatments of electron transfer reactions in solution have been reviewed recently,^{2,10} but precise mechanisms have yet to be formulated. Much of the existing data, such as that for the $\text{Fe(II)} - \text{Fe(III)}$ system may be interpreted by any of the inner-sphere, outer-sphere or hydrogen atom transfer mechanisms.

Electron transfer processes of interest in free radical polymer chemistry have been much less studied than the above types of ion-ion exchange reactions. However, the photochemical initiation of vinyl

monomers in aqueous and non-aqueous solutions by so-called ion pair complexes involving electron transfer is now well established.¹¹⁻¹⁷

Again, interest in polymer radical-ion interactions developed simultaneously with observations of electron transfer reactions in other fields of chemistry. For example, as early as 1932, Haber and Weiss^{18,19} had indicated that the decomposition of aqueous solutions of hydrogen peroxide by ferrous salts involved an initial electron transfer from Fe^{2+} to H_2O_2 :

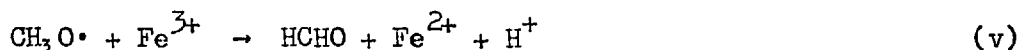
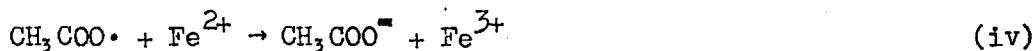


followed by:



whereby a single electron was transferred from Fe^{2+} to a hydroxyl radical. Other side reactions involving $\text{HO}\cdot$ and $\text{HO}_2\cdot$ radical attack on hydrogen peroxide also occurred.

The oxidation of organic compounds such as alcohol and alcohol/acetic acid mixtures by the hydrogen peroxide-ferrous iron system was studied in later years by other workers,^{20,21} who proposed other radical-ion single electron transfer reactions such as:



Clearly, electron transfer both from and to a radical in a radical-ion reaction was possible.

At the same time, interest in methods of generating radicals by electron transfer was created when initiation of polymerization of several monomers in aqueous solution was achieved by the hydrogen peroxide-ferrous ion system.²²⁻²⁴

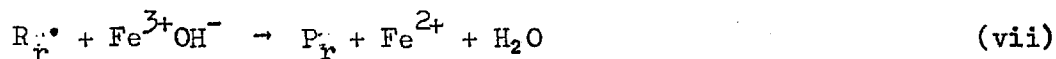
Early work by Rainard²⁵ and Cooper²⁶ using redox initiators revealed the possibility of polymer radical-metal ion reactions at high metal ion concentrations.

It is not proposed to review the later extensive application of these redox systems to initiation of vinyl polymerization in emulsions, since the early work²⁷ and some of the later work²⁸ has been reviewed elsewhere.

Dainton and co-workers, following extensive work on the irradiation of metal salts in various solutions appear to have been the first to show unequivocally that polymer radicals could undergo an electron transfer reaction with metal ions.^{29,30} Thus, in the polymerization of acrylamide in perchloric acid solution initiated by X-rays, they suggested that polyacrylamide radicals could be terminated by Fe^{3+} ions or $\text{Fe}^{3+}\text{OH}^-$ ion-pairs,



and



although the mechanism of these reactions remained obscure.

The presence of chromous ions was briefly reported to prevent the aqueous solution polymerization of acrylonitrile by an electron transfer process.²⁹

In a subsequent paper,³¹ it was concluded that oxidation and reduction of various organic radicals, including polymer radicals, by ions was a general phenomenon, the rate of reaction depending on the nature of the polymer radical and ion, and the solvent medium involved.

Polyacrylonitrile radicals in aqueous solution were shown to be terminated by ions such as V^{2+} , V^{3+} , Mo^{3+} , Ti^{3+} and U^{3+} .³²

A more extensive investigation of the polymerization of acrylonitrile in aqueous solution in the presence of added metal ions, especially ferric ions has been made by Dainton and co-workers involving initiation by Fenton's reagent,³³ photo-initiation using metal ions including ferrous and ferric ions,³⁴ and a more detailed study of photo initiation with the ferric ion at temperatures 15 - 50°C.³⁵

The effect of the cation of various cupric salts on aqueous polymerization of acrylonitrile initiated by ammonium persulphate has indicated that cupric nitrate, sulphate or acetate lead to increased rates, but that cupric chloride and bromide retard or inhibit polymerization.³⁶

A discussion of some of the factors affecting rates of termination of polymer radicals by metal ions has also been provided with respect to the aqueous polymerization of acrylamide initiated by γ -, and X-rays.³⁷

Further work on the kinetics of polymerization of acrylamide in aqueous solution initiated by 4,4'-azo-bis-4-cyanopentanoic acid and on the effect of added ferric salts has been reported by Cavell and co-workers.³⁸⁻⁴⁰

Although termination constants for the inner sphere complexes $Fe(H_2O)_5Cl^{2+}$ and $Fe(H_2O)_4SO_4^+$ have been determined at 25°C, there was a complication since rates of initiation seemed to be increased in the presence of added ferric salts. An electron transfer

mechanism has been suggested by this group to account for the effect of uranyl perchlorate on the same polymerizing system.⁴¹

Experimental investigations in non-aqueous systems have not been so extended, partly due to the difficulties in ensuring that all the initial reactants, including the added metal salt, and any resultant polymer always form a homogeneous system. One suitable solvent, however, was N,N-dimethylformamide, (DMF), and its solvent properties were exploited initially by Bamford and co-workers,⁴²⁻⁴⁴ who studied the polymerization of acrylonitrile, methylacrylonitrile and styrene, at 60°C, initiated by α, α' -azo-bisisobutyronitrile, (AIBN) in the presence of ferric chloride.

A detailed mathematical treatment of the kinetics, enabling rate constants for the electron transfer termination processes to be determined was also presented.⁴³ In the case of styrene, the polymer radical reactivity was so high that well-characterized induction periods were produced, enabling rates of initiation to be determined. The ferric chloride then behaved as an 'ideal' retarder.⁴²⁻⁴⁴

Unexpected accelerative effects of single valency state ions, such as Li^+ , were also observed in the polymerization of acrylonitrile.⁴⁴

The importance of primary radical termination in the polymerization of styrene in DMF initiated by AIBN, particularly at low $\frac{[\text{M}]}{[\text{In}]^{\frac{1}{2}}}$ values has also been suggested following work with ferric chloride.⁴⁵

Later, the polymerization of several monomers including methyl methacrylate and methyl acrylate was studied in the presence of ferric chloride, and from measurements in the absence and presence of monomer, it was concluded that rates of initiation were constant in all the monomers, implying that cage effects were unimportant.⁴⁶

The importance of polar effects in determining the reactivity of ferric chloride towards radicals has been stressed.⁴⁷

A similar type of study at 60 - 78°C using ferric chloride and styrene as scavengers for primary radicals from AIBN gave an initiator efficiency, f , about 0.73 almost independent of temperature.⁴⁸

The importance of the anion of various ferric salts added to monomers polymerized by AIBN or 4-4'-azo-bis-4-cyanopentanoic acid has been stressed by Entwistle.⁴⁹ The possibility of decarboxylation of the above substituted azo-pentanoic acid initiator by ferric chloride was also realized.

The use of ferric chloride in DMF as a simultaneous photo-initiator and terminator in the polymerization of acrylonitrile was complicated by the possible solvent participation in the initiation step.⁵⁰

More recently, Bengough and co-workers have studied the polymerization of methyl methacrylate,⁵¹ acrylonitrile,⁵² styrene⁵³ and methacrylonitrile⁵⁴ in DMF initiated by AIBN in the presence of cupric chloride. Of particular importance was the method of determining termination rate constants from kinetic data somewhat different from that previously reported by Bamford et al.⁴³

Cupric chloride behaves as an "ideal retarder" in the polymerization of methyl methacrylate,⁵¹ styrene⁵³ and methacrylonitrile⁵⁴ but the product of the primary retardation reaction, presumably cuprous chloride or its complexes with solvent or monomer, appears also to act as a retarder, in acrylonitrile polymerization.^{52,55,56}

Although the previous workers have successfully calculated many velocity constants for polymer radical-metal ion termination reactions, several problems remain.

These problems may be summarised:

- (a) The precise nature of the metal ion which reacts with the polymer radical in aqueous or DMF solutions remains obscure. Thus, co-ordination of solvent molecules around free metal ions must occur to some extent to form complex ions.
- (b) The role of the anion in determining reaction rates is not well understood. In particular, the possibility of the anion forming outer- or inner-sphere complexes with the metal ion must be considered. The kinetics of some ligand substitution processes have been discussed recently.⁵⁹⁻⁶¹
- (c) The effect of changing solvent on the velocity of a polymer radical-ion reaction is not known.

For example, previous workers have not compared reactions involving the same polymer radical $R_r^\cdot$ and complexes of an ion M^{x+} of the type $M(s_1)_n^{x+}$ and $M(s_2)_n^{x+}$ where s_1 and s_2 are non-aqueous solvent ligands.

(d) The detailed chemistry of the termination process is not clear. For example, when a polystyryl radical reacts with ferric chloride in DMF solution, the radical may be terminated by an acquired chlorine atom⁴⁹ or may donate a hydrogen atom and acquire an unsaturated $-\text{CH} = \text{CHPh}$ end group.⁴³

The work described later in this thesis was performed to obtain further information about certain of these outstanding problems. Attention was confined to an identification of various ferric complex ions existing in dimethylformamide- and dimethylsulphoxide-styrene systems, and to a consideration of the relative reactivities of these complex ions towards polystyryl radicals.

II THEORETICAL SECTION (62, 63, 64)

2.1. Simple Kinetic Scheme

2.1.1. Kinetic scheme for vinyl polymerization in the presence of an initiator producing free radicals

Initiation

The process of free radical initiation may be considered to involve two steps:

Decomposition of the initiator molecule, In , to give, usually, two radical fragments, $\text{R}_\text{C}^\bullet$;

(a) $\text{In} \rightarrow 2\text{R}_\text{C}^\bullet$ First order velocity constant = k_d and addition of $\text{R}_\text{C}^\bullet$ radicals to the monomer molecules, M ;

(b) $\text{R}_\text{C}^\bullet + \text{M} \rightarrow \text{R}_1^\bullet$ Rate of initiation = $\text{I} = \frac{d(\text{R}_1^\bullet)}{dt}$ (1)

However, some of the free radicals, $\text{R}_\text{C}^\bullet$, initially formed, are lost in various side reactions and as such, the efficiency, f , of an initiator is generally less than unity.

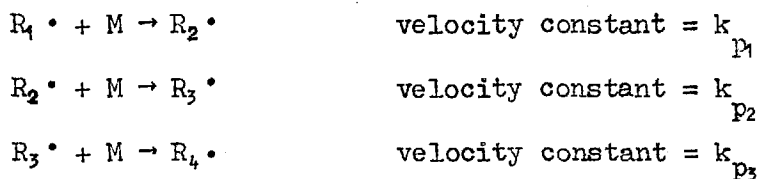
The efficiency, f , of the initiator, is equal to the fraction of free radicals, $\text{R}_\text{C}^\bullet$, formed by step (a), which are effective in initiating the subsequent chain by means of step (b). Hence, in any experiment;

$$\text{I} = 2k_\text{d} f [\overline{\text{In}}] \quad (2)$$

where $[\overline{\text{In}}]$ = the mean initiator concentration during that experiment.

Propagation

The growth of a polymer radical by successive addition of monomer molecules may be represented by:



or in general,



The same common velocity constant, k_p , may be used for each propagation step assuming that polymer radical reactivity is independent of chain length.

$$\text{So, } k_{p1} = k_{p2} = k_{p3} = \dots = k_{pr} = k_p \text{ (in general).}$$

$$\therefore \text{Rate of propagation, } R_p = k_p [M] [R \cdot] \quad (3)$$

where

$$r = \infty$$

$$[R \cdot] = \sum_{r=1}^{r=\infty} [R_r \cdot] = \text{the total concentration of polymer radicals.}$$

Transfer

(A) Transfer to monomer

A free radical, $R_r \cdot$ formed during propagation may attack monomer, and undergo a transfer reaction:



where P_r represents an inactive polymer containing r monomer units and $M \cdot$ is a new radical usually formed by transfer of a hydrogen atom from a polymer radical to a monomer molecule. In the polymerization

of styrene induced by an initiator, producing radicals, transfer to monomer is relatively unimportant in determining rates of polymerization and molecular weights, both in bulk and in solution. For example, the transfer constant to styrene monomer, $C_m (= \frac{k_f^m}{k_p})$ is only 6.023×10^{-5} at 60°C .⁶⁵

(B) Transfer to solvents

In the presence of a solvent, an additional transfer reaction must be considered, involving a polymer radical and a solvent molecule.



In the simplest case, where the $S^\bullet$ radicals are of similar reactivity to the polymer radicals, the solvent decreases the molecular weight but has a negligible effect on the rate of polymerization, other than that expected by mere dilution of monomer. The determination of the transfer constant of the solvent, $C_s (= \frac{k_f^s}{k_p})$ will be discussed in a later section.

Termination

The process of termination is a bimolecular reaction between a pair of polymer radicals causing annihilation of their active centres. It may be either termination by combination,



or, termination by disproportionation,



Most of the evidence to date suggests that the termination reaction between two polystyryl radicals is an exclusive combination

process for temperatures up to 80°C. Thus, for the sake of simplicity, a velocity constant, $2k_t$, without a subscript, will be used as the termination constant in this thesis, since only styrene was used as monomer.

The total rate of termination between polystyryl radicals, is given by

$$R_t = 2k_t [R\cdot]^2 \quad (4)$$

Once the steady state is achieved,

Rate of initiation = Rate of termination

$$\therefore 2k_d f [\overline{\text{In}}] = 2k_t [R\cdot]^2 \quad (5)$$

or

$$k_d f [\overline{\text{In}}] = k_t [R\cdot]^2 \quad (6)$$

Substituting the value of $[R\cdot]$ from eqn (5) in eqn (3),

$$R_p = k_p \left\{ \frac{f k_d [\overline{\text{In}}]}{k_t} \right\}^{\frac{1}{2}} [M] \quad (7)$$

Since the number of monomer molecules involved in initiation is insignificant in comparison with those involved in propagation, provided the chain length is great, R_p , may be identified with the rate of polymerization.

$$\therefore R_p = \text{Rate of polymerization}$$

$$= - \frac{d[M]}{dt}$$

$$= k_p [M] [R\cdot] \quad (8)$$

$$= k_p \left\{ \frac{f k_d [\overline{\text{In}}]}{k_t} \right\}^{\frac{1}{2}} [M] \quad (9)$$

Hence, according to eqn (7), the rate of polymerization should vary as the square root of the initiator concentration.

If f for α, α' -azobisisobutyronitrile, (AIBN), is constant and independent of the monomer concentration, $[M]$, then the rate of polymerisation, R_p , is first order^{64, 66, 67} in monomer concentration, $[M]$. There still remains some controversy about this particular point, however.

The determination of transfer constants

Since transfer to initiator is known to be negligible for AIBN,^{64, 66, 68} the degree of polymerization, $\overline{DP} = \frac{\text{Rate of growth}}{\text{Rate of all reactions leading to dead polymer}}$

$$= \frac{k_p [M] [R\cdot]}{k_f_m [M] [R\cdot] + k_f_s [S] [R\cdot] + k_t [R\cdot]^2}$$

$$\therefore \frac{1}{\overline{DP}} = \frac{k_f_m}{k_p} + \frac{k_f_s [S]}{[M]} + \frac{k_t^{\frac{1}{2}} \{k_d f [\overline{In}]\}^{\frac{1}{2}}}{k_p [M]}$$

$$\therefore 2 k_d f [\overline{In}] = 2 k_t [R\cdot]^2 \quad (5)$$

$$\therefore \frac{1}{\overline{DP}} = C_m + C_s \frac{[S]}{[M]} + \frac{k_t^{\frac{1}{2}} \{k_d f [\overline{In}]\}^{\frac{1}{2}}}{k_p [M]} \quad (10)$$

where C_m and C_s represent the transfer constants to monomer and solvent respectively.

For a series of experiments performed by varying $[M]$ and $[S]$ but maintaining $[\overline{In}]$ constant, from eqn (10)

$$[M] \left\{ \frac{1}{\overline{DP}} - C_m \right\} = C_s [S] + \text{constant} \quad (11)$$

provided that the various velocity constants and f do not vary with monomer-solvent composition. Hence, by plotting $[M] \left\{ \frac{1}{\overline{DP}} - C_m \right\}$ against $[S]$, C_s can be determined since it is equal to the slope of the line.

2.1.2. Generalised Kinetic Scheme for Retardation

The rate of polymerization of a vinyl monomer may be reduced or almost completely stopped by addition of relatively small quantities of certain substances termed retarders and inhibitors, respectively. On polymerizing styrene at 60°C, in the presence of the initiator, α, α' -azobisisobutyronitrile, (AIBN), and a complex A, (such as hexakis N,N-dimethyl formamide iron(III) tetrafluoroborate, $\text{Fe}(\text{DMF})_6-(\text{BF}_4)_3$, in the non-aqueous solvents (dimethyl formamide or dimethyl sulphoxide), retarded rates of polymerization were recorded dilatometrically.⁶⁹ The rate results may be analysed by the method of Kice.^{70, 71} The generalised kinetic scheme includes the steps of initiation, propagation and mutual termination of polymer radicals previously discussed, and also

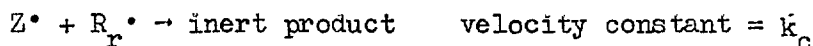
(h) Termination by transfer to Retarder



(i) Copolymerization, or reinitiation by $Z^\bullet$ species



(j) Cross termination



(k) Mutual termination of Z. species $Z^{\bullet} + Z^{\bullet} \rightarrow$ inert product

velocity constant = $2 k_z$

where $Z^{\bullet}$ represents any species formed by the reaction between a polymer radical and the complex, $A^{\bullet}$, $Z^{\bullet}$ a priori, might be radical.

Kice, by rigorous kinetic analysis, obtained the equation

$$R_p \sqrt{1 + \frac{c(1 - \phi^2)}{\phi^2}} = \frac{k_p k_x}{2k_t} \cdot \frac{\phi^2 (A)}{(1 - \phi^2)} \left\{ 1 + \sqrt{1 + \frac{c(1 - \phi^2)}{\phi^2}} \right\} - \frac{k_o k_p}{k_c} (M) \quad (12)$$

where, the reduced rate, $\phi = \frac{(R)_p}{(R)_p^o}$;

$$\begin{aligned} R_p &= - \left[\frac{d \ln (M)}{dt} \right]_{\text{inhibited}} \\ &= \left[- \frac{1}{(M)} \frac{d(M)}{dt} \right]_{\text{inhibited}}, \end{aligned}$$

which is thus a fractional rate of polymerization,

$$(R)_p^o = - \left[\frac{d \ln (M)}{dt} \right]_{\text{uninhibited}}$$

and c is a constant equal to $\frac{4 k_t k_z}{k_c^2}$.

The definition of R_p used by Kice, which is a fractional rate of polymerization, is not that used in many other kinetic schemes, including other sections of this thesis. Thus, the fractional rates of polymerization are in units of sec.^{-1} , rather than the more usual $\text{mole l.}^{-1} \text{sec.}^{-1}$. Normally, the value of c is chosen until a plot of the left hand side of the equation (12) against

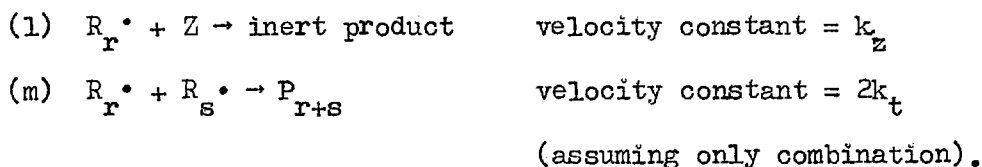
$\frac{\phi^2 (A)}{(1-\phi^2)} \left\{ 1 + \sqrt{1 + \frac{c(1-\phi^2)}{\phi^2}} \right\}$ at constant (M) gives a straight line of slope $\frac{k_p k_x}{2k_t}$ and an intercept of $-\frac{k_o k_p}{k_c}$ (M).

A low value of $\frac{k_o}{k_c}$ indicates a low tendency of $Z^\bullet$ species to attack monomer.

2.1.3. Kinetic Treatment of an "Ideal" Retarder

2.1.3.1. Treatment of Bamford et al.⁴³

An "ideal" retarder is a compound which reacts directly with a polymer radical to yield a completely inert product incapable of further reaction. For an "ideal" retarder a particularly simple reaction scheme of vinyl polymerization may be adopted. When the transfer reactions to solvent and monomer are of negligible importance, the reaction scheme involves the initiation steps (a) and (b), the propagation step (c) and two termination steps:



For this scheme:

$$\frac{d[R^\bullet]}{dt} = I - k_z [R^\bullet][Z] - 2k_t [R^\bullet]^2 \quad (13)$$

and

$$-\frac{dz}{dt} = k_z [R^\bullet][Z] \quad (14)$$

where

$$[R^\bullet] = \sum_{r=1}^{r=\infty} [R_r^\bullet] = \text{total polymer radical concentration.}$$

For, a steady state condition, in the presence of an ideal retarder, $\frac{d[R\cdot]}{dt} = 0$. The question remains whether this assumption is a reasonable one in the presence of an ideal retarder, and this assumption will therefore be examined more closely. From eqn (8), (13) and (14)

$$\frac{d[R\cdot]}{dt} = \frac{1}{k_p} \frac{1}{[M]} \cdot \frac{dR_p}{dt} = I - [2 k_t [R\cdot]^2 - \frac{d[Z]}{dt}] \quad (15)$$

If the steady state approximation is correct, $\frac{1}{k_p} \frac{1}{[M]} \frac{dR_p}{dt}$ must be a very small quantity, if not exactly equal to zero, and also I and $[2 k_t [R\cdot]^2 - \frac{d[Z]}{dt}]$ must be much greater than $\frac{1}{k_p [M]} \frac{dR_p}{dt}$. A typical polymerization - time curve is shown in Fig.30 (curve f), for the polymerization of styrene at 60°C, in dimethyl formamide initiated by AIBN in the presence of $[\text{Fe}(\text{DMF})_5] \text{Cl}^{2+}$ ions, which functioned as an "ideal retarder". In this experiment $[M]$ is 2.49 mole ℓ^{-1} , at 60°C, and k_p is 176 $\ell \cdot \text{mole}^{-1} \text{sec}^{-1}$, at 60°C.⁶⁵ During the first 80 minutes of the experiment $\frac{dR_p}{dt}$ is a very small quantity and hence, $\frac{1}{k_p [M]} \frac{dR_p}{dt}$ is much smaller than the measured value of I of 1.11×10^{-6} mole $\ell^{-1} \text{sec}^{-1}$.

Hence, assuming the steady state approximation during the initial stages,

$$I = k_z [R\cdot] [Z] + 2 k_t [R\cdot]^2 \quad (16)$$

Only towards the end of induction period does $\frac{dR_p}{dt}$ alter rapidly, and under these conditions the approximation may well break down.

When the inhibitor is completely exhausted $[Z]$ is zero and the concentration of polymer radicals attains its maximum value, $[R\cdot]_s$, given by

$$I = 2 k_t [R\cdot]_s^2 \quad (17)$$

The fraction of total termination occurring by mutual reaction of polymer radicals during the induction period is sufficiently small to be neglected. The assumption is reasonable, since $[R\cdot]$ is very small during the induction period, for experimental values of $k_z = 4.53 \times 10^4 \text{ l. mole}^{-1} \text{ sec.}^{-1}$ at 60°C , $[Z]_0 = 7.873 \times 10^{-3} \text{ mole l.}^{-1}$, and $2 k_t = 7.2 \times 10^7 \text{ l. mole}^{-1} \text{ sec.}^{-1}$, $k_z [Z]_0 [R\cdot] \gg 2 k_t [R\cdot]^2$.

Hence,

$$\frac{2 k_t [R\cdot]^2}{I} = \frac{k_t [R\cdot]^2}{k_t [R\cdot]_s^2} = \frac{(R_p)^2}{(R_p)_s^2} \quad (18)$$

Hence, during the induction period, using a simple reaction scheme:

$$I = k_z [R\cdot][Z] = - \frac{d[Z]}{dt} \quad (19)$$

By differentiation of eqn (16)

$$\frac{dZ}{dt} = - \left\{ \frac{I + 2 k_t [R\cdot]^2}{k_z [R\cdot]^2} \frac{d[R\cdot]}{dt} \right\}$$

Also, since $\frac{dZ}{dt} = k_z [R\cdot][Z]$ from eqn (16) and (17):

$$- \left\{ \frac{I + 2 k_t [R\cdot]^2}{k_z [R\cdot]^2} \right\} \frac{d[R\cdot]}{dt} = - I + 2 k_t [R\cdot]^2 \quad (20)$$

After re-arrangement and integration this becomes,

$$-\frac{[R\cdot]_s}{[R\cdot]} + \ln \left\{ \frac{[R\cdot]_s + [R\cdot]}{[R\cdot]_s - [R\cdot]} \right\} = k_z [R\cdot]_s t + A^* \quad (21)$$

where A^* is a constant and $[R\cdot]_s$ is the final steady radical concentration corresponding to $[Z] = 0$. If the 'reduced rate' ϕ_t is defined as the ratio of the rate at any time t in presence of the inhibitor, R_p , to the final maximum rate, R_{ps} , when all the inhibitor has disappeared and if the monomer concentration remains effectively constant, then we have,

$$\phi_t = \frac{k_p(M)(R\cdot)}{k_p(M)(R\cdot)_s} = \frac{(R\cdot)}{(R\cdot)_s} \quad (22)$$

Hence eqn (21) becomes

$$\frac{1}{\phi_o} - \frac{1}{\phi_t} + \ln \frac{(1 - \phi_o)(1 + \phi_t)}{(1 + \phi_o)(1 - \phi_t)} = k_z [R\cdot]_s t \quad (23)$$

where $\phi_o \ll 1$, equation (23) may be rewritten as,

$$\frac{1}{\phi_o} - \frac{1}{\phi_t} + \ln \frac{(1 + \phi_t)}{(1 - \phi_t)} = k_z [R\cdot]_s t \quad (24)$$

It is possible to choose a time $t = \tau$, such that

$$-\frac{1}{\phi_t} + \ln \frac{(1 + \phi_t)}{(1 - \phi_t)} = 0 \quad (25)$$

whence, $\phi_t = 0.648$, in which case eqn (24) becomes

$$\frac{1}{\phi_o} = k_z [R\cdot]_s \tau \quad (26)$$

τ is thus the time taken for the rate to reach 0.648 times the final maximum rate.

Again, from eqn (17), $(R^\bullet)_s = \left[\frac{I}{2k_t} \right]^{1/2}$, when all the inhibitor has been used up, i.e. when $[Z] = 0$.

From eqn (19) we know that during the induction period,
 $[Z] = \frac{I}{k_z [R^\bullet]}$ and corresponding to $t = 0$, $[R^\bullet]_0 = \frac{I}{k_z [Z]_0}$

$$\therefore \tau = \frac{1}{k_z \phi_0 [R^\bullet]_s} = \frac{1}{k_z [R^\bullet]_0} = \frac{[Z]_0}{I} = \frac{[Z]_0}{2 k_d f [In]} \quad (27)$$

where τ is the time corresponding to eqn (25) and $[Z]_0$ is the initial concentration of the ideal retarder. Bamford et al. used $FeCl_3$ as an ideal retarder.^{43, 44, 48} Equation (23) may be rewritten in the alternative form

$$-\frac{1}{\phi_t} + \ln \frac{(1 + \phi_t)}{(1 - \phi_t)} = k_z [R^\bullet]_s t + A^* \quad (28)$$

which enables ϕ_t to be plotted against $k_z [R^\bullet]_s t + A^*$.⁵¹

Again, since $(R_p)_s = -\frac{d[M]}{dt} = k_p [M] [R^\bullet]_s$

$$\therefore \frac{k_z (R^\bullet)_s (M)}{(R_p)_{\max}} = \frac{k_z}{k_p} \quad (29)$$

2.1.3.2. The Treatment of Bengough et al. ⁵¹⁻⁵⁴

Alternatively, a plot of the left hand side of eqn (28) against time, t , will give a straight line of slope $k_z (R^\bullet)_s$ and hence, k_z can be determined from eqn (29) using a measured value of $(R_p)_{\max}$ at a known monomer concentration (M) .

Again, re-arranging equation (13):

$$2 k_t (R^\bullet)^2 + k_z (R^\bullet)(Z) - I = 0$$

$$\therefore (R^\bullet) = \frac{-k_z (Z) + \sqrt{k_z^2 (Z)^2 + 8 k_t I}}{4 k_t} \quad (30)$$

when $(Z) = 0$,

$$(R^\bullet)_s = \left[\frac{I}{2k_t} \right]^{\frac{1}{2}} \quad (31)$$

$$\begin{aligned} \therefore \phi_t &= \frac{(R_p)}{(R_p)_s} = \frac{(R^\bullet)}{(R^\bullet)_s} \\ &= \frac{-k_z (Z) + \sqrt{k_z^2 (Z)^2 + 8 k_t I}}{2(2I k_t)^{\frac{1}{2}}} \end{aligned} \quad (32)$$

$$\therefore k_z = \frac{(1 - \phi_t^2)}{\phi_t} \cdot \frac{(2 I k_t)^{\frac{1}{2}}}{(Z)} \quad (33)$$

Now we require the variation of (Z) with time or with % polymerization.

$$\text{But } - \frac{dz}{dt} = k_z (R^\bullet) (Z) \quad (14)$$

$$\therefore - \frac{1}{k_z} \int_{(Z)_0}^{(Z)} \frac{dZ}{Z} = \int_0^t (R^\bullet) dt$$

Now in general,

$$- \frac{d(M)}{dt} = k_p (M) (R^\bullet) \quad (8)$$

$$\therefore \int_0^t (R^\bullet) dt = - \frac{1}{k_p} \int_{(M)_0}^{(M)} \frac{d(M)}{(M)} \quad (35)$$

$$\therefore \frac{1}{k_z} \int_{(Z)_0}^{(Z)} \frac{dZ}{Z} = \frac{1}{k_p} \int_{(M)_0}^{(M)} \frac{d(M)}{(M)}$$

or,

$$\left(\frac{k_p}{k_z} \right) \ln \frac{(Z)}{(Z)_0} = \ln \frac{(M)}{(M)_0} \quad (36)$$

$$\text{Hence, } (Z) = (Z)_0 \left\{ \frac{M}{M_0} \right\}^{k_z/k_p} \quad (37)$$

Now, if F = fractional conversion of monomer to polymer,

$$\text{equal to } \frac{(M)_0 - (M)}{(M)_0}$$

$$\frac{(M)}{(M)_0} = (1 - F)$$

$$\text{Hence, } (Z) = (Z)_0 (1 - F)^{k_z/k_p} \quad (38)$$

Substituting the value of Z in (33)

$$k_z = \left\{ \frac{(1 - \phi_t^2)}{\phi_t} \frac{(2 I k_t)^{\frac{1}{2}}}{(Z)_0 (1 - F)^{k_z/k_p}} \right\} \quad (39)$$

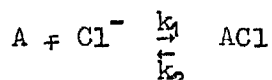
$$\therefore \log \left\{ \frac{(1 - \phi_t^2)}{\phi_t} \right\} = \log \left\{ \frac{k_z (Z)_0}{(2 I k_t)^{\frac{1}{2}}} \right\} + \frac{k_z}{k_p} \log (1 - F) \quad (40)$$

Thus, keeping I and $(Z)_0$ fixed if we plot $\log \left\{ \frac{(1 - \phi_t^2)}{\phi_t} \right\}$ against $\log (1 - F)$, we should get a straight line of slope $\frac{k_z}{k_p}$. The above equation was used by Bengough et al. for the polymerization of some monomers in presence of CuCl_2 .^{51,53,54}

However, because of the shape of the % polymerization against time curves, it is difficult to determine accurately the value of time corresponding to any value of ϕ if it is < 0.15 or > 0.8 . In this thesis, the values of ϕ were determined from the smoothed curves of % polymerization vs. time, at convenient intervals of time for the range of ϕ -values 0.15 - 0.8.

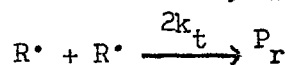
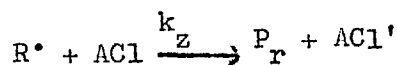
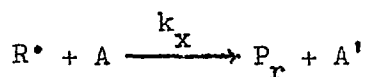
2.1.3.3. Extension of the Treatment of Bengough et al. to the Equilibrium $A + Cl^- \rightleftharpoons AC1$

It is assumed that in the presence of LiCl and an organic ferric complex, A, the following equilibrium is established.



where AC1 represents a substituted inner- or outer-sphere complex.

Now if the velocity constant for the reaction of a polystyryl radical with A and AC1 are represented by k_x and k_z respectively, the different termination steps will be



$$\therefore 2k_t(R^\bullet)^2 + (R^\bullet) \{k_x(A) + k_z(AC1)\} - I = 0 \quad (41)$$

$$\therefore (R^\bullet) = \frac{-\{k_x(A) + k_z(AC1)\} + \sqrt{\{k_x(A) + k_z(AC1)\}^2 + 8k_t I}}{4k_t}$$

$$\text{But, } (R^\bullet)_s = \left[\frac{I}{2k_t} \right]^{\frac{1}{2}}$$

[cf eqn (31)]

Proceeding as before, we can show that,

$$\{k_x(A) + k_z(ACl)\} = (2k_t I)^{\frac{1}{2}} \left\{ \frac{1 - \phi_t^2}{\phi_t} \right\} \quad (43)$$

$$\text{Now, } -\frac{d(ACl)}{dt} = k_z(R\cdot)(ACl) + k_2(ACl) - k_1(A)(Cl^-)$$

and if the equilibrium is always attained,

$$k_1(A)(Cl^-) = k_2(ACl)$$

$$\therefore -\frac{d(ACl)}{dt} = k_z(R\cdot)(ACl) \quad (44)$$

Hence, it can be shown as before

$$(ACl) = (ACl)_0 (1 - F)^{k_z/k_p} \quad (45)$$

[cf (38)]

If $k_x(A) \ll k_z(ACl)$ i.e. if the equilibrium is somewhat to the right hand side, and $k_z \gg k_x$

$$\text{then } k_z(ACl) = (2k_t I)^{\frac{1}{2}} \left\{ \frac{1 - \phi_t^2}{\phi_t} \right\} \quad (46)$$

In our experiments, k_z is of the order $10^4 \text{ l.mole}^{-1}\text{sec}^{-1}$ while k_x is of the order $10^2 \text{ l.mole}^{-1}\text{sec}^{-1}$, only.

$$\therefore k_z = \frac{(2k_t I)^{\frac{1}{2}}}{(ACl)_0 (1-F)^{k_z/k_p}} \left\{ \frac{1 - \phi_t^2}{\phi_t} \right\} \quad (47)$$

whence,

$$\log \left\{ \frac{1 - \phi_t^2}{\phi_t} \right\} = \log \left\{ \frac{k_z(ACl)_0}{(2k_t I)^{\frac{1}{2}}} \right\} + \frac{k_z}{k_p} \log (1 - F) \quad (48)$$

Hence, a plot of $\log \left\{ \frac{1 - \phi_t^2}{\phi_t} \right\}$ against $\log (1 - F)$ should give a straight line of slope $\frac{k_z}{k_p}$.

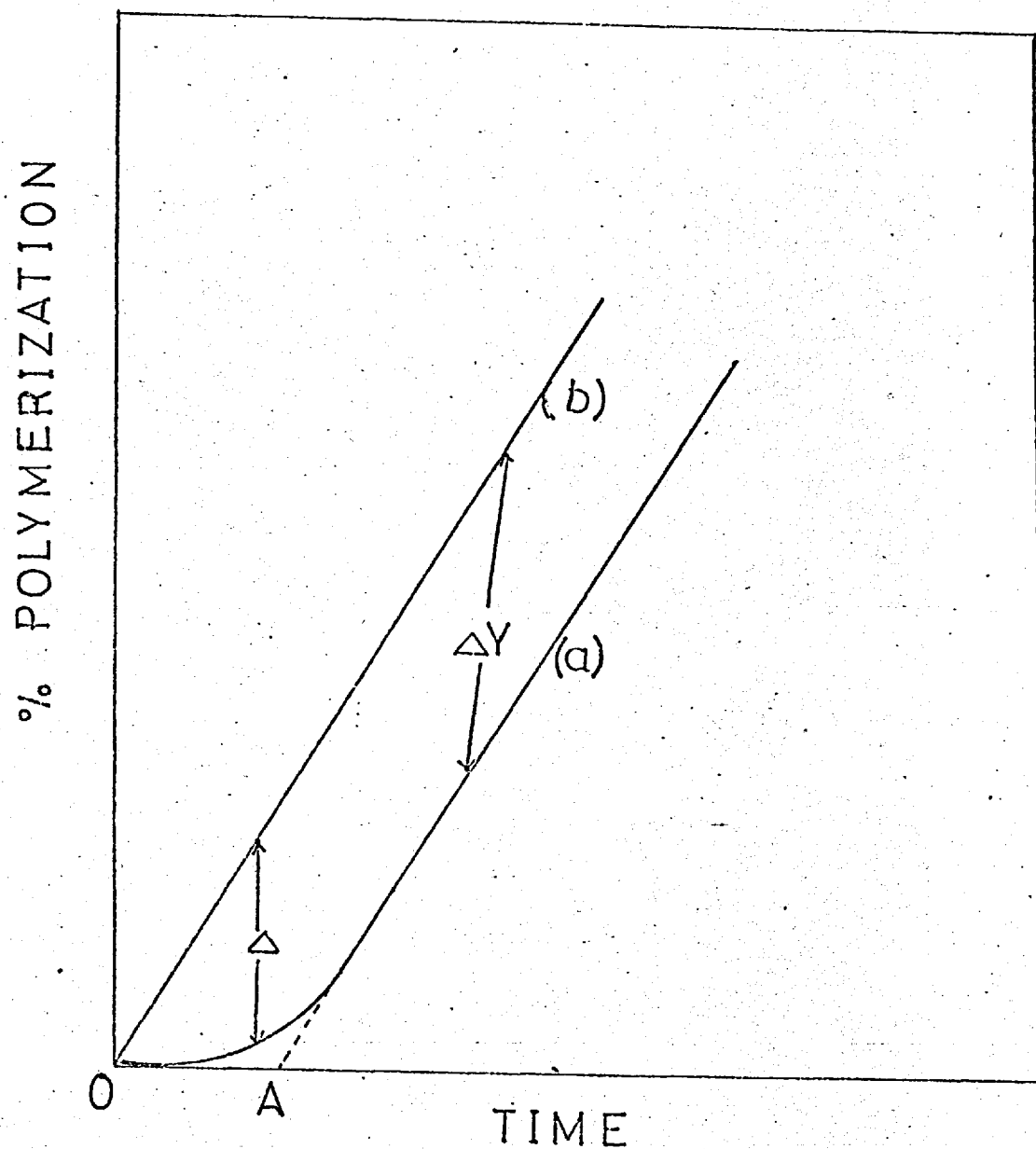


Fig.1. A conversion against time plot showing the significance of ΔY .

2.1.4. Relationship between τ and the Induction Period^{43,51}

In Figure 1, curve (a) represents the period of acceleration to the steady retarded rate following inhibition, and (b) is a straight line drawn through the origin parallel to the linear portion of the curve (a). We have

$$\frac{1}{\phi_0} - \frac{1}{\phi_t} + \ln \left[\frac{(1 - \phi_0)(1 + \phi_t)}{(1 + \phi_0)(1 - \phi_t)} \right] = k_z [R^\bullet]_s t \quad (23)$$

Differentiating eqn (23) and for convenience omitting the subscript t of ϕ_t , and replacing, for convenience here, the symbol ϕ by θ :

$$d\theta \left\{ \frac{1}{\theta^2} + \frac{1}{1+\theta} + \frac{1}{1-\theta} \right\} = k_z [R^\bullet]_s dt$$

Now, let the vertical distance between curves (b) and (a) be equal to Δ and ΔY be the value of Δ when (a) becomes linear (i.e. when (b) and (a) are parallel). The extrapolated linear portion of the curve (a) intersects the time axis at A. Hence, Induction Period, I.P. = OA.

Again,

Δ = difference in % polymerization achieved at any time t .

$$\begin{aligned} &= k_p [M] \int_0^t \{ [R^\bullet]_s - [R^\bullet] \} dt \\ &= k_p [M] \int_{\text{value of } \theta \text{ at } t=0}^{\text{value of } \theta \text{ at time, } t} \left\{ \frac{(R^\bullet)_s - (R^\bullet)}{k_z (R^\bullet)_s} \left(\frac{1}{\theta^2} + \frac{1}{1+\theta} + \frac{1}{1-\theta} \right) d\theta \right\} \end{aligned} \quad (49)$$

$$\text{But } \frac{(R^\bullet)}{(R^\bullet)_s} = \theta$$

Hence,

$$\begin{aligned}
 k_z \Delta &= k_p(M) \int_{\theta_0}^{\theta} (1 - \theta) \left\{ \frac{1}{\theta^2} + \frac{1}{1+\theta} + \frac{1}{1-\theta} \right\} d\theta \\
 &= k_p(M) \int_{\theta_0}^{\theta} \left(1 + \frac{1}{1+\theta} - \frac{\theta}{1+\theta} + \frac{1}{\theta^2} - \frac{1}{\theta} \right) d\theta \quad (50)
 \end{aligned}$$

Now, when $\theta = 1$, Δ becomes ΔY .

Hence, integrating (50) between θ_0 and 1

$$\begin{aligned}
 k_z \Delta Y &= k_p(M) \int_{\theta_0}^1 \left(1 + \frac{1}{1+\theta} - \frac{\theta}{1+\theta} + \frac{1}{\theta^2} - \frac{1}{\theta} \right) d\theta \\
 &= k_p(M) \left\{ 2 \ln 2 - 2 - 2 \ln (1+\theta_0) + \frac{1}{\theta_0} + \ln \theta_0 + \cancel{\theta_0} \right\} \quad (51)
 \end{aligned}$$

But $\frac{\Delta Y}{\text{intercept on OA}} = \frac{\Delta Y}{\text{I.P.}} = \text{rate of polymerization}$

$$= k_p(M) (R^*)_s \quad (52)$$

$$\therefore \text{I.P.} = \text{OA} = \frac{\Delta Y}{k_p(M)(R^*)_s} = \frac{1}{k_z (R^*)_s} \left\{ 2 \ln 2 - 2 - 2 \ln (1+\theta_0) + \frac{1}{\theta_0} + \ln \theta_0 + \cancel{\theta_0} \right\} \quad (53)$$

Again, since $\frac{1}{\theta_0} = k_z [R^*]_s \tau$ (26)

where τ is the time when the rate is 0.648 x maximum rate.

$$\therefore \tau - \text{I.P.} = \frac{1}{k_z (R^*)_s} \left\{ 2 - 2 \ln 2 - \ln \theta_0 \right\} \quad (54)$$

Since, $\ln (1 + \theta_0) \simeq \theta_0$ with $\theta_0 \rightarrow 0$. So τ is always greater than

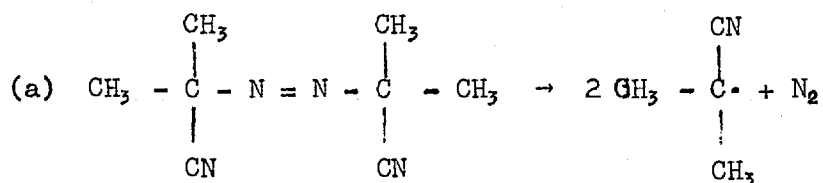
I.P. Bamford et al.⁴³ gave

$$\tau - \text{I.P.} = \frac{1}{k_z (R^\bullet)_s} \{1 - 2\ln 2 - \ln \theta_o\}$$

2.2. Decomposition of α, α' -azobisisobutyronitrile, (AIBN)

Azo-initiators are favoured for many kinetic studies because unlike peroxides they undergo no induced decomposition. The most widely used initiator with styrene is α, α' -azobisisobutyronitrile (AIBN). Its thermal decomposition in solution has been followed by nitrogen evolution, by spectrophotometry and by radical scavengers such as iodine, oxygen, α, α' -diphenyl- β picrylhydrazyl and ferric chloride, and is found to be first order.⁷²

Initially,



Tetramethylsuccinodinitrile is the main product in solution though other side products are formed.^{28, 67} A spectrophotometric method may be applied to determine the first order rate constant, k_d , using the expression⁷³

$$k_d = \frac{1}{t} \ln \left(\frac{A_o - A_\infty}{A_t - A_\infty} \right) \quad (55)$$

where, A_o , A_t and A_∞ represent the absorbancies corresponding to times zero, time t and time infinity, respectively. The value of $\ln (A_o - A_\infty)$ was found by an extrapolation procedure involving a plot of $\ln (A_t - A_\infty)$ against time, t , since during the early stages

of the experiment the spectroscopic cell contents had to warm up to the thermostatted cell holder temperature. The value of A_{∞} in practice, was determined after three or four weeks, when there was no measurable further change.

2.3. Measurement of Rates of Polymerization Dilatometrically

The density of styrene is less than that of polystyrene. Consequently, polymerization of styrene is accompanied by a decrease in volume and the rate of contraction in volume in a dilatometer enables the rate of polymerization to be determined.

If V ml. is the initial volume of the solvent and monomer (styrene) in the dilatometer at the experimental temperature and v is the volume of 1 cm of the capillary of radius, r ,

$$v = \pi r^2$$

$$V = \left\{ \begin{array}{l} \text{volume of the dilatometer bulb to the lower mark} \\ + \pi r^2 l_0 \end{array} \right\} \text{ cc}$$

where l_0 is the initial height of the liquid above the lower mark in cm, when the reaction time is zero and r is the radius of the capillary in cm.

In practice, different values of the height of the meniscus above the lower mark, are plotted against time of polymerization and l_0 is determined by extrapolating back to zero time. Now, if l_1 is the height above the lower mark at any time, t_1 min., % contraction in volume = $\left\{ \frac{(l_0 - l_1) v}{V} \right\} \times 100$ at any time t_1 min.

If all the styrene present in the reacting mixture of volume, V ml. are converted into polymer and if the initial volume of styrene at 60°C is $V_{\text{styrene}}(\text{ml})$, then

$$100\% \text{ polymerization} = \left\{ \frac{V_{\text{styrene}} - V_{\text{polymer}}}{V} \right\} \times 100 \% \text{ volume contraction.}$$

$\therefore$ corresponding to time, t_1 min., at 60°C

$$\begin{aligned} \% \text{ polymerization} &= \frac{(l_0 - l_1)v \times 100}{\left\{ \frac{V_{\text{styrene}} - \frac{V_{\text{styrene}} \times 0.8712}{1.0563}}{V} \right\} \times \frac{1}{V}} \\ &= \left\{ \frac{(l_0 - l_1)v \times 100}{V_{\text{styrene}} - \frac{V_{\text{styrene}} \times 0.8712}{1.0563}} \right\} \% \quad (56) \end{aligned}$$

since the densities of monomer and polymer at 60°C are 0.8712 and 1.0563 g.ml.⁻¹, respectively.

The percent polymerization can be calculated from eqn (56) and the plot of % conversion (of monomer to polymer) against time is found frequently to be linear.

Now, for 1 litre of styrene/solvent mixture converted at the rate of 1% per minute we have, $\left(\frac{1}{100} \times w\right)$ gm. of polystyrene formed in 1 litre of the mixture at 60°C .

In other words,

$$1\% \text{ polymerization per minute} = \left[\frac{1}{100} \times \frac{w}{104.1} \times \frac{1}{60} \right] \text{ mole of styrene } l^{-1} \text{sec}^{-1}.$$

$$\therefore X\% \quad " \quad " \quad " \quad \equiv X \left[\frac{1}{100} \times \frac{w}{104.1} \times \frac{1}{60} \right] \text{ mole } l^{-1} \text{sec}^{-1} \quad (57)$$

The following densities were used in this thesis,

Table 1

Compounds	Density at 20°C (gm.ml. ⁻¹)	Density at 60°C (gm.ml. ⁻¹)
Styrene ⁷⁴	0.9063	0.8712
Polystyrene in styrene ⁷⁴	-	1.0563
Dimethyl formamide ⁷⁴ (DMF)	0.9494	0.9150
Dimethyl sulphoxide* (DMSO)	1.1003	1.0609

(* Determined in these laboratories)

2.4. The Viscosity Measurement⁷⁵

The intrinsic viscosity of a polymer is related to the viscosity average molecular weight by the Mark-Houwink equation

$$[\eta] = K \bar{M}_v^\alpha,$$

where K and α are constants for a given polymer, solvent and temperature.

Measurements of solution viscosity are usually made by comparing the time, t , required for a given volume of polymer solution to flow through a capillary tube with corresponding time, t_0 , for the solvent.

The relative viscosity is given by $\eta_r = \frac{t}{t_0}$

$$\text{Specific viscosity, by } \eta_{sp} = \frac{t - t_0}{t_0}$$

$$\begin{aligned} \text{and intrinsic viscosity, by } [\eta] &= \left[\frac{\eta_{sp}}{c} \right]_{c=0} \\ &= \left[\frac{\ln \eta_r}{c} \right]_{c=0} \end{aligned}$$

$$\text{for } \eta_r < 2 \quad 68$$

The intrinsic viscosity is obtained by plotting both $\frac{\eta_{sp}}{c}$ and $\frac{\ln \eta_r}{c}$ against c and extrapolating back to zero concentration, and using a mean value if the two extrapolated values do not coincide.

The intrinsic viscosity is independent of concentration. The constant, K, may be replaced by the appropriate calculated constant to yield the number average molecular weight ($\bar{M}_n$) directly. For example, for unfractionated vinyl polymers terminated exclusively by disproportionation⁷⁵ of polymer radicals of low conversion,

$$K'' = K\Gamma(2 + \alpha) \text{ and } [\eta] = K'' \bar{M}_n^\alpha \quad (58)$$

and for unfractionated vinyl polymers terminated exclusively by combination,

$$K''' = \frac{K\Gamma(3 + \alpha)}{2^{1+\alpha}} \text{ and } [\eta] = K''' \bar{M}_n^\alpha \quad (59)$$

where Γ is the "Gamma Function".⁷⁶ Bawn et al.⁷⁷ established the following values for polystyrene in toluene at 25 - 30°C,

$$[\eta] = 1.729 \times 10^{-4} (\bar{M}_n)^{0.71} \text{ dl. g.}^{-1} \quad (60)$$

for unfractionated polystyrene

and

$$[\eta] = 1.34 \times 10^{-4} (\bar{M}_n)^{0.71} \text{ dl. g.}^{-1} \quad (61)$$

for fractionated polystyrene.

The above equations, suitably modified when necessary, were used in all later calculations.

2.5. Osmotic Pressure Measurements

2.5.1. Determination of Molecular Weight, ($\bar{M}_n$)

According to the theory of dilute polymer solutions^{66,68}, the osmotic pressure, π is a function of concentration, c and it is established that

$$\frac{\pi}{c} = \left(\frac{\pi}{c}\right)_0 [1 + \Gamma_2 c + g\Gamma_2^2 c^2]$$

where Γ_2 is the parameter depending on the polymer-solvent interaction; g is a slowly varying function of polymer-solvent interaction with values near zero for poor solvents and near 0.25 for good

solvents, and $(\frac{\pi}{c})_0$ represents the limiting value at infinite dilution. For very dilute solutions, the above equation may be approximated as

$$\left(\frac{\pi}{c}\right) = \frac{RT}{\bar{M}_n} [1 + \Gamma_2 c] \text{ where } \left(\frac{\pi}{c}\right)_0 = \frac{RT}{\bar{M}_n} \quad (62)$$

Owing to the omission of the higher terms in eqn (62), its application is restricted to solutions of low concentration only.

2.5.2. Calculation of the gas constant, R.

$$R = 8.205 \times 10^{-2} \text{ l.atmos. deg.}^{-1} \text{ mole}^{-1}.$$

$\therefore$ if d_t = density of toluene at temperature, $t^\circ\text{C}$,

$$R = 8.205 \times 10^{-2} \left(\frac{76 \times 13.595}{d_t} \right) \text{ l. cm of toluene at } t^\circ\text{C deg.}^{-1} \text{ mole}^{-1}.$$

$\therefore$ At a temperature of $t^\circ\text{C}$,

$$RT = \left\{ \frac{84.776}{d_t} \times (273.16 + t) \right\} \text{ l. cm of toluene mole}^{-1}.$$

$$\therefore \left(\frac{\pi}{c}\right)_0 = \frac{RT}{\bar{M}_n} = \frac{84.78 (273.16 + t)}{d_t \cdot \bar{M}_n} \quad (63)$$

In this thesis, the following density values⁷⁸ were used:

Table 2

Temperature ($^\circ\text{C}$)	Density of toluene (gm. ml. $^{-1}$)
20	0.866
25	0.861
30	0.856

The plot of densities of toluene against temperature (range 0°C to 99°C) gives a straight line (Fig.2) and the densities corresponding to intermediate temperatures were calculated from this plot.

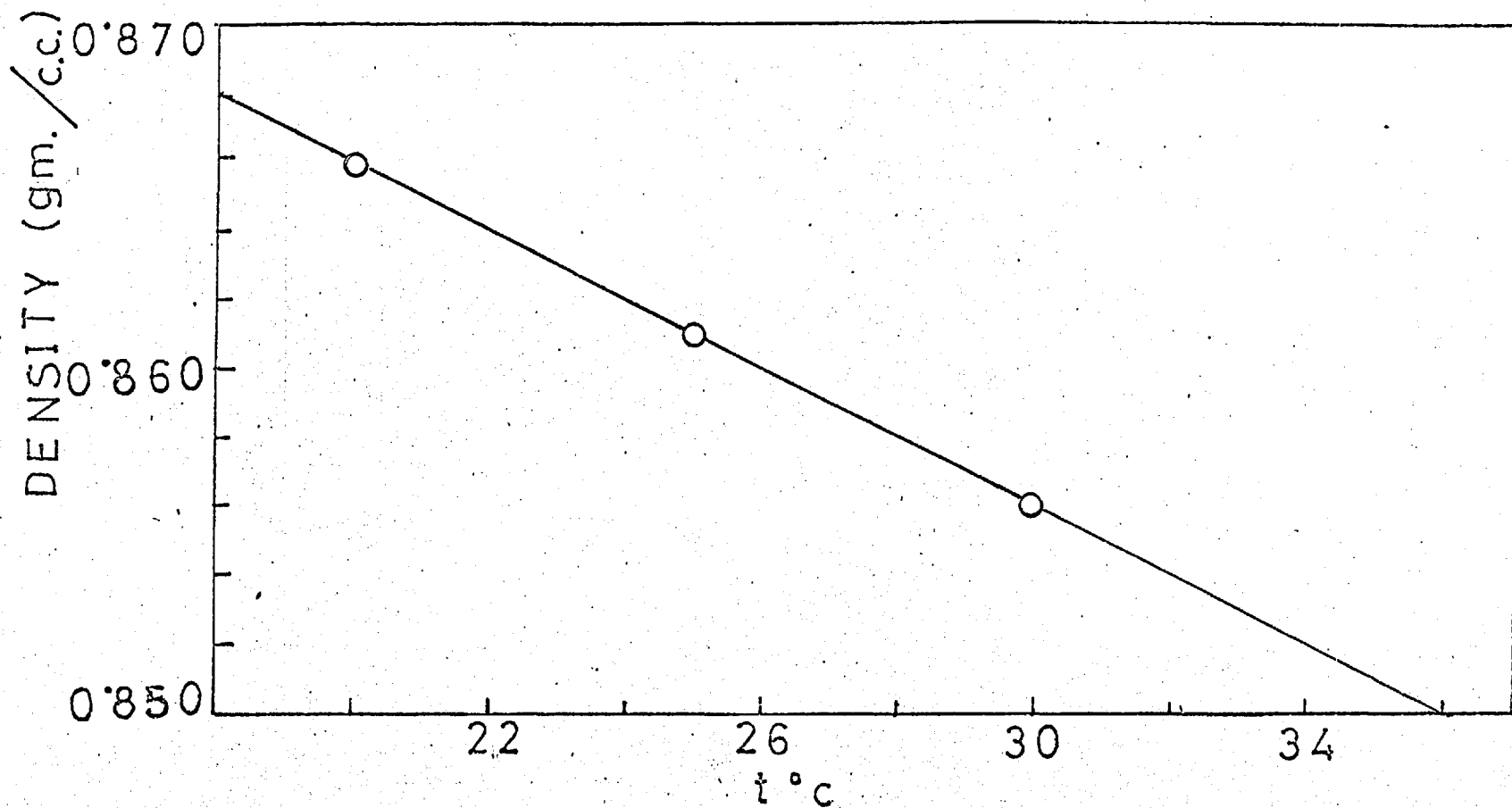


Fig.2. Densities of toluene at different temperatures..

III MATERIALS

(Preparation, Purification and Storage)

3.1. Monomer

3.1.1. Styrene

The styrene, (supplied by B.D.H.), contained 0.001 to 0.002 per cent of tert. - Butyl catechol as the stabilizer. It was purified⁷⁹ by washing three times with 40 per cent aqueous sodium hydroxide (A.R., Hopkin and Williams) followed by five times with distilled water, and drying overnight over anhydrous calcium sulphate. The filtered liquid was distilled under vacuum and the middle fraction was collected.

Oxygen-free nitrogen was then bubbled through the purified styrene and it was stored in "Cardice" (solid carbon dioxide) in a Quickfit stoppered flask. The styrene was discarded when a few ml. of methanol added to a small test sample of monomer at room temperature produced a faint precipitation of polystyrene. The purity of the styrene was checked with methanol in this way from time to time.

3.2. Solvents

3.2.1. N,N Dimethyl Formamide (DMF)^{74,80}

Commercial N,N dimethyl formamide (B.D.H.) was dried by treating it successively with A.R. potassium hydroxide pellets (Hopkin and Williams), anhydrous calcium sulphate and calcium hydride (Hopkin and Williams). After filtration, it was distilled under reduced pressure

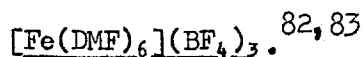
and the middle fraction was collected. It was stored in a stoppered bottle over a trace of calcium hydride until required.

3.2.2. Dimethyl sulphoxide (DMSO).⁸¹

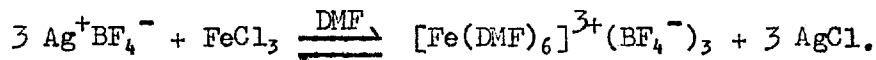
Commercial dimethyl sulphoxide (B.D.H.) was dried over Linde 4A molecular sieve, distilled under reduced pressure and the middle fraction was collected. It was stored over Linde 4A molecular sieve until needed.

3.3. Organic Ferric Compounds

3.3.1. Hexakis N,N-dimethyl formamide iron(III) Tetrafluoroborate,



To 2.6869 gm (0.0138 mole) of anhydrous silver boron tetrafluoride (Alfa Inorganic) dissolved in 30 ml. of N,N-dimethyl formamide (DMF), 0.75 gm. (0.0046 mole) of anhydrous ferric chloride (Hopkin and Williams) dissolved in 20 ml. DMF were added. To ensure complete precipitation, the mixture was allowed to stand for about twelve hours and then the precipitate of silver chloride was filtered off through a dry No.3 sintered glass crucible. 300 ml. of dried anhydrous ether (M and B) were added to the filtrate and the mixture was kept overnight. The solid formed was filtered off, washed with ether, and dried under vacuum in a desiccator over silica gel.

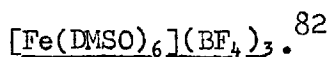


The yellow crystalline compound was recrystallised from a mixture of DMF/absolute alcohol and stored in the dark over silica gel until required. The entire operation was carried out in a dry box.

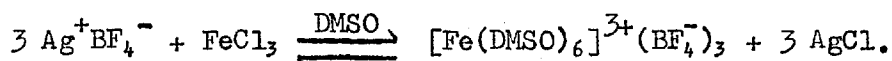
Analytical results:

Calculated for C, 28.64%; H, 5.61%; N, 11.13%

Found C, 28.76%; H, 5.82%; N, 11.26%.

3.3.2. Hexakis Dimethyl Sulphoxide Iron(III) Tetrafluoroborate,

To 2.6869 gm (0.0138 mole) of anhydrous silver boron tetrafluoride (Alfa Inorganic) dissolved in 30 ml. of dimethyl sulphoxide (DMSO), 0.75 gm (0.0046 mole) of anhydrous ferric chloride (Hopkin and Williams) dissolved in 20 ml. of DMSO were added. To ensure complete precipitation, the mixture was allowed to stand for twenty four hours and then the precipitate of silver chloride was filtered off through a dry No.3 sintered glass crucible. 300 ml. of dried anhydrous ether (M. and B.) were added to the filtrate and the mixture was kept in the dark for forty eight hours. The solid formed was filtered off, washed with ether and dried under vacuum in a desiccator over silica gel.



The greenish yellow crystalline compound was then dissolved in DMSO and reprecipitated twice by absolute alcohol. It was dried in vacuo and stored in the dark over silica gel until required. The entire operation was carried out in a dry box.

Analytical results:

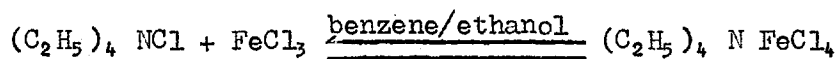
Calculated for, $\text{C}_{12}\text{H}_{36}\text{S}_6\text{O}_6\text{B}_3\text{F}_{12}\text{Fe}$

C, 18.36%; H, 4.59%

Found C, 18.36%; H, 4.64%

3.3.3. Tetraethylammonium Tetrachloroferrate(III).⁸²

Tetraethylammonium tetrachloroferrate was prepared by dissolving iron(III) chloride (Hopkin and Williams) in a benzene/ethanol mixture (1:1, by volume). To the solution was added the stoichiometric quantity of tetraethylammonium chloride (B.D.H.). Precipitation of yellow needle-like crystals occurred immediately.



The crystals were filtered off and washed with anhydrous ether, and dried in a vacuum desiccator over phosphorous pentoxide. The compound was stored in the dark in vacuo over phosphorus pentoxide until required.

Analytical results:

Calculated for $\text{C}_8\text{H}_{20}\text{NFeCl}_4$:

C, 29.28%; H, 6.10%; N, 4.27%

Found C, 29.23%; H, 5.98%; N, 4.22%.

3.4. Initiator

3.4.1. Purification of α, α' -azobisisobutyronitrile (AIBN)

About 6 gm. of commercial α, α' -azobisisobutyronitrile (Aldrich Chemical Company) were placed in a 500 ml. round bottom flask and about 400 ml. of anhydrous ether (M. and B.) were added progressively, in small quantities. The mixture was stirred in a bath of warm water, (30 - 35°C), until the AIBN dissolved to form a clear solution. For the sake of safety, this operation was performed outdoors. Some ether was then evaporated using a water pump to reduce the

volume to about 200 ml. The solution became cloudy and was kept overnight in a refrigerator, in a stoppered round-bottomed flask wrapped in aluminium foil.

The crystalline material was isolated by filtration, dissolved in ether once more, and the whole operation was repeated.

The final white, crystalline material was stored in a small stoppered bottle covered completely with aluminium foil.

The purity of the compound was checked spectroscopically.

3.5. Lithium salts

Lithium fluoride, lithium chloride, lithium bromide and A.R. lithium sulphate supplied by B.D.H. were used directly without further purification.

IV APPARATUS

4.1. The High Vacuum System

It has been noted that atmospheric oxygen has a profound influence upon the kinetics of polymerization of vinyl monomers. Further, the effect of oxygen is so varied and unpredictable that it is absolutely essential to remove all atmospheric oxygen from the reaction vessel to achieve reproducible kinetic results. The high vacuum system used for filling reaction vessels and degassing reactants is shown in Fig.3.

The pumping system consisted of one small mercury diffusion pump D_1 and a large mercury diffusion pump D_2 arranged in series, backed by an Edwards "Speedivac" high vacuum oil rotary pump (2 SC 20 A).

The oil pump used in conjunction with the mercury diffusion pumps enabled the pressure to be reduced to as low as 10^{-6} mm of mercury. The small bulb F together with a large "equalizing pressure bulb", E, prevented oil from being sucked into the main system in the event of power failure. The liquid air trap, A, prevented the condensable vapours released during degassing procedures from contaminating the mercury in the diffusion pump or the oil in the rotary pump. A section of the apparatus, P, with two taps, T_3 and T_4 , enabled the mercury diffusion pumps D_1 and D_2 to be by-passed if desired. In some experiments in which large quantities of air were released from materials being degassed, initial degassing was achieved using

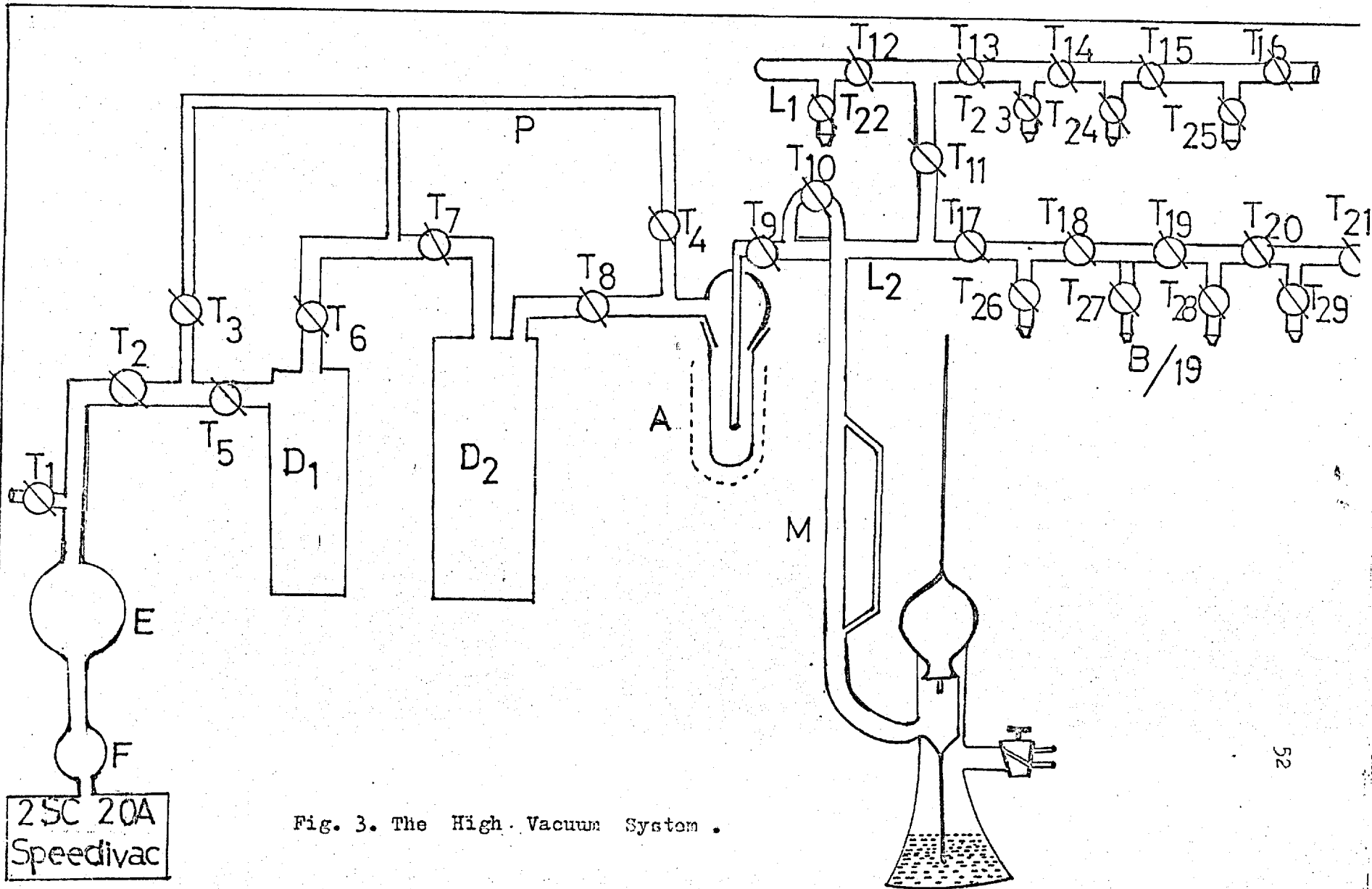


Fig. 3. The High Vacuum System .

the rotary pump alone, by closing the taps T_5 , T_6 , T_7 and T_8 and opening taps T_3 and T_4 . The degassing procedure could be completed using both diffusion pumps and rotary pump by closing taps T_3 and T_4 and opening taps T_5 , T_6 , T_7 and T_8 .

The main vacuum line, connected to the diffusion pumps, was made of tubing of large bore (2 cm) in order to facilitate efficient outgassing and consisted of two parts L_1 and L_2 with an inter-connecting tap T_{11} . The vacuum lines L_1 and L_2 contained a series of isolating high vacuum taps $T_{12} - T_{16}$ and $T_{17} - T_{21}$, respectively. L_1 and L_2 also contained a series of side arms fitted with taps $T_{22} - T_2$, and each side arm had a B/19 cone at the free end.

A conventional McLeod gauge which could be isolated by tap T_{10} , if necessary, was incorporated in the vacuum line for measurement of pressure.

Pyrex glass was used throughout and all the taps are lubricated with Apiezon N high vacuum grease (Edwards High Vacuum Co.Ltd.).

4.2. The Dilatometers

The density of most vinyl monomers is less than that of the polymers formed from them and as such rates of polymerization can be followed by measuring the contraction in volume. The rate of contraction is generally measured in a reacting vessel known as a dilatometer, (Fig.4). Dilatometers were usually made of Veridia precision bore capillary of diameter 2 mm and of length 10 cm, joined to a bulb of size about 8 cc. In some experiments dilatometers with a bulb capacity of about 30 ml., and a capillary of 1.0 mm

diameter were used to increase the accuracy of measuring reduced rates of polymerisation. Dilatometers were calibrated using distilled water, the density of which is known precisely at any given temperature. Two marks, C and D, were made on the capillary by means of a glass knife as shown in Fig.4. The volume of each dilatometer to the lower mark, C, as well as the radius of the capillary and the distance between the top and bottom marks, C and D, were determined accurately.

The Filler Tube with Dilatometer

To avoid any extraneous effects due to atmospheric oxygen, the dilatometers were filled and sealed off in vacuum. The apparatus for doing this is shown in Fig.5. The dilatometer was attached to a tube filler furnished with a B/19 socket at the top. The reaction mixture was first introduced into the tube filler through a dropping funnel. The mixture was then frozen by immersing the tube filler in liquid nitrogen and the whole system was evacuated. By alternately isolating the tube filler and contents from the rest of the vacuum line by means of a tap and melting the contents in the tube filler, degassing was accomplished. The reactants were assumed to be free from air, when no bubbles were evolved on melting the solid. In practice, degassing was usually carried out three times. With the tube filler frozen in liquid nitrogen, the tube filler was sealed at the constriction, A, by an oxy-gas flame. Finally some of the liquid was tipped into the dilatometer so that the meniscus of the liquid in the capillary tube would stand about 3 cm below the top

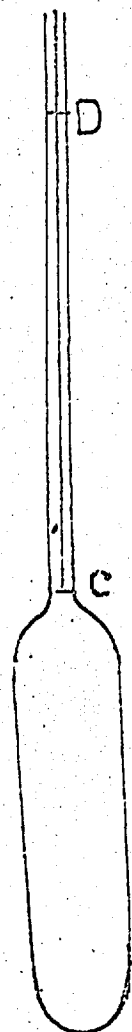


Fig.4. Dilatometer .

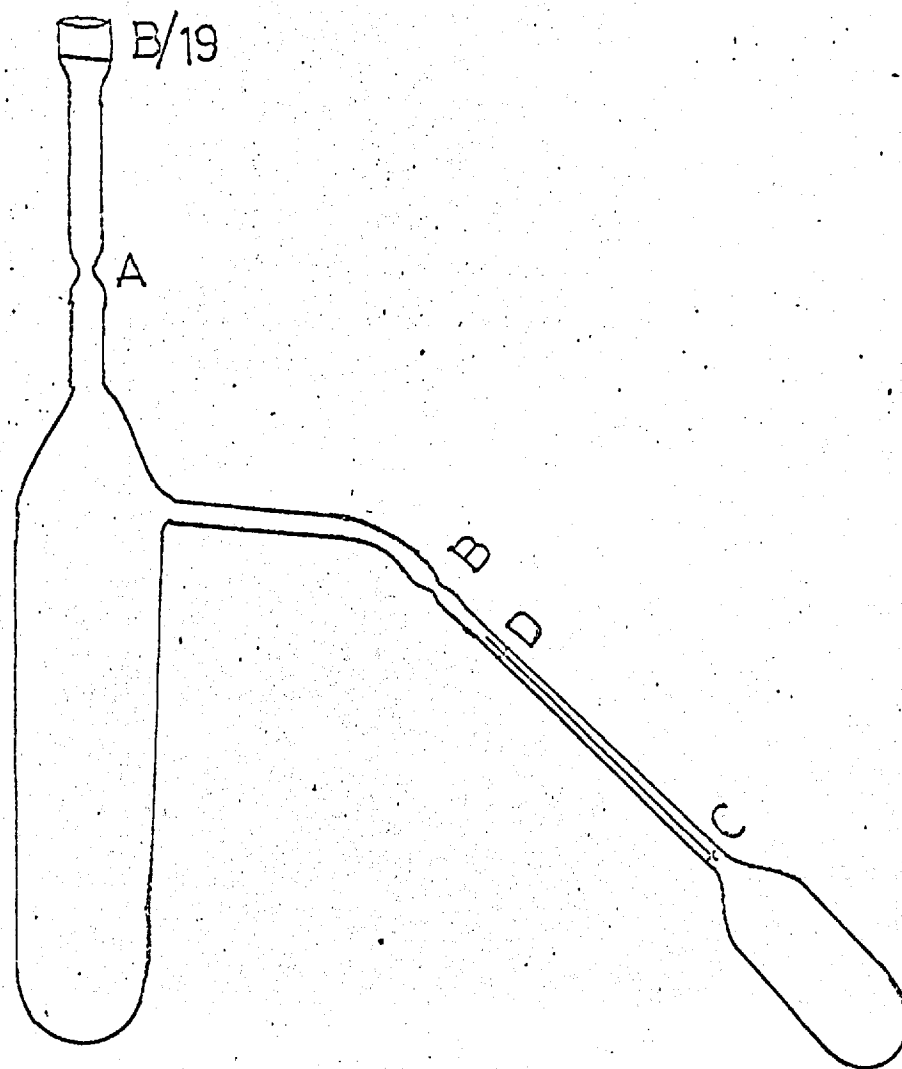


Fig.5. Dilatometer attached to the
Tube Filler .

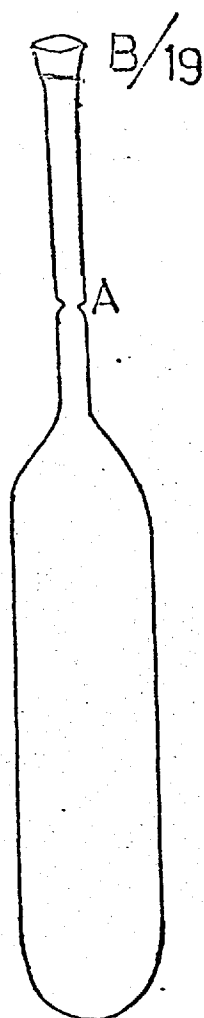


Fig. 6. Simple tube.

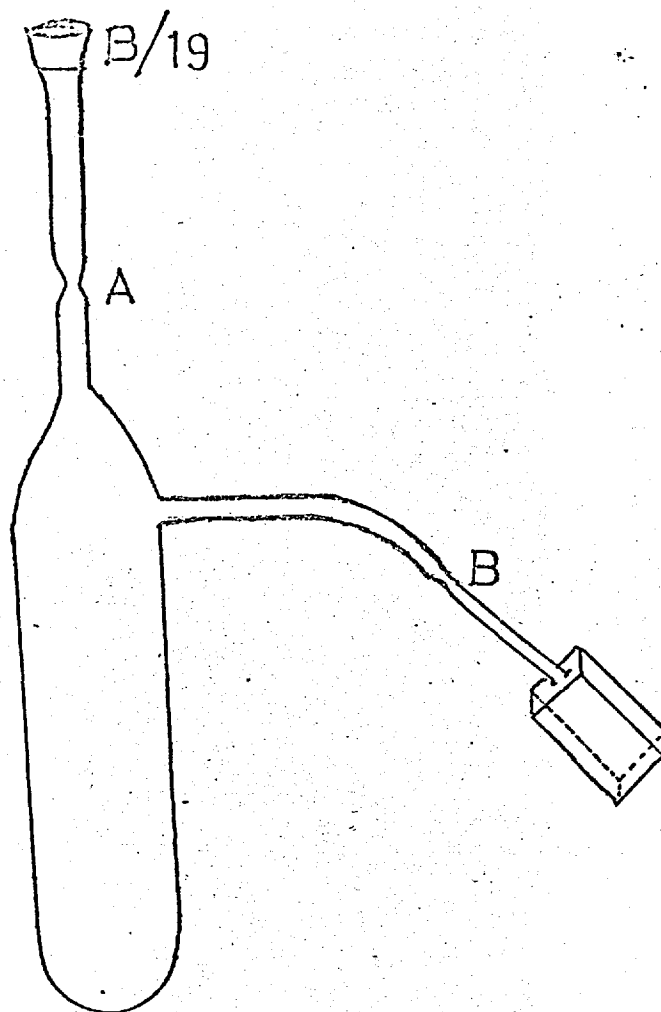


Fig. 7. Spectroscopic cell attached to tube filler.

mark, D, when thermostatted at 60°C . The liquid in the dilatometer and that left in the filler tube were then both frozen in liquid nitrogen and the dilatometer was sealed at the constriction, B, and detached from the tube filler. The fall in the meniscus height in the dilatometer was followed by means of a cathetometer. Usually a 50 cm cathetometer with a vernier reading to ± 0.001 cm was used.

4.3. The Thermostat

A cylindrical glass bath of height 45 cm and diameter of 30 cm, was used as a thermostat. It was filled with water and covered by a layer of paraffin oil of about 1 cm depth, about 4 cm below the bath top, in order to reduce excessive evaporation of water.

The temperature of the bath was controlled at 60°C ($\pm 0.01^{\circ}\text{C}$) by a contact thermometer (Jumo Contact Limited, MS 121) connected to a heater through an electronic control relay (Electro Methods Limited, England, Type No. 213B). In order to keep the temperature of the bath uniform, the contents in the bath were constantly stirred by an electrical stirrer. A standard thermometer (certified by Sugden, Powell Limited), immersed completely in the bath, served as a reference thermometer. A similar bath filled with distilled water maintained at 30°C , by a similar method was used for viscometric work.

4.4. Gravimetry

For gravimetric work, reactions were carried out in simple tubes (Fig.6), fitted with B/19 sockets at the top. The reaction mixture of monomer (styrene), solvent and initiator in each tube was degassed

and sealed in vacuo exactly as in dilatometric work. The sealed tube was then introduced into the bath at 60°C . The conversion was not allowed to exceed ten per cent. The tube was then cracked open and the contents were poured into a 400 ml. beaker containing about 200 ml. of methanol in which had been dissolved a trace of hydroquinone. The polystyrene precipitated, and the precipitate was allowed to settle overnight and filtered through a clean previously-weighed sintered glass crucible (No.3). It was washed with methanol and dried at 60°C , under vacuum, to constant weight. (In practice, the samples were dried under vacuum until the loss in weight did not exceed 5 milligrams per day). The rate of polymerization was calculated from the amount of polystyrene formed and the sample could be subsequently used in osmometry and/or viscometry for the determination of the degree of polymerization.

4.5. Viscometry

The molecular weight of polystyrene was determined using an Ubbelohde viscometer fitted with a pumping device as shown in Fig.8. The three limbs of the viscometer, A, B and C were covered, when necessary, with glass lids, D, E and F, respectively, to prevent dust from contaminating the solution inside the viscometer. There were two etched marks X and Y on the limb C,

In order to obtain reproducible results, the apparatus must be clean, dry and completely free from dust particles. Hence, the apparatus was soaked in chromic acid for 24 hours, rinsed with distilled water and dried overnight in an air oven before use.

The apparatus was placed in the thermostat at 30°C, and 5 ml. of dust free "AnalaR" toluene were pipetted through A. About 15 minutes were allowed for temperature equilibrium to be attained.

The pumping system was then connected to A and air, previously filtered through a sintered glass filter S, was pumped into the viscometer keeping a moistened finger over B, till the solvent level rose well above the top etched mark, X. Then the pressure was released by opening the tap T on the pumping device and a few seconds later the finger from B was removed and the liquid began to flow down the capillary. The time of flow of the solvent from the upper to lower etched mark was measured with a stopwatch. The experiment was repeated until three consecutive readings agreed within 0.2 second. If the times were found to be inconsistent the apparatus was cleaned with chromic acid once more, as some dust particles were suspected to be present.

The apparatus was dried in an oven and 5 ml. of a standard solution (about 1%) of polystyrene in dust free "AnalaR" toluene (B.D.H.) were pipetted into A and the time of flow of the solution from X to Y was measured as before. A known volume of dust free "AnalaR" toluene was added to A to reduce the concentration of the solution to about 0.8%. The solution was made homogeneous by holding a finger over C and applying pressure by means of the pumping device at B to bubble air through the solution. The time of flow was determined by the stopwatch as before and the operation was repeated by further additions of solvent till the concentration of the solution fell to about 0.25%.

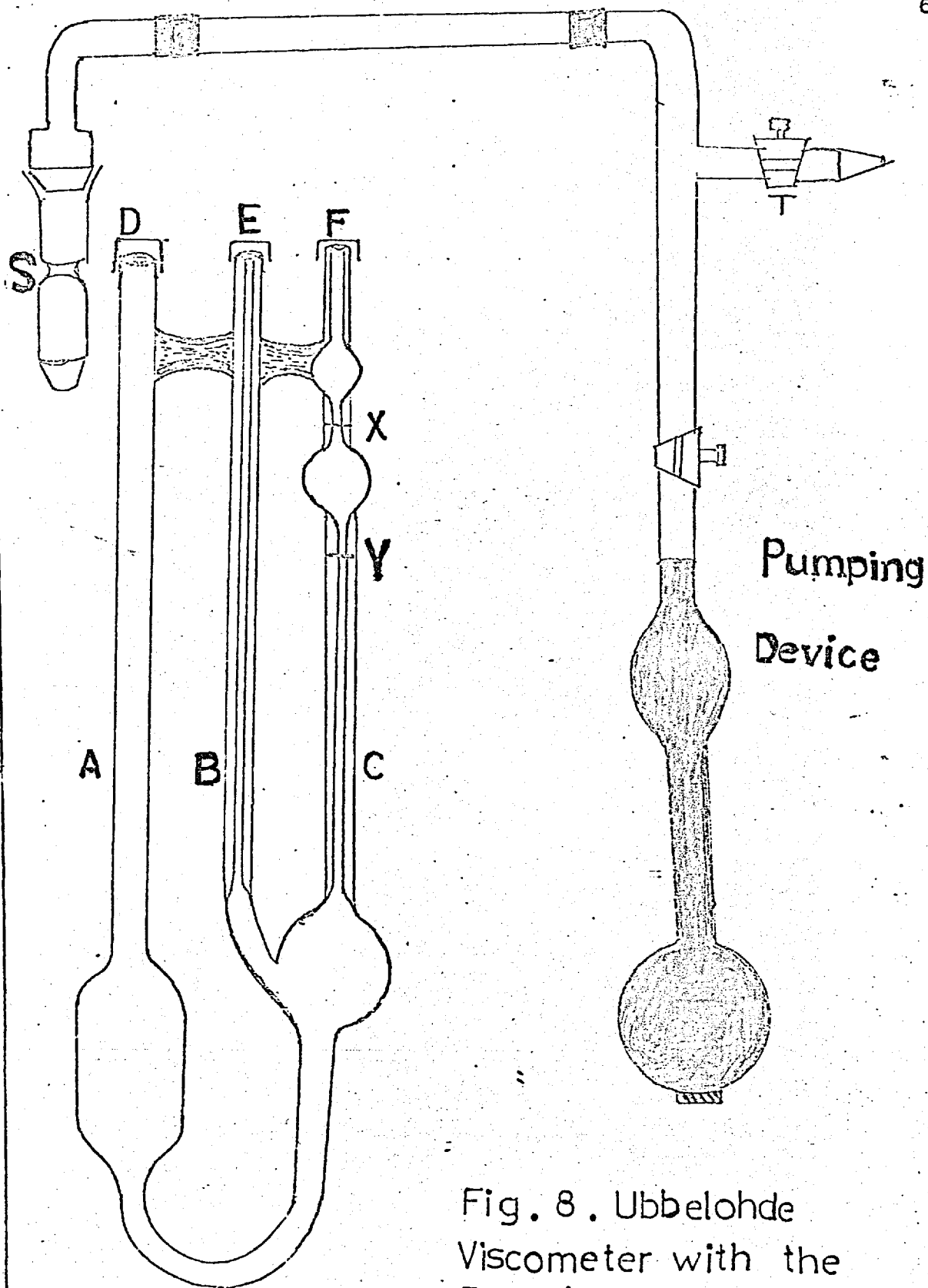


Fig. 8 . Ubbelohde
Viscometer with the
Pumping Device .

4.6. Osmometry

The osmometer used for the determination of the molecular weight of the polystyrenes was a Mechrolab model 502 High Speed Membrane Osmometer, with a Schleicher and Schuell type 0 - 8 regenerated cellulose membrane. The instrument was sensitive within the number-average molecular weight range of 20,000 to 1,000,000, and permitted operation from room temperature to 130°C. The instrument was operated at room temperature with "AnalaR" toluene (B.D.H.) as the solvent.

The working principle of the osmometer is shown in Fig.9. Fundamental to the operation of the Mechrolab 502 were a semipermeable membrane and an air bubble. The air bubble was trapped in a capillary which was filled with solvent and attached to a lower membrane clamp. In the control position, the light source was focused on the upper meniscus of the air bubble. The photo-detector cell was located at an angle of 90° from the light beam.

The counter pressure servo system consisted of a photo-detector cell, an amplifier and a servo-motor connected to the elevator that adjusted the pressure on the solvent side of the membrane.

Initially a standard solution of polystyrene (about 1%) was introduced. This caused solvent flow towards the membrane causing distortion of the air-solvent meniscus. This distortion of the meniscus changed its light scattering properties, and, hence changed the intensity of light reaching the detector cell. The detector cell analysed this change and sent a signal through the

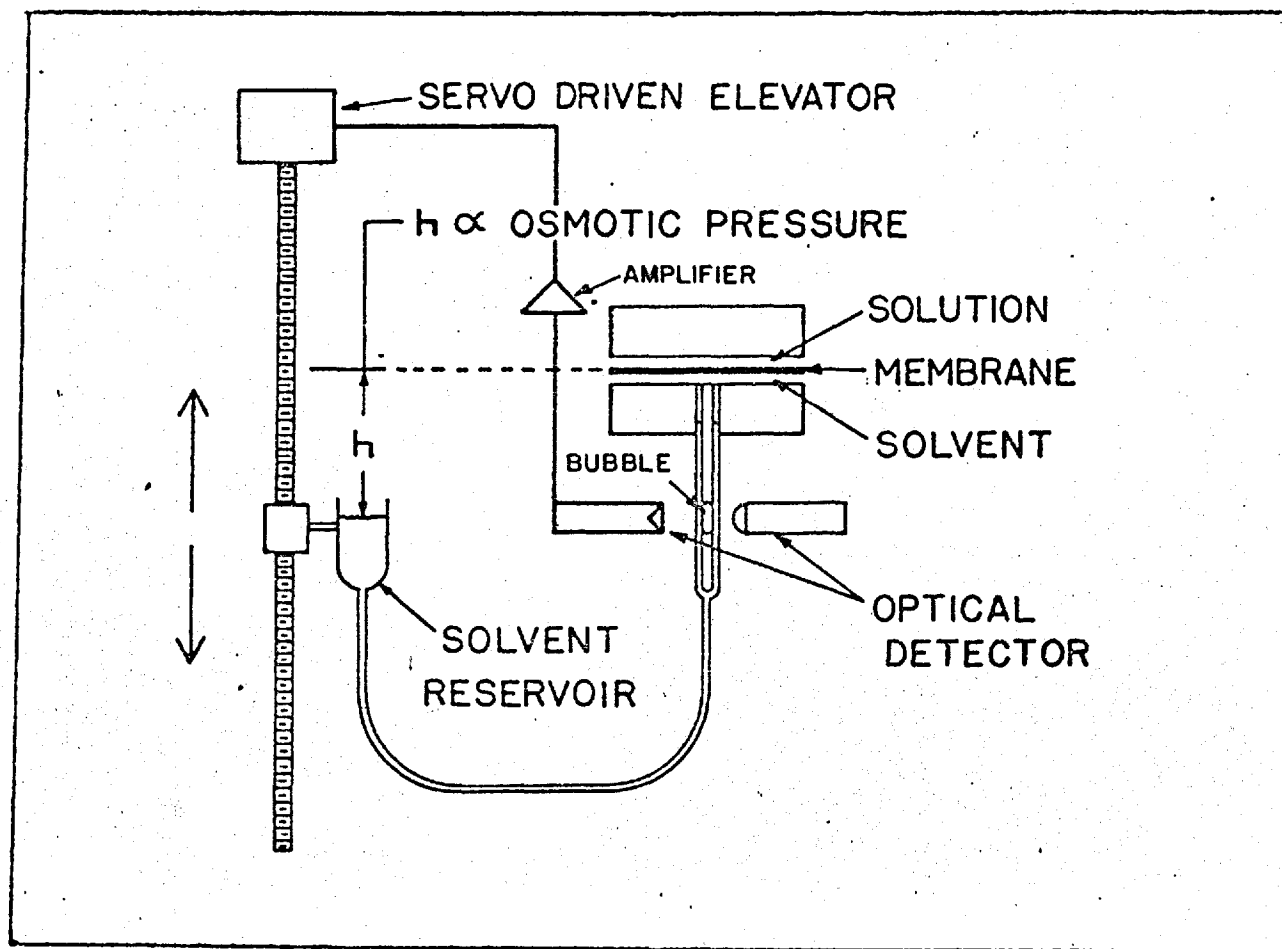


Fig.9. The Working Principle of the Mechrolab 502

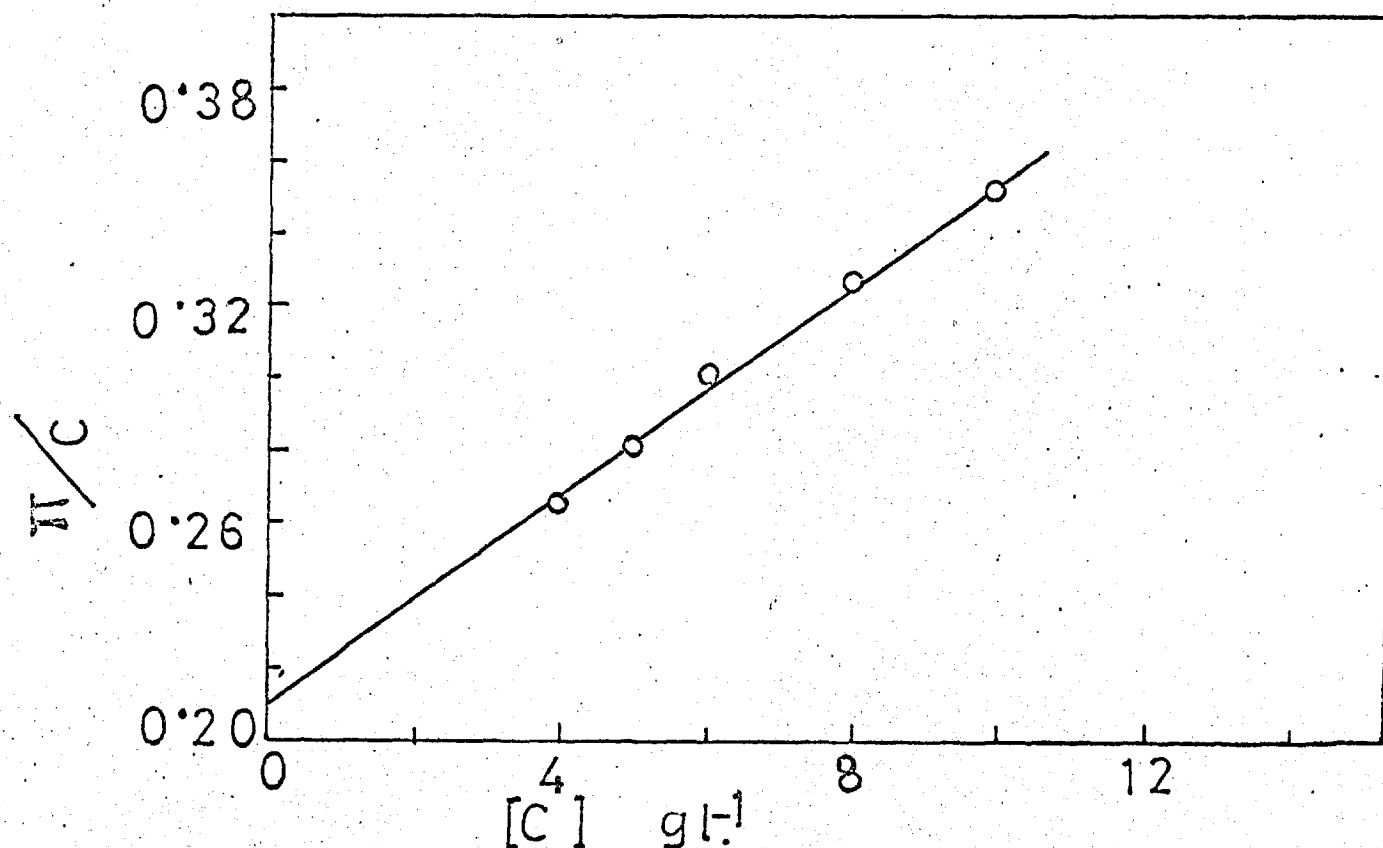


Fig.10. Plot of $\frac{\pi}{C}$ vs. concentration, C for Pressure Chemical Co. Special Polystyrene in toluene. $(\frac{\pi}{C})_0 = 0.216$ cm. toluene 100 ml.g.⁻¹ at 20°C. Values quoted for the Special Polystyrene $\frac{\bar{M}_w}{\bar{M}_n} < 1.06$ and $\bar{M}_n = 97,200$.

amplifier to the servo system. The servo system then made the appropriate pressure adjustment. The pressure applied was read on a digital counter in cm of solvent and was equivalent to the osmotic pressure of the solution. The osmotic pressures at a series of three or four concentrations were measured and the results were represented graphically. Extrapolation to zero concentration of $(\frac{\pi}{c})$ was made, and the molecular weight was calculated from this value. A typical extrapolation is shown in Fig.10, using a fractionated polystyrene sample supplied by The Pressure Chemical Company.

The servo system was capable of reading osmotic pressures to well within ± 0.01 cm of the solvent. A recorder was used in conjunction with the osmometer. The recorder demonstrated the graphic display of the dynamics of the system.

4.7. Spectroscopy

The spectrometers used were the Unicam S.P. 800 and S.P. 500 models and a Perkin-Elmer 137 U.V. model. The first spectrometer was used for recording spectra at room temperature whilst the other two were used for spectra at room temperature as well as at 60°C . A Churchill thermo circulator was used in conjunction with the spectrometers for thermostating the cells at 60°C . To avoid any extraneous effects due to oxygen, reactions were performed under vacuum in plain reaction tubes (Fig.6). At suitable times, reaction tubes were removed from the thermostat rapidly cooled in liquid nitrogen, cracked open, mixed with an appropriate amount of 1,10 phenanthroline hydrate (Hopkin and Williams) and then the mixture transferred to spectroscopic

cells. In some cases, the cells were filled in vacuo and the reactions were followed directly. Aluminium foil was used to protect cells containing reactant solutions from stray light. The apparatus for filling such cells is shown in Fig.7. The degassing was performed as previously described for dilatometry. 10 mm. path length rectangular quartz cells (Thermal Syndicate Ltd) were usually used for ultra-violet spectroscopy. The cells were matched against DMF and DMF-styrene mixture containing lithium chloride when appropriate.

V. RESULTS AND DISCUSSIONS

5.1. Spectroscopic Identification of α, α' -azobisisobutyronitrile

The melting point of α, α' -azobisisobutyronitrile, (AlBN), is not a good criterion of purity, and therefore the purity of the recrystallised material was checked spectroscopically. A solution of AlBN of strength 10.35 g.l.^{-1} in absolute alcohol at 20°C , was used for spectroscopic analysis. The maximum extinction coefficient was found to be $13.0 \text{ l.mole}^{-1}\text{cm.}^{-1}$ at a wavelength of 3450°A , (Fig.11), and was in reasonable agreement with other literature values.^{85,86}

5.2. Decomposition of AlBN in Dimethyl Sulphoxide

The decomposition of AlBN in dimethyl sulphoxide, (DMSO) was followed spectroscopically at 60°C , using a 137 Perkin-Elmer spectrometer. Freshly distilled DMSO was used and the experimental procedure has already been outlined (Section 4.7). Some of the spectroscopic curves recorded are shown in Fig.12, corresponding to different times of reaction. As the decomposition proceeded, the intensity of the peak at $350 \text{ m}\mu$ gradually decreased while that at $300 \text{ m}\mu$ increased, initially, giving an approximate isosbestic point at $327 \text{ m}\mu$. The peak at $350 \text{ m}\mu$ is characteristic of the azo-group in AlBN, and the absorption in the region of $300 \text{ m}\mu$ is due in part to tetramethylsuccinodinitrile, which is the main decomposition product,⁸⁷ although some dimethyl-N- (2 cyano-2 propyl) ketenimine, $(\text{CH}_3)_2 \text{C} = \text{C} = \text{N} - \text{C}(\text{CN})(\text{CH}_3)_2$, which also absorbs in the same region,⁸⁸ may be formed.⁷²

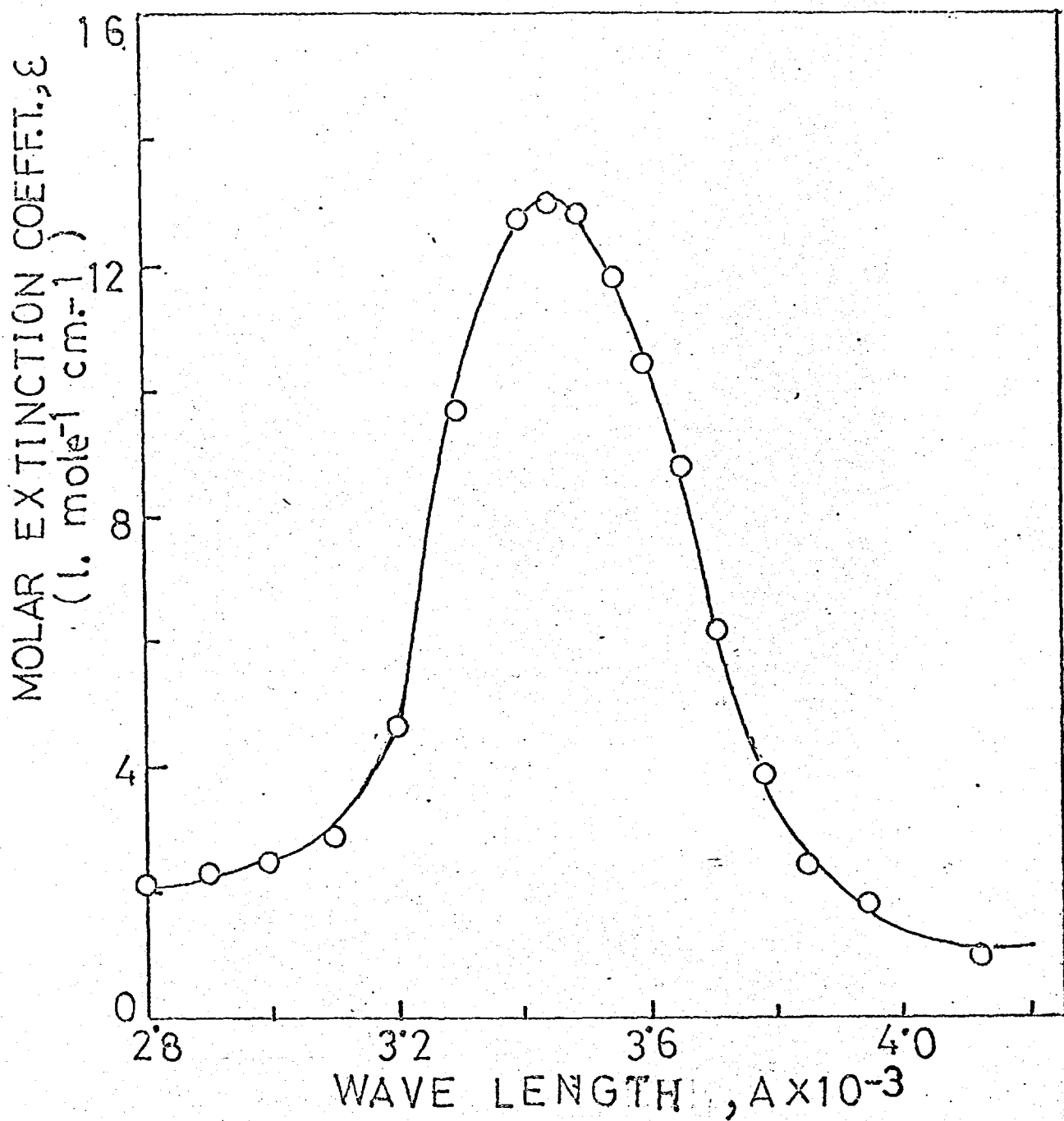


Fig.11. Absorption spectrum of α, α' -azobisisobutyronitrile (AIBN).

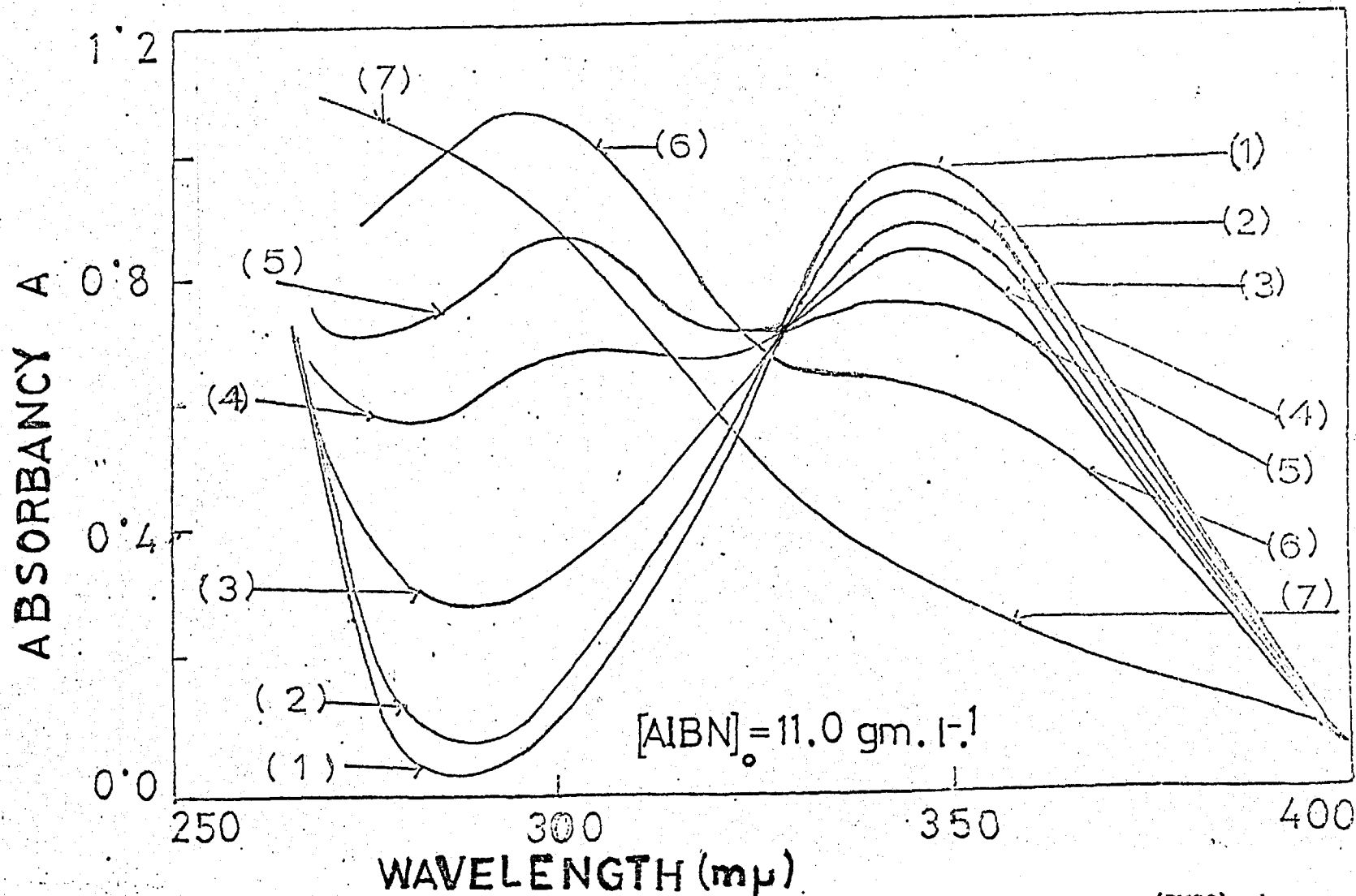


Fig.12. Decomposition of α, α' -azobisisobutyronitrile, (AIBN) in Dimethyl sulphoxide (DMSO), at 60°C . : Reaction time; (1) 10 min., (2) 45 min., (3) 180 min., (4) 250 min., (5) 720 min., (6) 1440 min., and (7) 4 weeks.

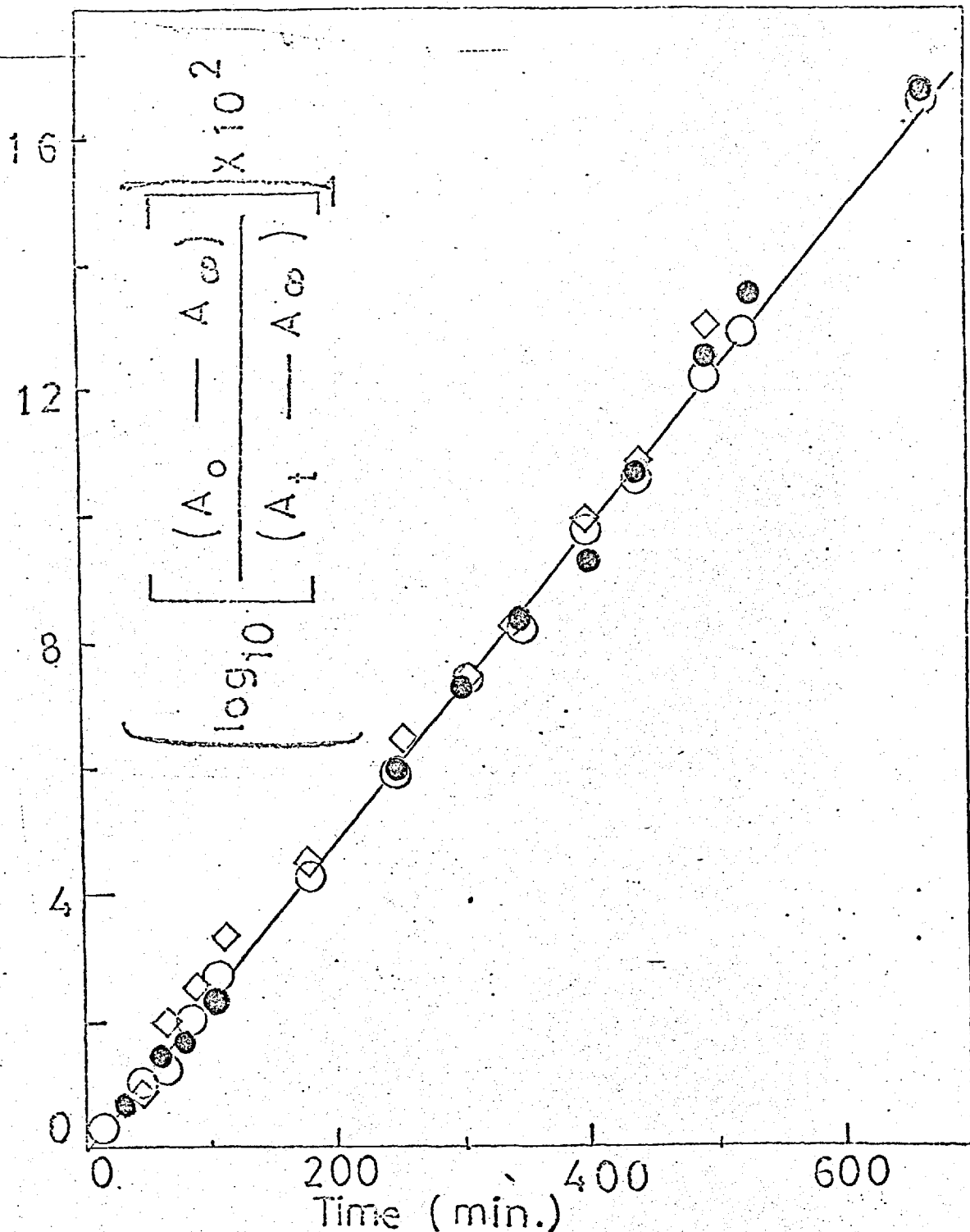


Fig.13. A plot of $\log \left[\frac{A_0 - A_\infty}{A_t - A_\infty} \right]$ against time of reaction corresponding to wavelengths 345 mμ (●), 350 mμ (○) and 360 mμ (◇). [Total concentration of α,α'-azobis-isobutyronitrile in DMSO = 11.0 gm.l.⁻¹]. Temperature = 60°C.

The first order rate constant, k_d , for AlBN decomposition was determined using the expression:

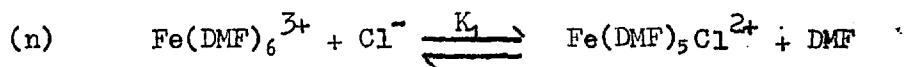
$$k_d = \frac{1}{t} \ln \left[\frac{A_o - A_\infty}{A_t - A_\infty} \right] \quad (55)$$

where A_o , A_t and A_∞ represent the absorbancies of AlBN at a suitable wavelength corresponding to time zero, time t and time infinity.

The plots of $\log \left[\frac{A_o - A_\infty}{A_t - A_\infty} \right]$ against time t , corresponding to wavelengths, 345, 350 and 360 mμ, gave a reasonably straight line (Fig.13) and the mean value of k_d was found to be $0.94 \times 10^{-5} \text{sec.}^{-1}$ at 60°C . The value of k_d for AlBN in DMF, which is also a relatively inert solvent with respect to transfer, is reported as $1.2 \times 10^{-5} \text{sec.}^{-1}$.^{67,89}

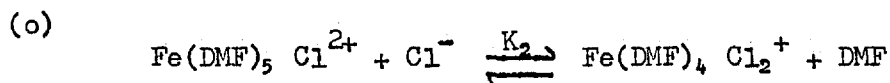
5.3. Spectroscopic Investigation of Iron(III) Chloro Complexes in N,N Dimethyl Formamide and Mixed Solvents

The spectra of $[\text{Fe}(\text{DMF})_6] (\text{BF}_4)_3$ in dimethyl formamide (DMF) solution containing different concentrations of added lithium chloride are shown in Fig.14. Assuming the usual co-ordination number of six for all cationic iron(III) species, curve (a) may be associated with the presence of $\text{Fe}(\text{DMF})_6^{3+}$ ions. Adding lithium chloride to give a LiCl/A molar ratio of 0.25 produced an increase in absorption over the entire wavelength range, curve (b), attributed to the formation of $\text{Fe}(\text{DMF})_5\text{Cl}^{2+}$ ions. The formula $\text{Fe}(\text{DMF})_5\text{Cl}^{2+}$ is used for simplicity here, and does not necessarily imply inner sphere complexing; but could also refer to outer sphere complexes of the type $\text{Fe}(\text{DMF})_6^{3+}, \text{Cl}^-$. The equilibrium reaction involved is:



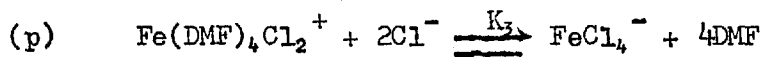
The intensity of absorption at 265 mμ subsequently decreased progressively on increasing the LiCl/A molar ratio to 0.5:1 and 1:1.

These changes were due to disappearance of $\text{Fe}(\text{DMF})_5\text{Cl}^{2+}$ and formation of $\text{Fe}(\text{DMF})_4\text{Cl}_2^+$ species, which by analogy with other results involving $\text{Fe}(\text{DMA})_4\text{Cl}_2^+$ were expected to absorb most strongly at 320 mμ.



where K_2 is the corresponding equilibrium constant.

A relatively large increase in absorption over all wavelengths occurred for a LiCl/A molar ratio of 2:1 [curve (e)], presumably due to the increased concentration of $\text{Fe}(\text{DMF})_4\text{Cl}_2^+$ ions, and a hump also appeared in the region 340 - 360 mμ. For a LiCl/A molar ratio of 3:1, the intensity at 265 mμ again decreased, there was a peak at 305 mμ, and the absorption at 350 mμ increased [curve (f)]. There is strong independent evidence^{82,90} that an absorption in the region of 360 mμ is due to FeCl_4^- ions, which are presumably formed in this instance by the process.



where K_3 is the appropriate equilibrium constant.

This was confirmed also by recording the spectrum of $(\text{C}_2\text{H}_5)_4\text{N FeCl}_4$; B, in DMF at 20°C, as shown in Fig.15 [curve (a)].

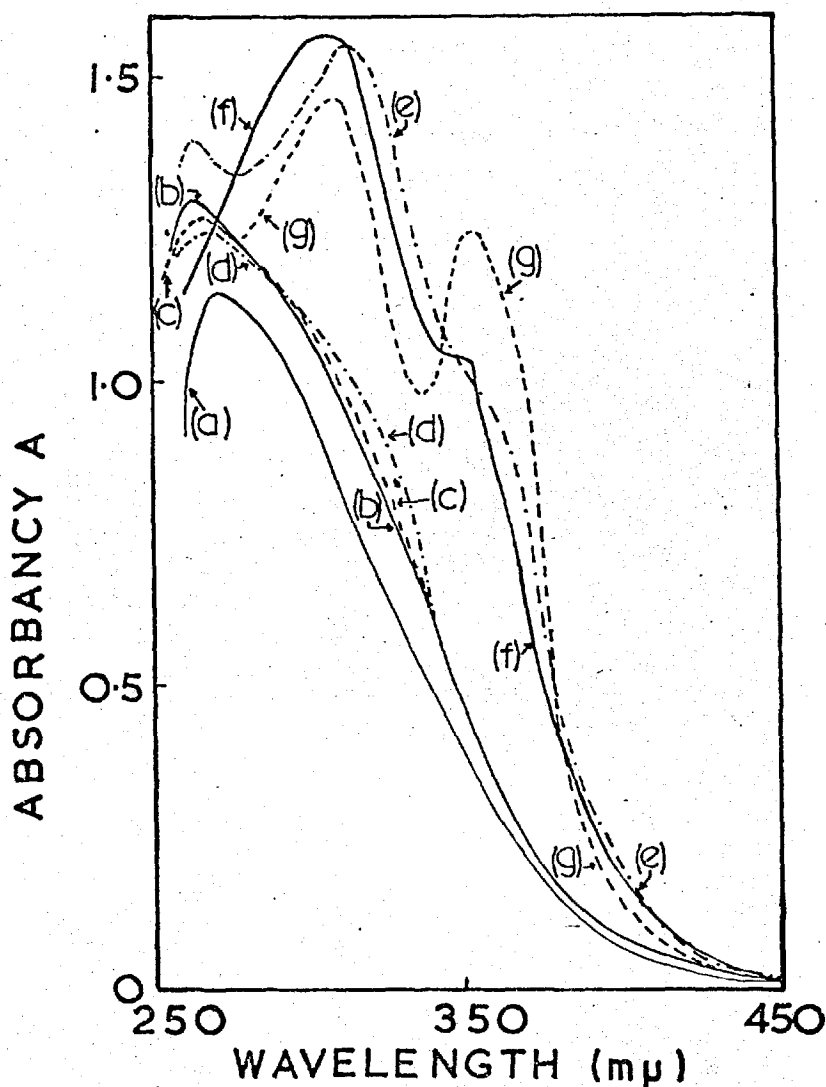


Fig.14. Ultraviolet spectra of the complex (A), $\text{Fe}(\text{DMF})_6-(\text{BF}_4)_3$, with added LiCl in DMF at 20°C . [Total Fe(III) concentration is 2.2×10^{-4} mole l^{-1}]: (a) complex (A) alone; LiCl/(A) molar ratios are 0.25:1 in (b); 0.50:1 in (c); 1:1 in (d); 2:1 in (e); 3:1 in (f); and 4:1 in (g).

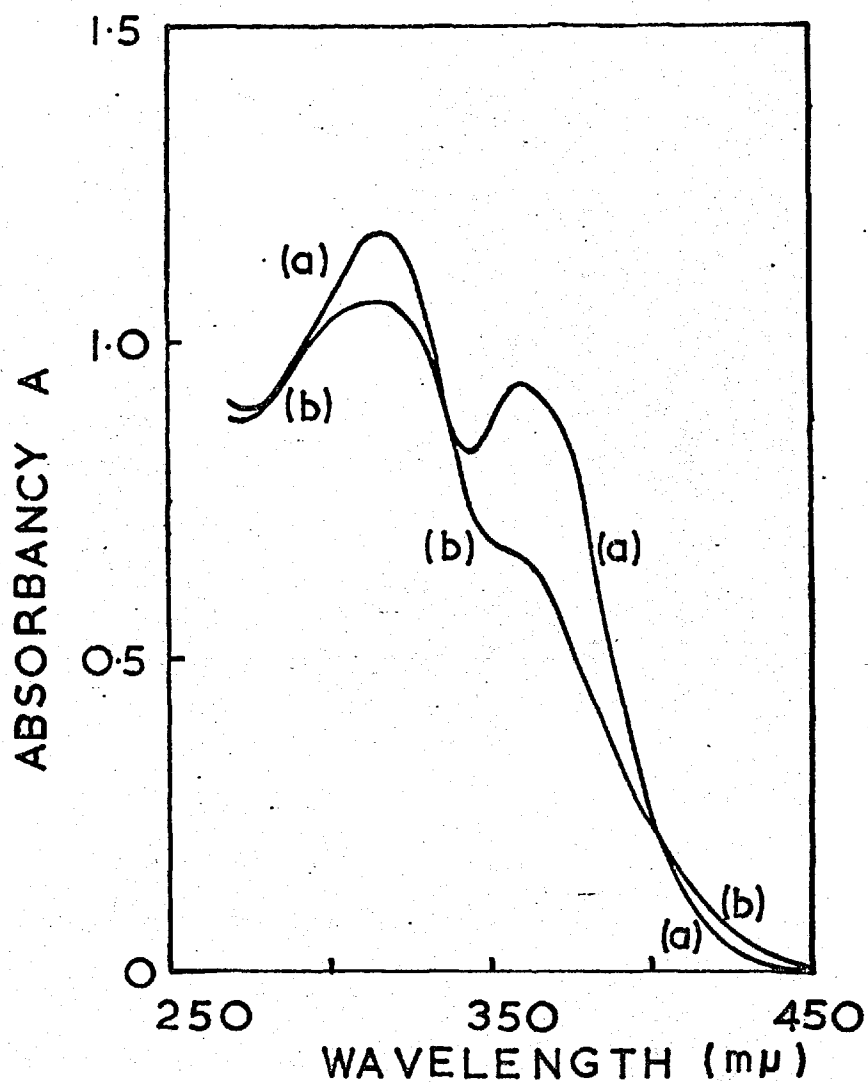


Fig.15. Ultraviolet spectra in DMF at 20°C. [Total Fe(III) concentration is 1.37×10^{-4} mole l^{-1}]: (a) tetraethylammonium tetrachloroferrate(III); (b) iron(III) chloride.

The intensity due to compound, B, was only slightly affected on adding lithium chloride to the solution to give a molar ratio of LiCl/B of 3:1, indicating the stability of FeCl_4^- under these conditions. Again, in agreement with this rationalization, the absorbancy at 360 m μ increased markedly on increasing the LiCl/A molar ratio to 4:1 as shown in Fig.14 [curve (g)]. The intensity of the peak at 360 m μ thereafter increased by 1.4% on increasing the LiCl/A molar ratio to 9:1, indicating that most of the iron(III) species beyond a 4:1 molar ratio existed as FeCl_4^- .

The equilibrium constant for the formation of the monochloro species could not be calculated accurately from the spectroscopic results but there were indications that the equilibrium constant, K_1 , was very high. Again the plot of τ against added LiCl for a molar ratio of $\text{Cl}^- : \text{A} < 1:1$ was found to be linear (Fig.31) which also suggests a high value for K_1 . The equilibrium constant of formation of the dichloro species was estimated to be about 5×10^4 from the spectroscopic results shown in Fig.16. The spectroscopic results in DMF and DMF/styrene mixtures suggest that uncharged FeCl_3 species are not involved in the equilibria. This point is well supported by the fact that the trichloro iron(III) species can exist in only strongly acidic aqueous solution⁹⁰. The values of the equilibrium constants for the stepwise formation of iron(III) complexes generally decrease with progressive addition of chloride ions,⁹¹ so that $K_1 > K_2$. K_1 may thus be of the order of 10^8 .

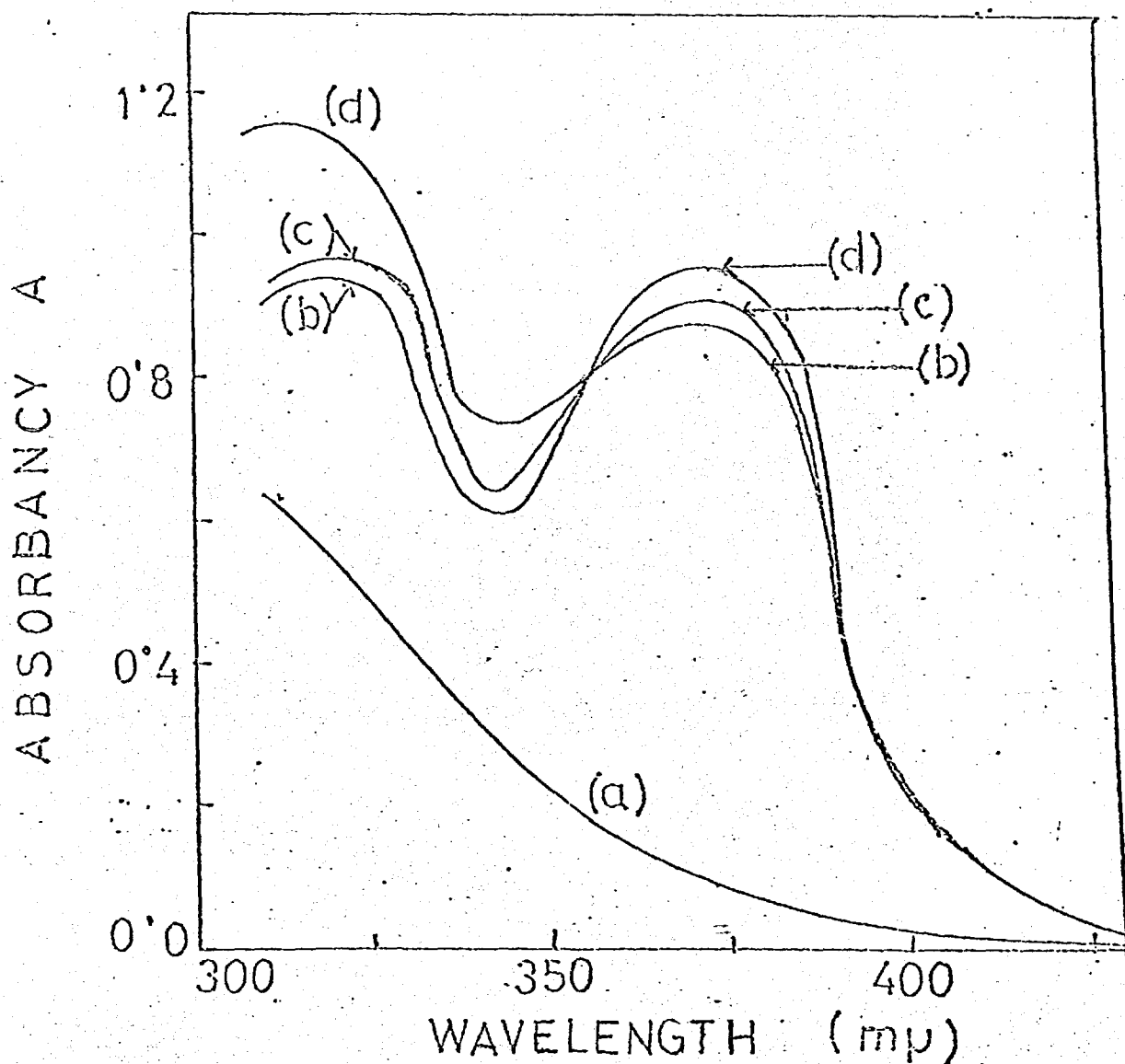


Fig.16. Ultraviolet spectra of the complex A, $\text{Fe}(\text{DMF})_6-(\text{BF}_4)_3$, with added LiCl in DMF/styrene (1:1 by volume) mixture at 20°C . [Total Fe(III) concentration is 1.2×10^{-4} mole l^{-1}] : (a) complex, A, alone; LiCl/A molar ratios are 1:1 in (b); 3:2 in (c) and 2:1 in (d).

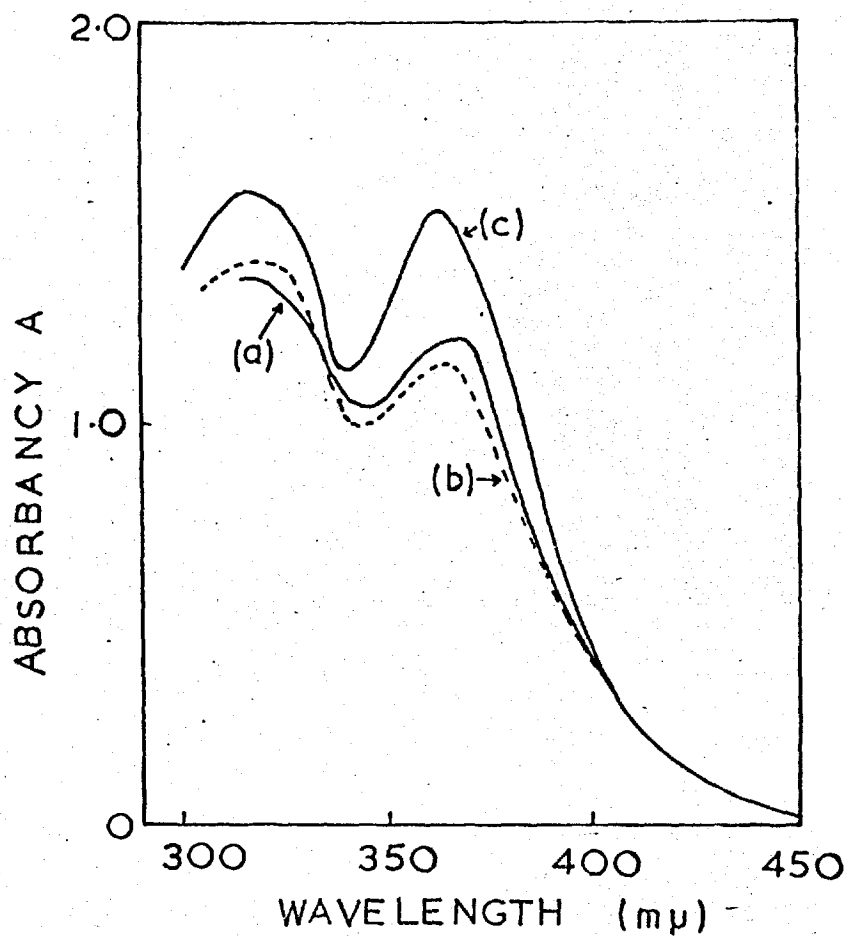


Fig. 17. Ultraviolet spectra in a DMF/styrene mixture at 60°C. [DMF] = 8.79 mole l.⁻¹; [styrene] = 2.49 mole l.⁻¹ [Total Fe(III) concentration is 2.2×10^{-4} mole l.⁻¹]: (a) iron(III) chloride; (b) LiCl/(A) molar ratio is 3:1; (c) tetraethylammonium tetrachloroferrate(III).

Similar spectroscopic studies were made with DMF/styrene mixtures at 20°C and 60°C, with the concentrations of styrene similar to those employed in many kinetic studies.^{43,69} In these mixed solvent systems, at both temperatures there was a tendency for FeCl_4^- ions to be present to a greater extent than in the pure DMF alone, the other principal ionic species again being $\text{Fe}(\text{DMF})_4\text{Cl}_2^+$ at relatively high LiCl/A molar ratios. Figure 17 shows some of the spectroscopic results at 60°C. From the spectroscopic results, the equilibrium constant K_3 was estimated to be at least 10^8 . In pure N,N-dimethyl acetamide, a similar type of equilibrium was established⁸² with an estimated equilibrium constant of 10^{10} .

The spectroscopic results were unaffected by addition of traces of water to the solutions studied, and were not markedly time dependent, indicating that the various equilibria were rapidly attained.

5.4. Spectroscopic Investigations of Iron Complexes in Dimethyl Sulphoxide (DMSO) and in Mixed Solvents

The spectra of $[\text{Fe}(\text{DMSO})_6](\text{BF}_4)_3 \cdot \text{D}$, in DMSO containing different concentrations of added lithium chloride are shown in Fig.18. Assuming the usual coordination number of six for all cationic species, curve (a) may be associated with the presence of $\text{Fe}(\text{DMSO})_6^{3+}$ ions. Adding lithium chloride to give a LiCl:D molar ratio of 1:1 changed the spectrum in the 335 mμ region. This was in accordance with the published results of Drago⁸¹ and Wada et al.⁹² However on addition of further chloride ions the intensity in the 335 mμ region was found

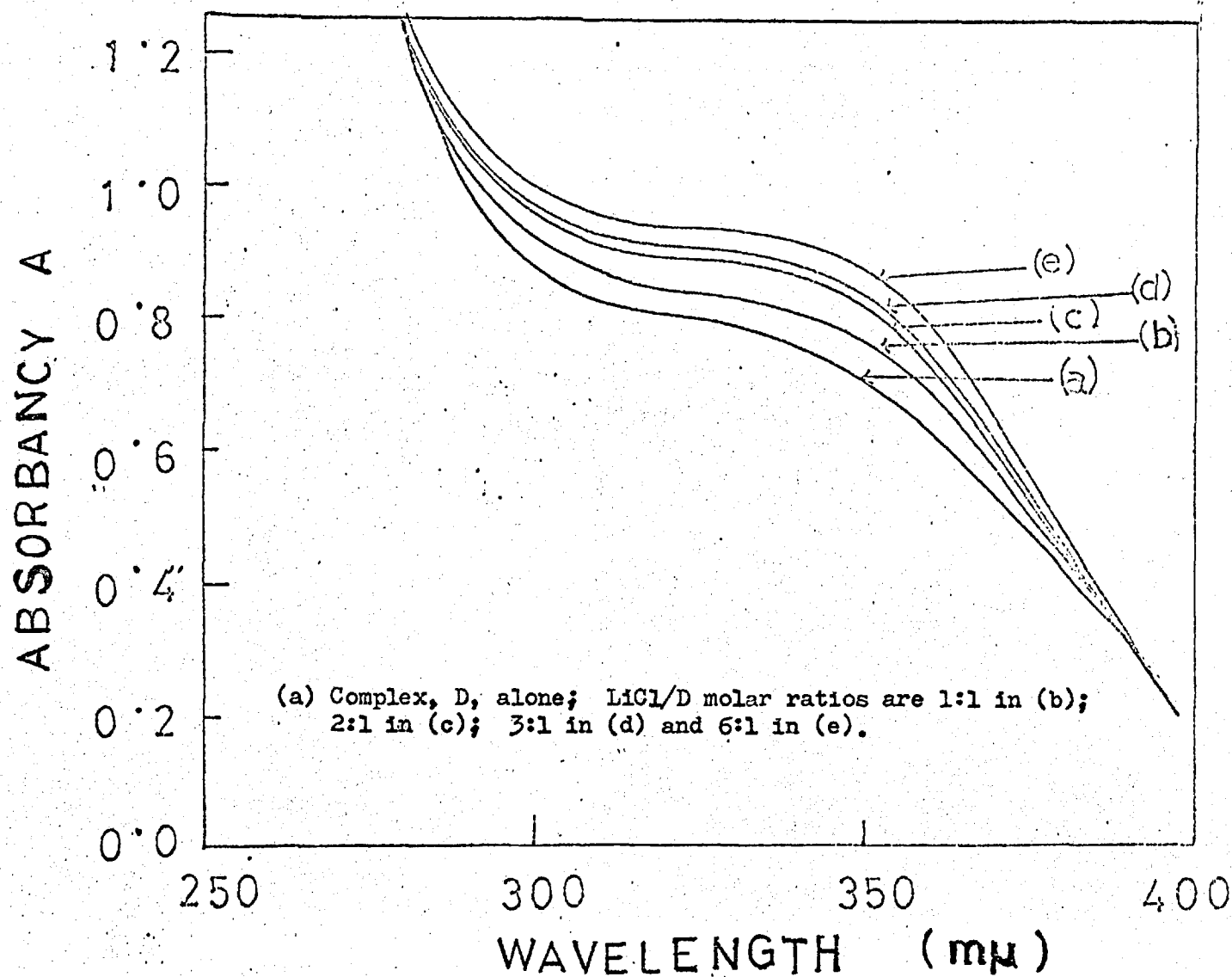


Fig.18. Ultraviolet spectra of $[\text{Fe}(\text{DMSO})_6](\text{BF}_4)_3$, D with LiCl at 20°C.
Total Fe(III) concentration is 2.0×10^{-4} mole ℓ^{-1} .

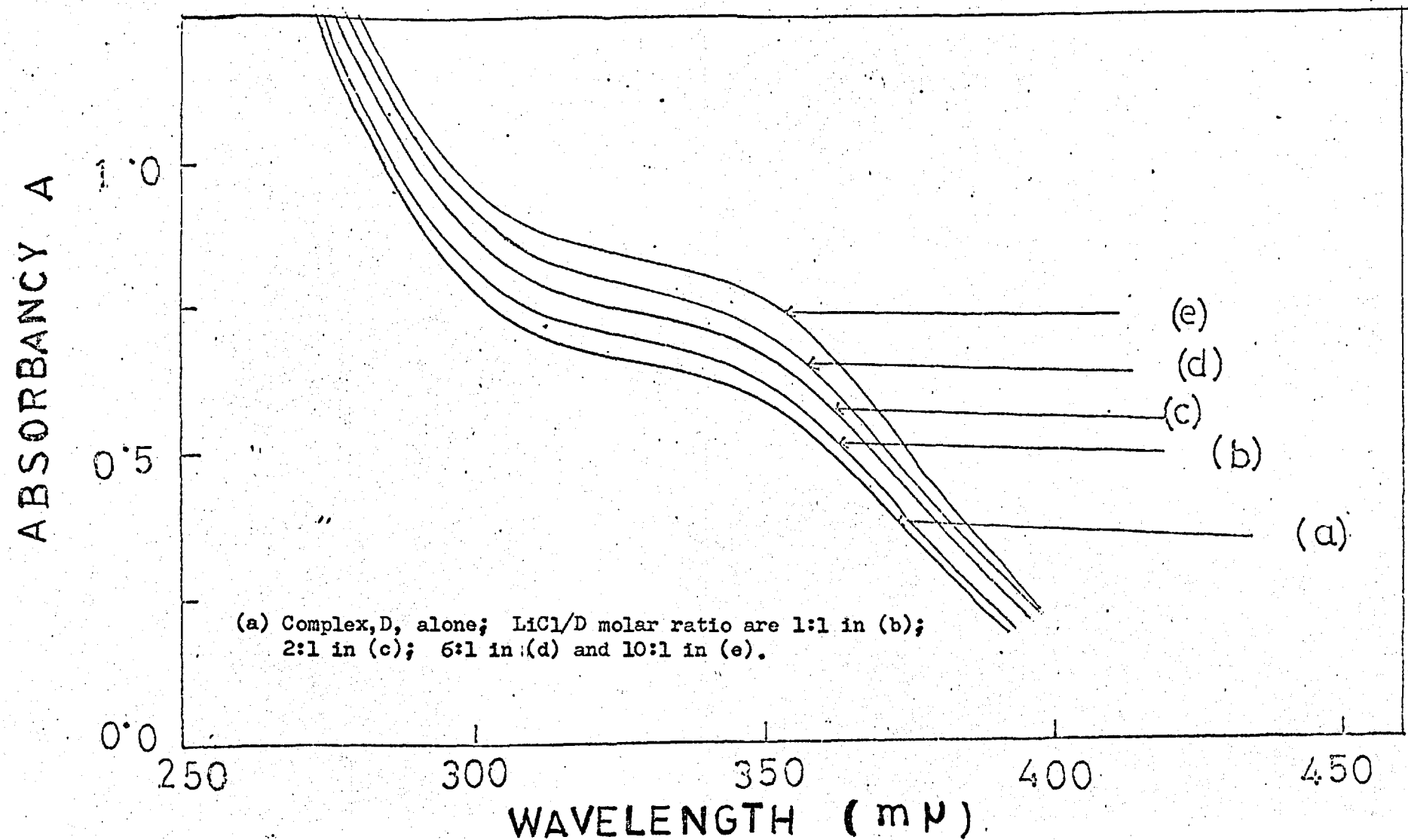


Fig.19. Ultraviolet spectra of the complex, D, $[\text{Fe}(\text{DMSO})_6](\text{BF}_4)_3$, with added LiCl in DMSO at 60°C .
Total Fe(III) concentration is 2.0×10^{-4} mole l^{-1} .

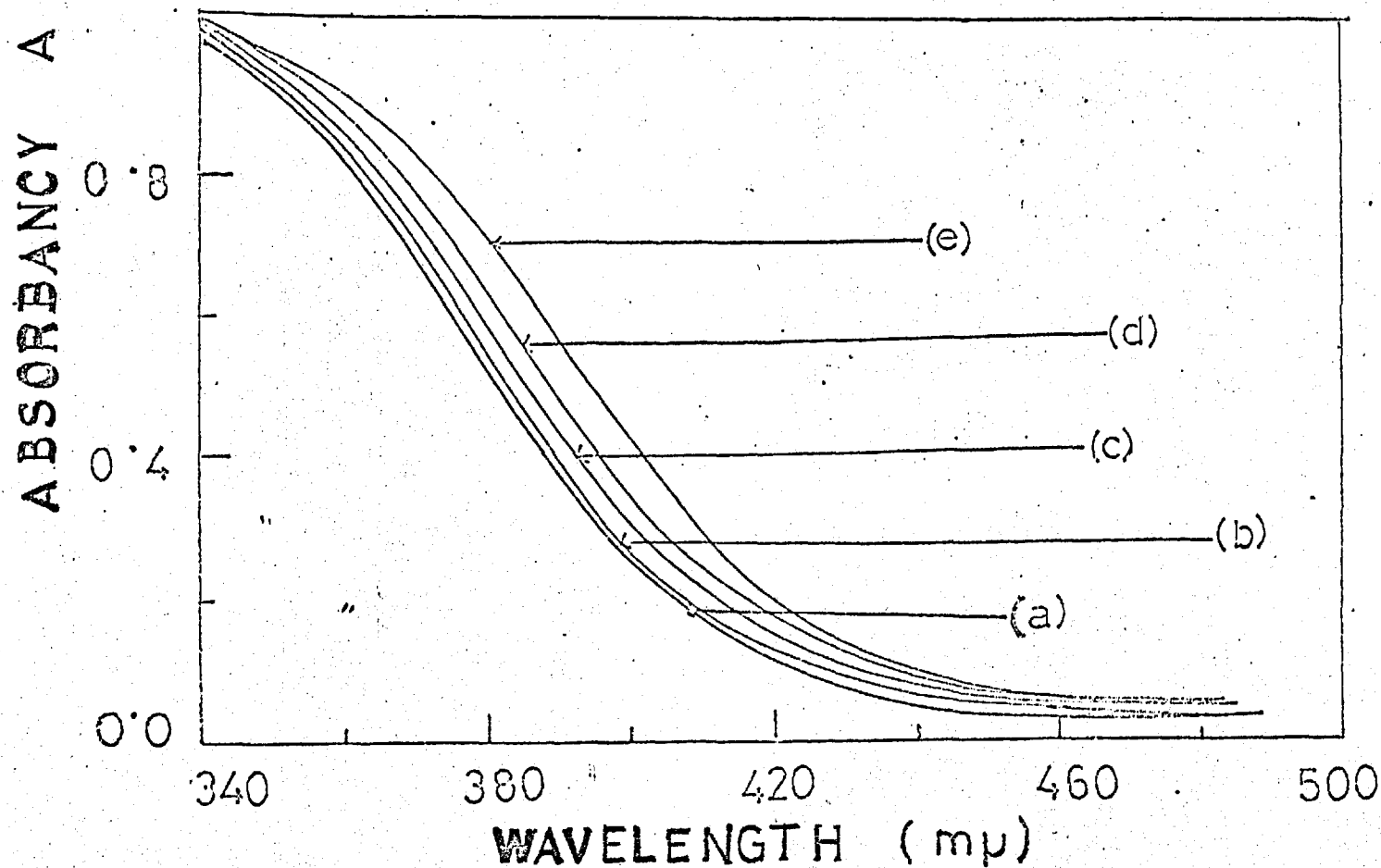


Fig.20. Ultraviolet and visible spectra of the complex, D, $[Fe(DMSO)_6](BF_4)_3$, with added LiCl in styrene/DMSO mixture at $60^\circ C$.
 $[Fe(DMSO)_6](BF_4)_3 = 2.0 \times 10^{-4}$ mole l^{-1} .
 $[Styrene] = 1.74$ mole l^{-1} .
 $[DMSO] = 10.75$ mole l^{-1} .
 Curve (a) for the complex alone; LiCl/D molar ratios are 1:1 in (b); 2:1 in (c); 6:1 in (d) and 10:1 in (e).

to increase and did not reach a limit for a molar ratio of 2:1 as previously reported,⁸¹ but required a minimum molar ratio of about 10:1. This is quite expected as DMSO is a stronger ligand than the chloride ion.⁹³ Drago et al.⁸¹ also reported the absence of FeCl_4^- in DMSO at a 5×10^{-4} M iron concentration with a very large chloride ion to iron(III) molar ratio. They also stated that the spectrum of iron(III) chloride dissolved in DMSO is qualitatively the same as that of a 1:1 molar ratio of chloride ion to iron(III). These spectroscopic results suggested that only the monochloro species was stable in DMSO; the dichloro and the tetrachloro species were consequently very unstable. The spectra of the same systems in DMSO at 60°C, were almost identical with those at 20°C, as shown in Fig.19. The same conclusion can be drawn from the spectra recorded at 60°C. (Fig.20) in DMSO/styrene mixtures, but the interpretation may be complicated by the possible precipitation of polystyrene formed by thermal polymerization when the cells were thermostatted for long times. The equilibrium constant, K, for the system,

$$(q) \quad \text{Fe}(\text{DMSO})_6^{3+} + \text{Cl}^- \xrightleftharpoons{K} \text{Fe}(\text{DMSO})_5\text{Cl}^{2+} + \text{DMSO}$$

at 60°C in DMSO and DMSO/styrene is estimated to be about 10^3 from the spectroscopic results and is much smaller than the equilibrium constant of the corresponding system in DMF.

5.5. Densities of Dimethyl Sulphoxide (DMSO) at Different Temperatures

The densities of DMSO at different temperatures were determined experimentally by calculating the total volume of a known weight of DMSO using a calibrated dilatometer. The results are recorded in

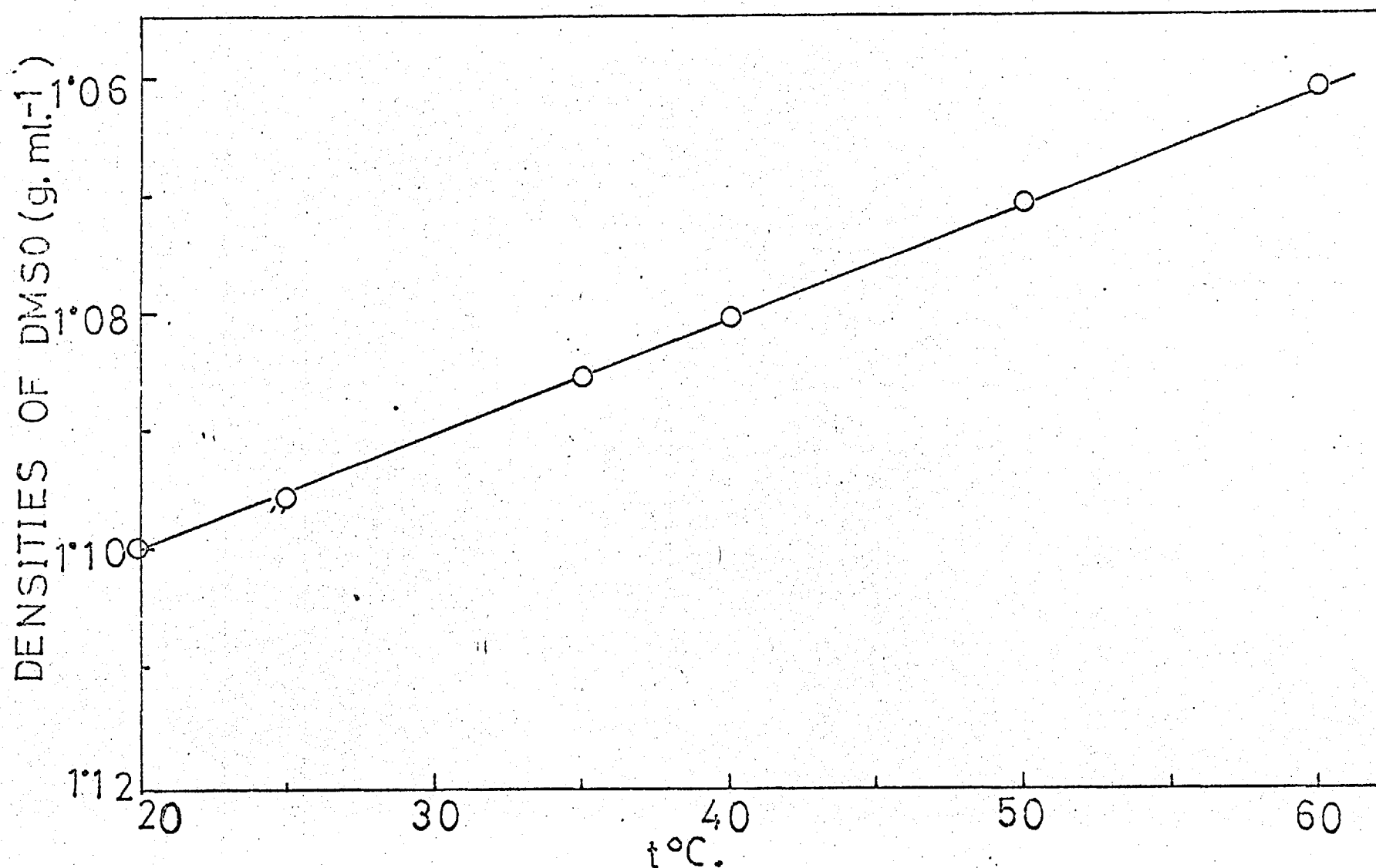


Fig.21. Densities of Dimethyl sulphoxide at different temperature.

Table 3 and plotted in Fig.21.

Table 3

Variation of densities of dimethylsulphoxide with temperature

Temperature (°C)	Density (g.ml. ⁻¹)
20	1.1003
25	1.0958
35	1.0861
40	1.0807
50	1.0709
60	1.0609

5.6. Determination of Rates of Polymerization of Styrene in Dimethyl Sulphoxide (DMSO).

According to eqn (9),

$$\text{Rate of polymerization, } R_p = k_p \left\{ \frac{f k_d [\overline{\text{In}}]}{k_t} \right\}^{\frac{1}{2}} [\overline{\text{M}}]$$

so if f , k_d , $[\overline{\text{In}}]$ and k_t remain constant, and independent of monomer and solvent concentrations, then a plot of R_p against $[\overline{\text{M}}]$ should be linear. Since DMSO is not a good solvent for polystyrene, k_t is expected to fall with increasing solvent concentration due to polymer radical coiling and eventual radical occlusion by precipitated polymer,

R_p will then increase due to occlusion of some of the free radicals. However, for a conversion of less than 10%, no noticeable increase in rate was observed for homogeneous or heterogeneous systems. The data for different times of reaction are collected in Table 5. The reason for the relatively small change of rate of polymerization with increasing % conversion may be due to the fact that DMSO is not an extremely poor solvent for polystyrene, and polystyrenes of low molecular weight are soluble. It was found experimentally that precipitation of polystyrene did not occur if the concentration of DMSO was less than about 5 mole ℓ^{-1} . The three points marked with an asterisk in Table 4 were within that range and gave homogeneous systems throughout the course of the reaction. A plot of the rate of polymerization against average monomer concentration is shown in Fig. 22 and the data are collected in Table 4.

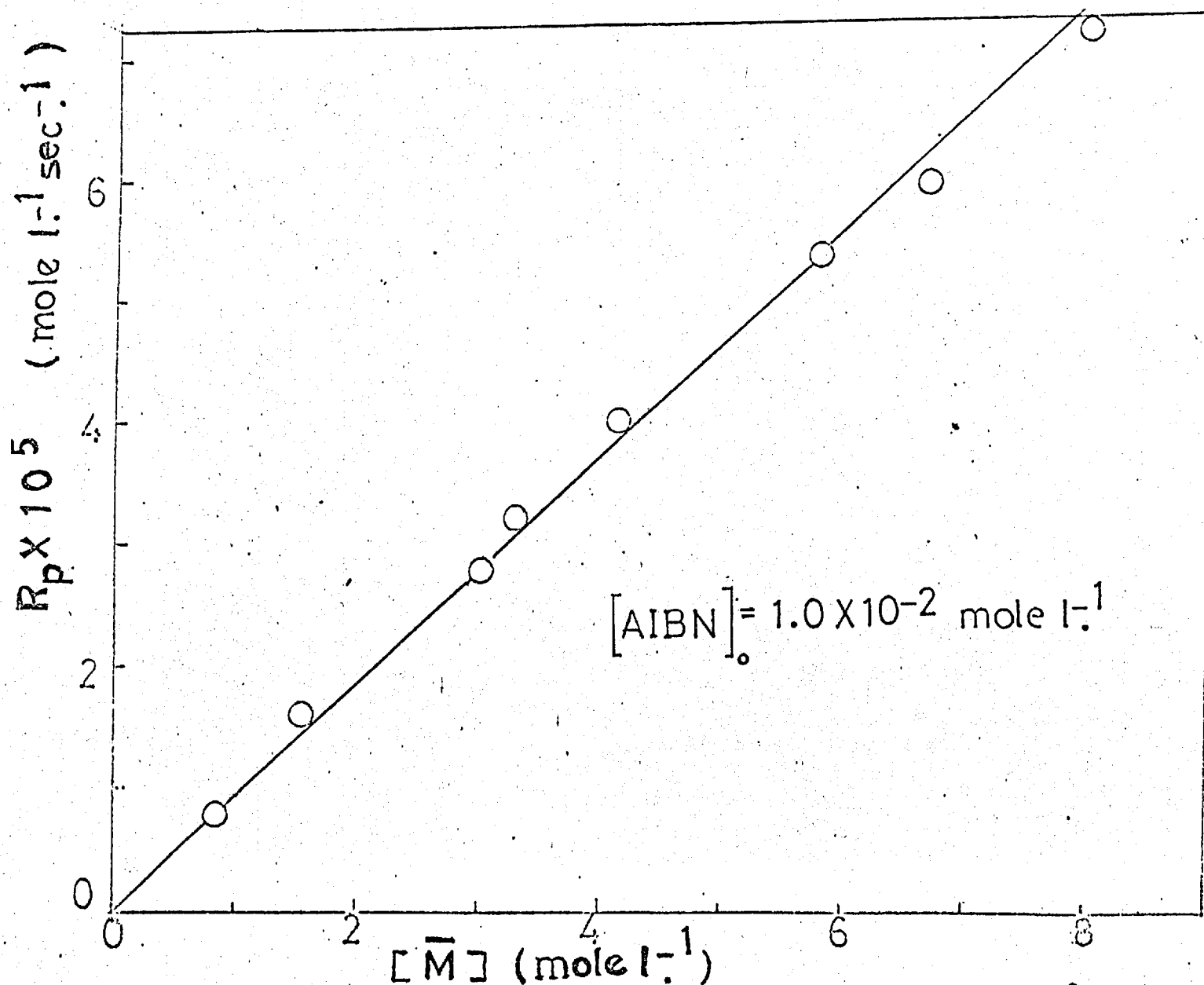


Fig.22. Rate of polymerization as a function of $[M]$, in DMSO at 60°C .

Table 4

Polymerization of styrene in DMSO at 60°C. $[\text{In}]_0 = 1.0 \times 10^{-2} \text{ mole } \ell^{-1}$.

Reaction Times about 3 hours.

$[\bar{M}]$ (mole ℓ^{-1})	$[\text{S}]_0$ (mole ℓ^{-1})	$R_p \times 10^5$ (mole ℓ^{-1} sec. $^{-1}$)	$[\eta]$ (dl. g. $^{-1}$)	$\overline{DP} \times 10^{-4}$	$[\bar{M}] \times \left[\frac{1}{\overline{DP}} - C \right] \times 10^4$ (mole ℓ^{-1})
8.071	0.000*	7.294	0.7154	11.930	6.296
6.680	2.281*	6.028	0.6153	9.647	6.521
5.838	3.693*	5.408	0.5695	8.65	6.399
4.153	6.517	4.026	0.4640	6.483	6.156
3.739	7.229	3.553	0.4270	5.813	6.206
3.311	7.929	3.279	0.4065	5.371	5.964
3.041	8.644	2.869	-	-	-
1.660	10.753	1.544	0.3220	3.875	4.184
0.827	12.165	0.819	0.2553	2.796	2.897

* These systems remained homogeneous throughout the course of the experiments.

Table 5

Effect of % conversion on $\overline{DP}$ and Rate of Polymerization of Styrene in DMSO at 60°C. $[In]_0 = 1.0 \times 10^{-2}$ mole ℓ^{-1}

$[M]_0$ (mole ℓ^{-1})	$[M]$ (mole ℓ^{-1})	Time of re- action (hours)	$[S]_0$ (mole ℓ^{-1})	$R_p \times 10^5$ (mole $\ell^{-1} \text{sec}^{-1}$)	$[\eta]$ dl.g^{-1}	$\overline{DP} \times 10^{-4}$	$[M] \left(\frac{1}{\overline{DP}} - C_m \right) \times 10^4$ (mole ℓ^{-1})
1.741	1.718	1	10.753	1.412	0.2985	2.960	5.705
1.741	1.660	3	10.753	1.544	0.3320	3.875	4.184
0.870	0.857	1	12.165	0.779	0.2051	1.995	4.308
0.870	0.827	3	12.165	0.819	0.2553	2.796	2.897

5.7.1. Molecular Weight Determination by Osmometry and Viscometry

Degrees of polymerization, $\overline{DP}$, and molecular weights, $\overline{M}_n$ of the polystyrenes prepared at various solvent/monomer concentrations, with constant initiator concentration, $(In)_0$, were determined osmotically and viscometrically. Details of these methods were discussed in Sections 2.4, 2.5, 4.5 and 4.6. A comparison of the $\overline{DP}$'s determined by the two methods is shown in Table 6. In general, osmotic molecular weights were much higher than the $\overline{M}_n$ values determined by viscometry, though the general trend of the results was similar. The experimental techniques and results were checked more carefully with a highly fractionated polystyrene, $\left(\frac{\overline{M}_w}{\overline{M}_n} < 1.06 \right)$, supplied by the Pressure Chemical Company (Lot No. 42) with a nominal stated weight of 97,200. $\overline{M}_n$ found by osmometry (Fig. 10) was 133,500

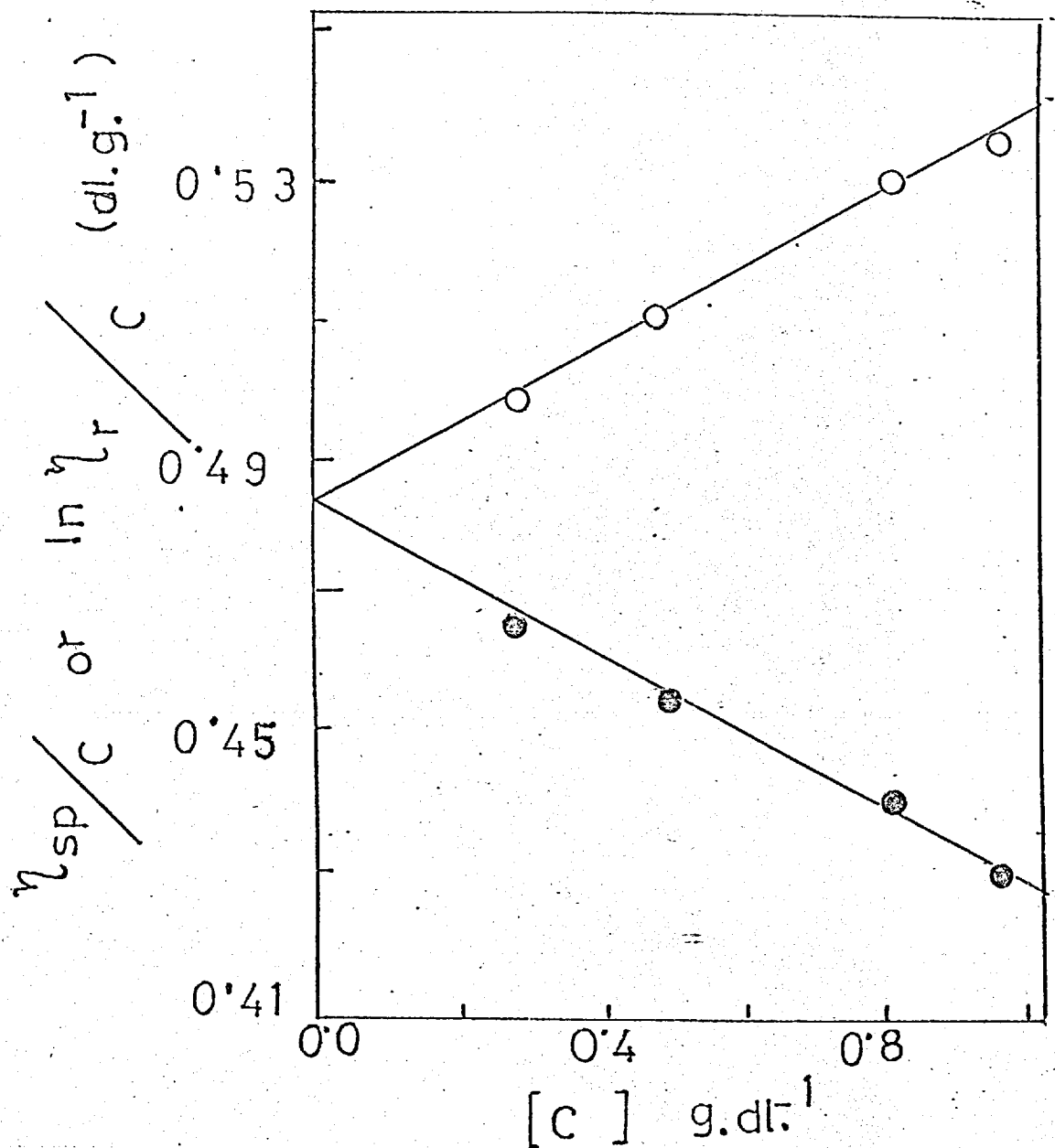


Fig.23. Double plot of viscosity number (open circles) and logarithmic viscosity number (closed circles) against concentration for standard polystyrene in toluene.

Value quoted for the polystyrene supplied by

Pressure Chemical Co., $\bar{M}_n$

Nominal $\bar{M}_n = 97,200$, $\frac{\bar{M}_w}{\bar{M}_n} < 1.06$. Temperature = 30°C .

and $\bar{M}_n$ by viscosity (Fig.23) was 103, 100. So the molecular weights of polystyrenes determined viscometrically were taken to be more accurate and were used in calculations for the determination of the transfer constant of Dimethyl sulphoxide.

Table 6

$\overline{DP}$ Values of Unfractionated Polystyrenes, Prepared by the Polymerization of Styrene at 60°C, in Dimethylsulphoxide, Determined by Viscometry and Osmometry.

Viscometric Method $\overline{DP} \times 10^{-2}$	Osmotic Method $\overline{DP} \times 10^{-2}$
11.930	13.069
9.647	12.305
8.650	11.202
5.371	7.254
3.875	4.514

5.7.2. Variation of the Intrinsic Viscosity of a Standard Polystyrene

Sample in Different Mixtures of DMSO/Styrene

The intrinsic viscosity of a highly fractionated polystyrene (Pressure Chemical Company Polystyrene, $\frac{\bar{M}_w}{\bar{M}_n} < 1.06$, Lot No.42, Nominal $\bar{M}_n = 97,200$) was found to decreaseⁿ with increase of [DMSO] in a mixture of DMSO/styrene (Table 7), Fig. 24. Precipitation of the standard polystyrene did not occur over the concentration

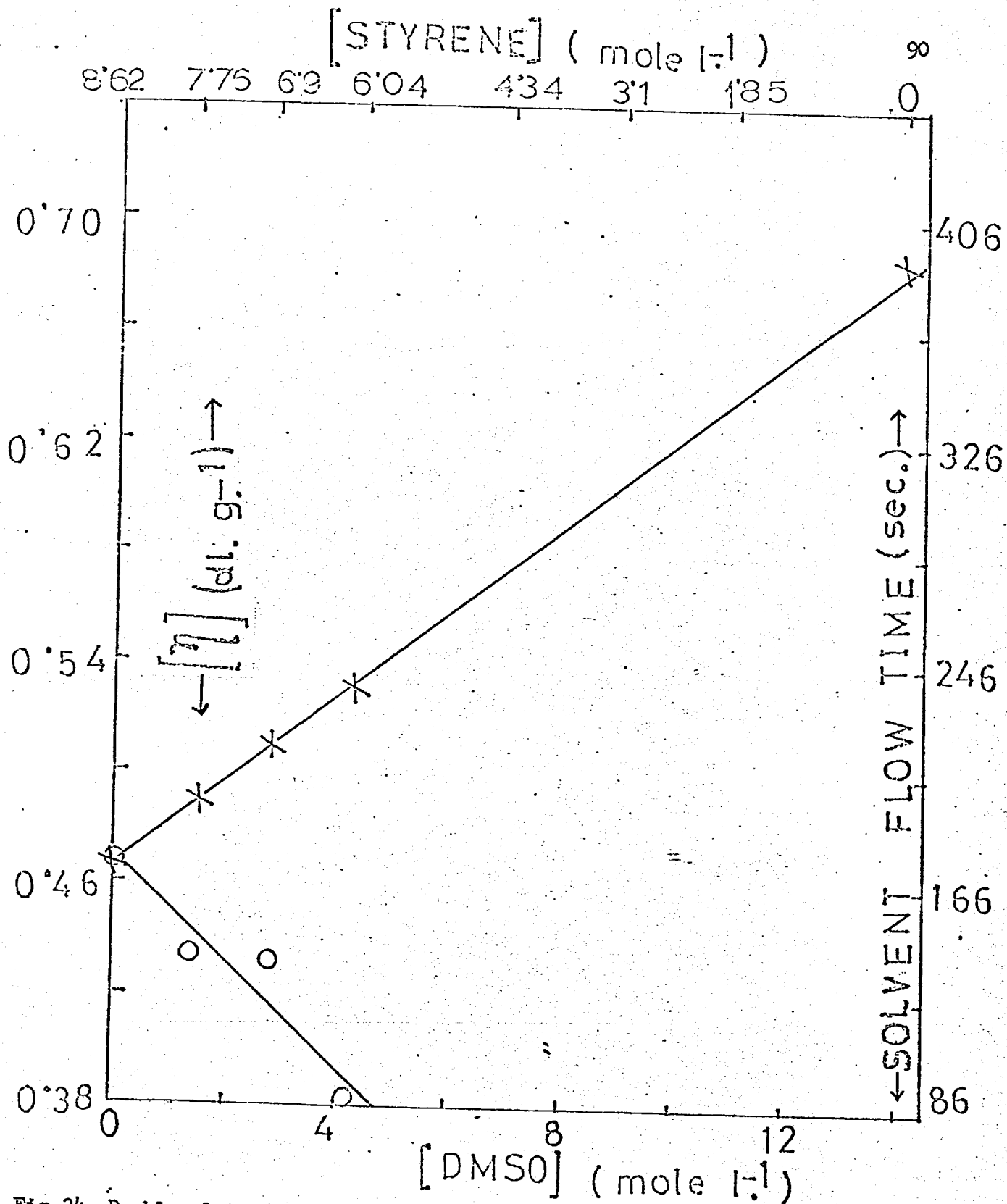


Fig.24. Double plot of intrinsic viscosity (O) of the standard polystyrene (Nominal $\bar{M}_n = 97,200$; $\bar{M}_w/\bar{M}_n < 1.06$) and the mixed solvent flow time (X) against concentrations of the constituents of the mixed solvents DMSO/styrene. Temperature = 30°C .

range studied. From these results, it is concluded that there is no preferential solvation of polystyrene over the range considered.

Table 7

Molecular weight of the special polystyrene supplied by Pressure Chemical Co. (Lot No. 42) Nominal, $\bar{M}_n = 97,200$, $\frac{\bar{M}_w}{\bar{M}_n} < 1.06$.
The following data were obtained for solutions at 30°C .

[Styrene] (mole ℓ^{-1})	[DMSO] (mole ℓ^{-1})	Flow time of Mixed Solvent (sec.)	$[\eta]$ dl. g^{-1}
8.622	0.000	173.5	0.4685
7.760	1.395	195.7	0.4335
6.897	2.790	215.1	0.4320
6.035	4.185	235.0	0.3815
0.000	13.949	391.9	-

5.8. Determination of the Transfer Constant for Dimethylsulphoxide

The usual reaction scheme for vinyl polymerization in solution, using a constant initiator concentration, in which termination occurs by combination of radicals leads to the equation:

$$[\bar{M}] \left(\frac{1}{\overline{DP}} - C_m \right) = C_s [S] + \text{constant} \quad (11)$$

where C_s and C_m are transfer constants to solvent and monomer, respectively, and $\overline{DP}$ is the degree of polymerization. If, as has been observed for certain other systems,^{64,74} the initiator efficiency

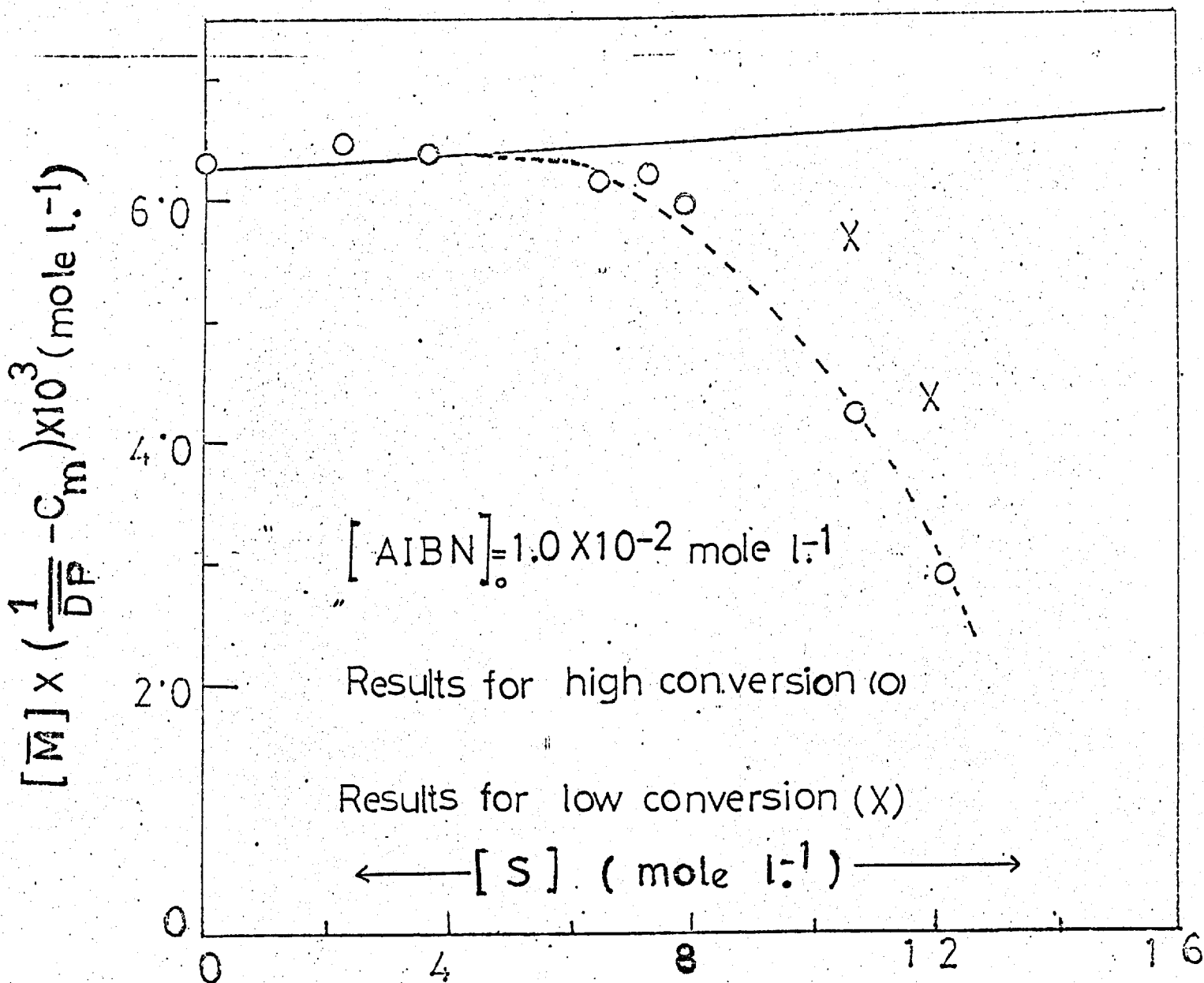


Fig. 25: Plot of $[M] \left\{ \frac{1}{\overline{DP}} - C_m \right\}$ as a function of solvent concentration, $[S]$.

Temperature of polymerization = 60°C.

and velocity constants involved remain constant, then a plot of the left hand side of eqn (11) against values of $[S]$ should be linear with a slope equal to C_s . Experimentally it was found that the first three points (marked with an asterisk in Table 4) gave a reasonably straight line (Fig.25) and assuming a value⁶⁵ of $C_m = 6.023 \times 10^{-5}$, C_s was found to be equal to 2.42×10^{-5} . White et al.⁹⁴ obtained a value of 1.1×10^{-5} for DMSO in a DMSO/acrylonitrile system.

It has been shown that the velocity constant, k , for a polymer radical - substrate reaction, is related to the velocity constant, k_T , for the transfer reaction with toluene, by the equation:

$$\log k = \log k_T + \alpha\sigma + \beta,$$

where α and β are characteristic constants for the substrate, for example monomer or transfer agent, and σ is a constant for a particular polymer radical.

Using the value of C_s as above for the DMSO/styrene systems, α and β for DMSO were found to be -2.59 and +0.245, respectively. Other numerical values, taken from literature^{47,65} and used in this calculation were (a) for the polystyrene radical $\sigma = -0.01$, $k_p = 176 \text{ l.mole}^{-1}\text{sec}^{-1}$ and $k_T = 2.11 \times 10^{-3} \text{ l.mole}^{-1}\text{sec}^{-1}$ at 60°C , and (b) for the polyacrylonitrile radical, $\sigma = +0.66$, $k_p = 2458 \text{ l.mole}^{-1}\text{sec}^{-1}$, and $k_T = 0.785 \text{ l.mole}^{-1}\text{sec}^{-1}$, at 60°C .

The negative value of α indicates that DMSO tends to accept an electron from the polystyryl radical in the transition state and that polar effects are important, but the relatively low value of β shows that DMSO is relatively unreactive. This may be due to the high

dissociation energy of the H - C bond which is probably broken during the transfer reaction.

However, $\overline{DP}$ values were found to be greater than expected when DMSO exceeded about 5 mole ℓ^{-1} . In this particular system, $\overline{DP}$ might increase due to occlusion of the polystyryl radicals by the precipitated polystyrene. Thus there was no precipitation of polystyrene in the experiments corresponding to the first three values in Table 4, while $\overline{DP}$ increased markedly and rates of reaction increased slightly (Table 5) for the heterogeneous systems studied.

5.9. Interaction of Polystyryl Radicals with Ferric Ions and Complexes Followed Dilatometrically

5.9.1. With Ferric Chloride

Some experiments were performed using ALBN to initiate the polymerization of styrene in DMF at 60°C, in the presence and absence of anhydrous ferric chloride. Typical results, in excellent agreement with Bamford et al.⁴³, are shown in Fig.30.

Further experiments with ferric chloride at 60°C, indicated that with constant $[M]$, $[DMF]$ and $[FeCl_3]_0$, there was a linear relationship between τ^{-1} and $[ALBN]$ (Fig.26, Table 8), as expected from eqn (27). Assuming a value of k_d of $1.2 \times 10^{-5} \text{ sec}^{-1}$ 67,89, f was found to be 0.60 from the slope of the curve.

Again, for a series of experiments in which $[ALBN]_0$ was maintained constant but $[FeCl_3]_0$ was varied, there was a linear relationship between $[ALBN] \tau$ and $[FeCl_3]_0$ (Fig.27, Table 8), as expected from

eqn 27. From the slope of the curve, the value of f was found to be 0.57. Analysis of ϕ_t -time data by the method of Bamford et al.⁴³ gave a value of k_5 of $8.62 \times 10^4 \text{ l.mole}^{-1}\text{sec}^{-1}$ at 60°C , which compares well with the value of Bamford et al.⁴³ (using $k_p = 176 \text{ l.mole}^{-1}\text{sec}^{-1}$ at 60°C .⁶⁵ instead of $100 \text{ l.mole}^{-1}\text{sec}^{-1}$, makes Bamford's value $9.43 \times 10^4 \text{ l.mole}^{-1}\text{sec}^{-1}$.)

However, the above treatment is only approximate since it had already been shown that when iron(III) chloride was dissolved at low concentrations in DMF/styrene mixtures at 60°C , the principal ionic species present were $\text{Fe}(\text{DMF})_4\text{Cl}_2^{2+}$ and FeCl_4^{-} .⁸³ So the precise significance of the previous values of f and k_5 are difficult to assess from the results obtained with ferric chloride alone.

Table 8

Experiments performed with Anhydrous FeCl_3 . At 60°C ,
 $[\text{styrene}] = 2.49 \text{ mole l.}^{-1}$. $[\text{DMF}] = 8.792 \text{ mole l.}^{-1}$.

$[\text{AIBN}] \times 10^2$ (mole l.^{-1})	$[\text{AIBN}] \times 10^2$ (mole l.^{-1})	τ (sec.)	$\frac{1}{\tau} \times 10^4$ (sec.^{-1})	$\tau [\text{AIBN}]$ (sec.mole l.^{-1})	$[\text{FeCl}_3]_0 \times 10^3$ (mole l.^{-1})
3.809	3.630	14100	0.709	-	7.873
7.618	7.598	7860	1.27	597.20	7.873
15.236	15.201	3480	2.87	-	7.873
7.618	7.611	1920	-	146.13	2.620
7.618	7.576	15900	-	1204.58	15.746

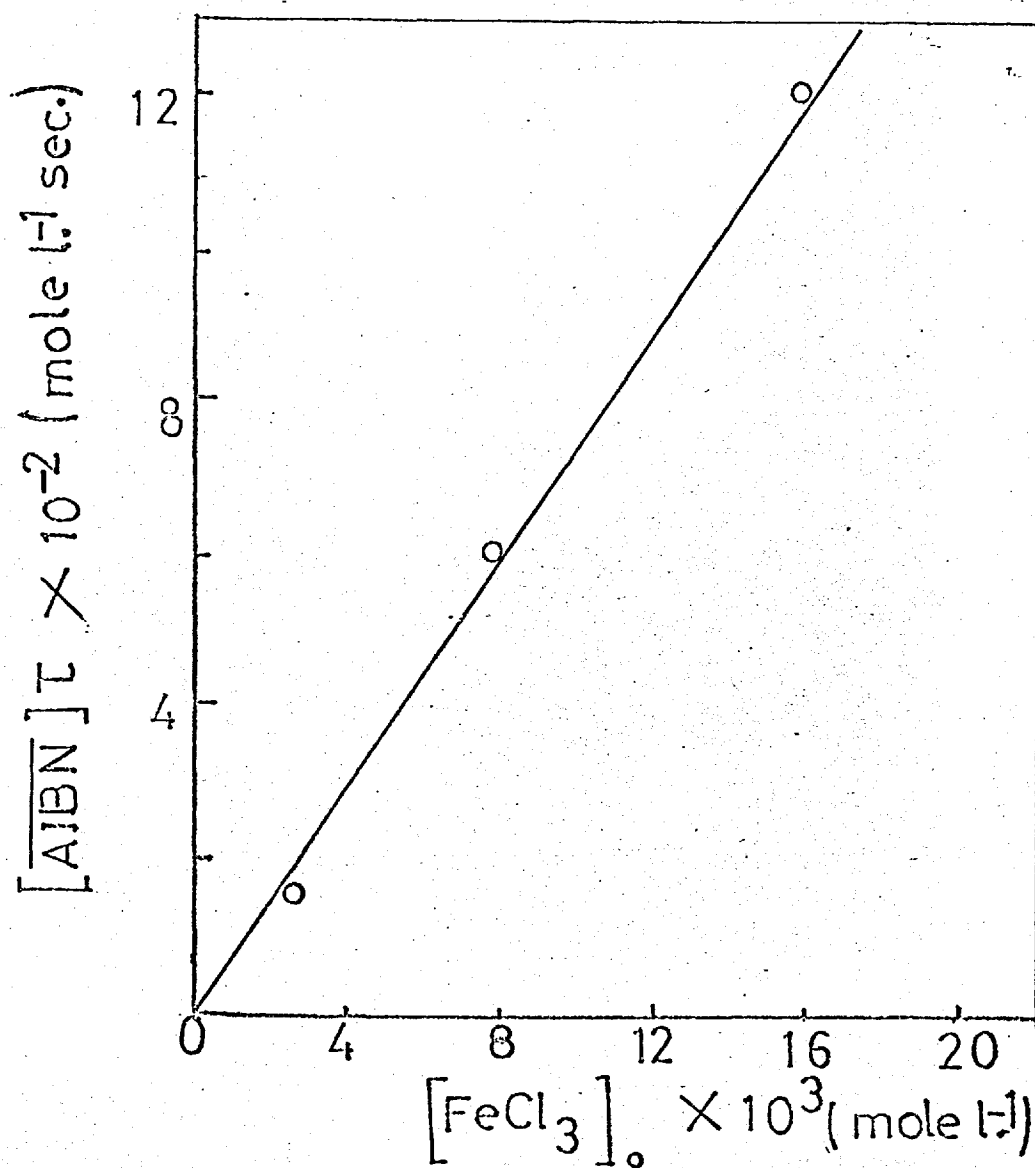


Fig. 27. Dependence of induction period, τ , on initial ferric chloride concentration $[FeCl_3]_0$.
 $[AIBN]_0 = 7.618 \times 10^{-2} \text{ mole l.}^{-1}$; $[styrene] = 2.490 \text{ mole l.}^{-1}$; and $[DMF] = 8.792 \text{ mole l.}^{-1}$ at 60°C .

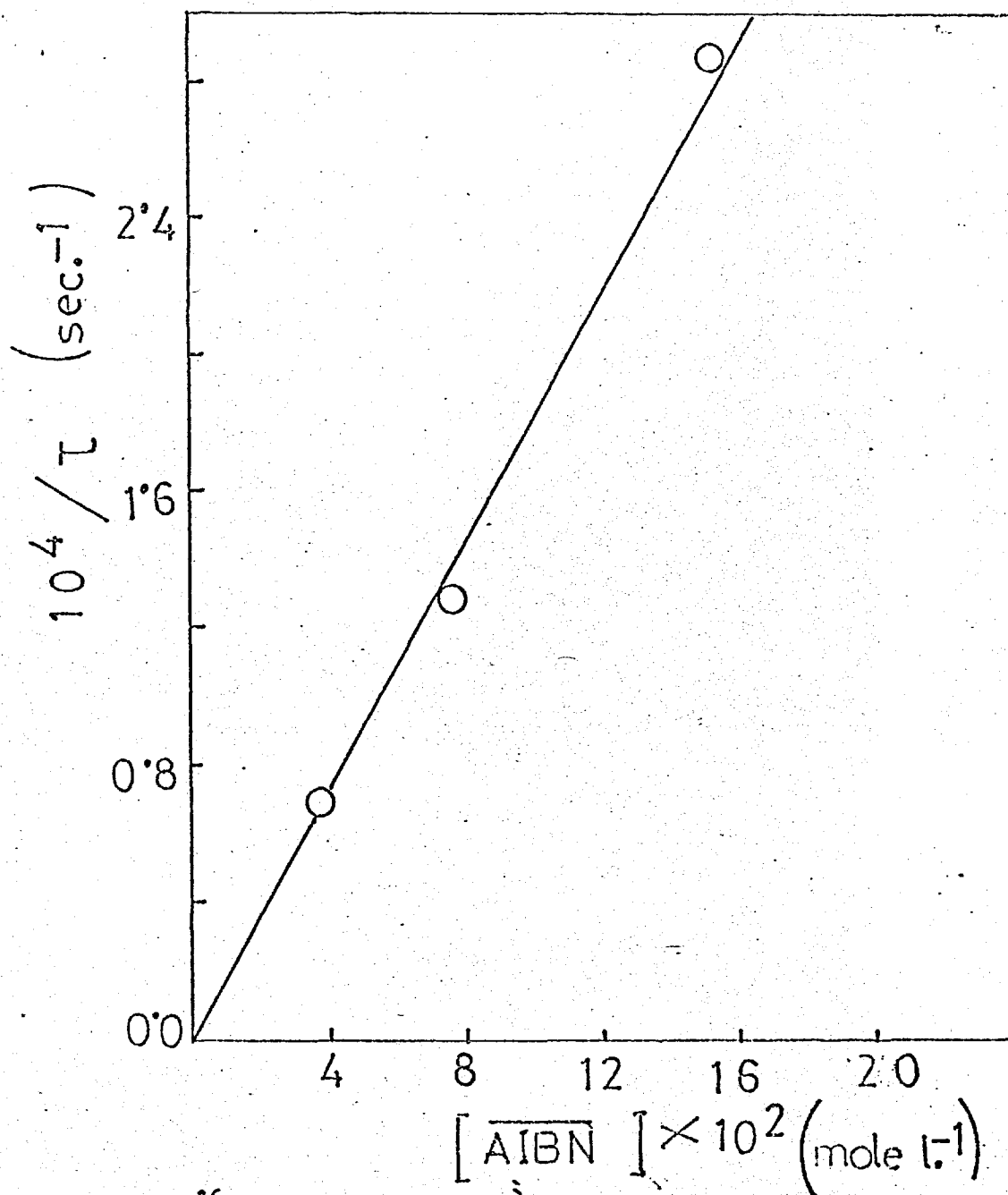


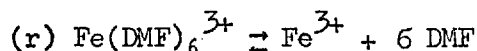
Fig. 27. Dependence of the induction period, τ , on mean azo-bisisobutyronitrile concentration, $[AIBN]$.
 $[Styrene] = 2.490 \text{ mole l.}^{-1}$; $[FeCl_3]_0 = 7.873 \times 10^{-3} \text{ mole l.}^{-1}$; and $[DMF] = 8.792 \text{ mole l.}^{-1}$, at 60°C .

5.9.2. Rate Measurements using the Complex, $[\text{Fe}(\text{DMF})_6]^{3+} 3(\text{BF}_4^-)$, A;

Evaluation of k_x

The tetrafluoroborate salt, A, $\text{Fe}(\text{DMF})_6^{3+} 3(\text{BF}_4^-)$ was selected for study since the BF_4^- ion shows little tendency to complex and $\text{Fe}(\text{DMF})_6^{3+}$ ions are formed in DMF/Styrene mixtures.

On polymerization of styrene at 60°C in the presence of AIBN, DMF and A, retarded rates of polymerization were recorded dilatometrically (Fig.28). The rate results were analysed by the method of Kice, assuming that the equilibrium (r) was well over to the left hand side.



According to Kice equation,

$$R_p \sqrt{1 + \frac{c(1-\phi^2)}{\phi^2}} = \frac{k_p k_x}{2k_t} \cdot \frac{\phi^2(A)}{(1-\phi^2)} \left\{ 1 + \sqrt{\frac{1 + c(1-\phi)^2}{\phi^2}} \right\} - \frac{k_o k_p}{k_c} (M) \quad (12)$$

The equation and the significance of the terms involved are discussed in Section 2.1.2.

A plot of the left hand side of equation (12) against

$$\frac{\phi^2(A)}{(1-\phi^2)} \left\{ 1 + \sqrt{1 + \frac{c(1-\phi^2)}{\phi^2}} \right\}$$

at constant (M) should give a slope of $\frac{k_p k_x}{2k_t}$ and an intercept on the vertical axis of $-\frac{k_o k_p}{k_c} (M)$. A value of c equal to 1×10^{-6} was

chosen to give the least deviation of the experimental points from a straight line and the results are collected in Table 9 and plotted

Table 9

Effect of Complex A on the Polymerization of Styrene Initiated by ALBN in DMF Solution

at 60°C

(M) = 2.490 mole ℓ^{-1} ; (DMF) = 8.792 mole ℓ^{-1} . Value of c chosen = 1.0×10^{-6}

(ALBN) $\times 10^2$ (mole ℓ^{-1})	Rate of Poly- merization $\times 10^5$ (mole $\ell^{-1} \text{sec}^{-1}$)	Retarder Concentration (A) $\times 10^3$ (mole ℓ^{-1})	$\frac{\phi^2(A)}{(1-\phi^2)} \left[1 + \sqrt{\frac{1+c(1-\phi^2)}{\phi^2}} \right]$ $\times 10^3$ (mole ℓ^{-1})	$\frac{R_p}{\phi^2} \sqrt{\frac{1+c(1-\phi^2)}{\phi^2}}$ $\times 10^3$ (sec. $^{-1}$)
7.618	3.979	0.000	-	-
7.618	2.390	3.936	4.443	9.598
7.618	2.035	5.904	4.183	8.173
7.618	1.701	7.873	3.521	6.831
7.618	1.037	11.909	1.736	4.165
1.404	1.859	0.000	-	-
1.404	0.500	7.873	1.228	2.008

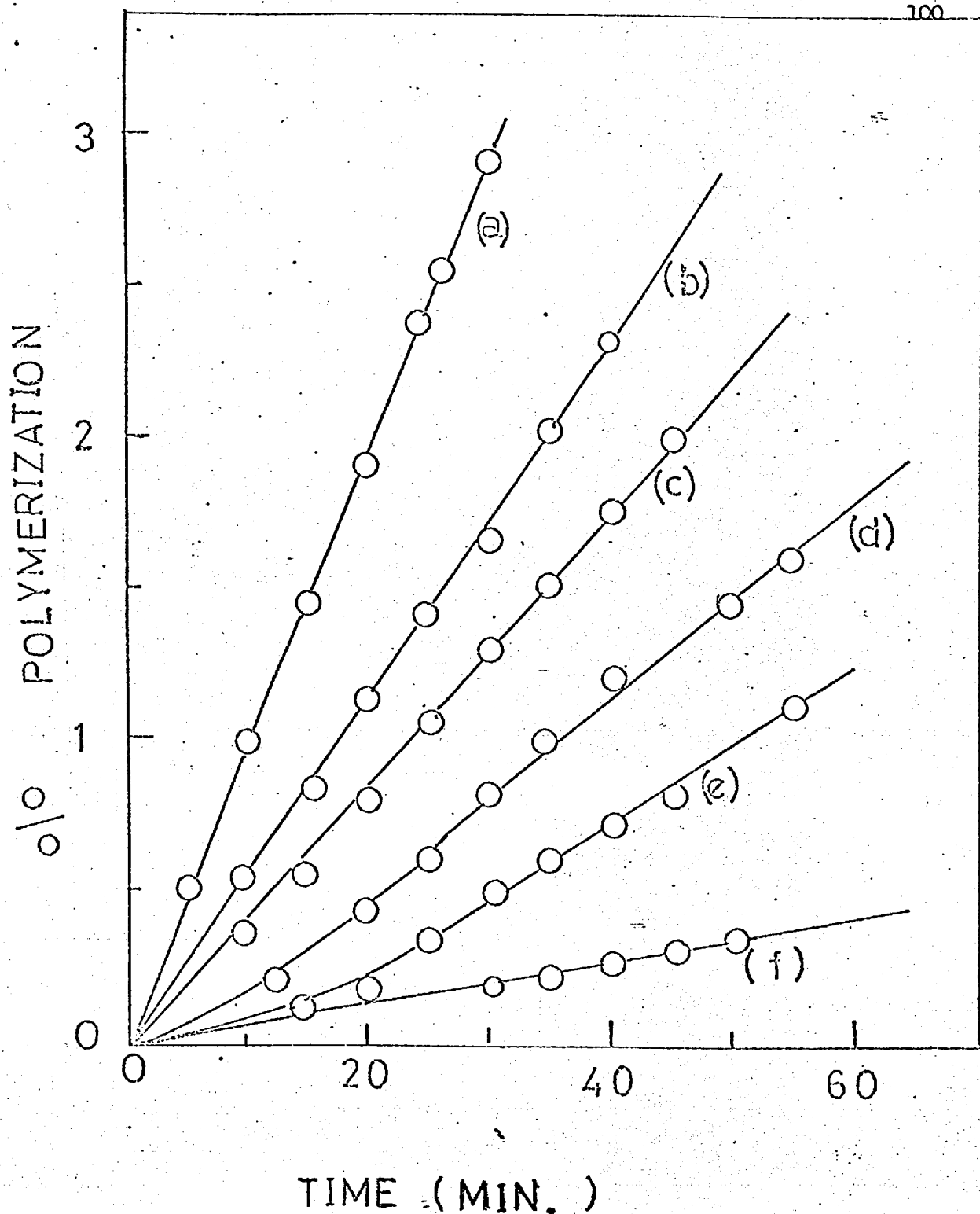


Fig.28. Effect of Complex, A, on the polymerization of styrene initiated by AIBN in DMF solution at 60°C.
 $[M] = 2.490 \text{ mole l.}^{-1}$; $[DMF] = 8.792 \text{ mole l.}^{-1}$; $[AIBN]_0 = 7.618 \times 10^{-2} \text{ mole l.}^{-1}$; (b) $(A)_0 = 3.936 \times 10^{-3} \text{ mole l.}^{-1}$;
 (c) $(A)_0 = 5.904 \text{ mole l.}^{-1}$; (d) $(A)_0 = 7.873 \times 10^{-3} \text{ mole l.}^{-1}$;
 (e) $(A)_0 = 11.909 \text{ mole l.}^{-1}$ and (f) $(A)_0 = 7.873 \times 10^{-3} \text{ mole l.}^{-1}$,
 $[AIBN]_0 = 1.404 \times 10^{-2} \text{ mole l.}^{-1}$.

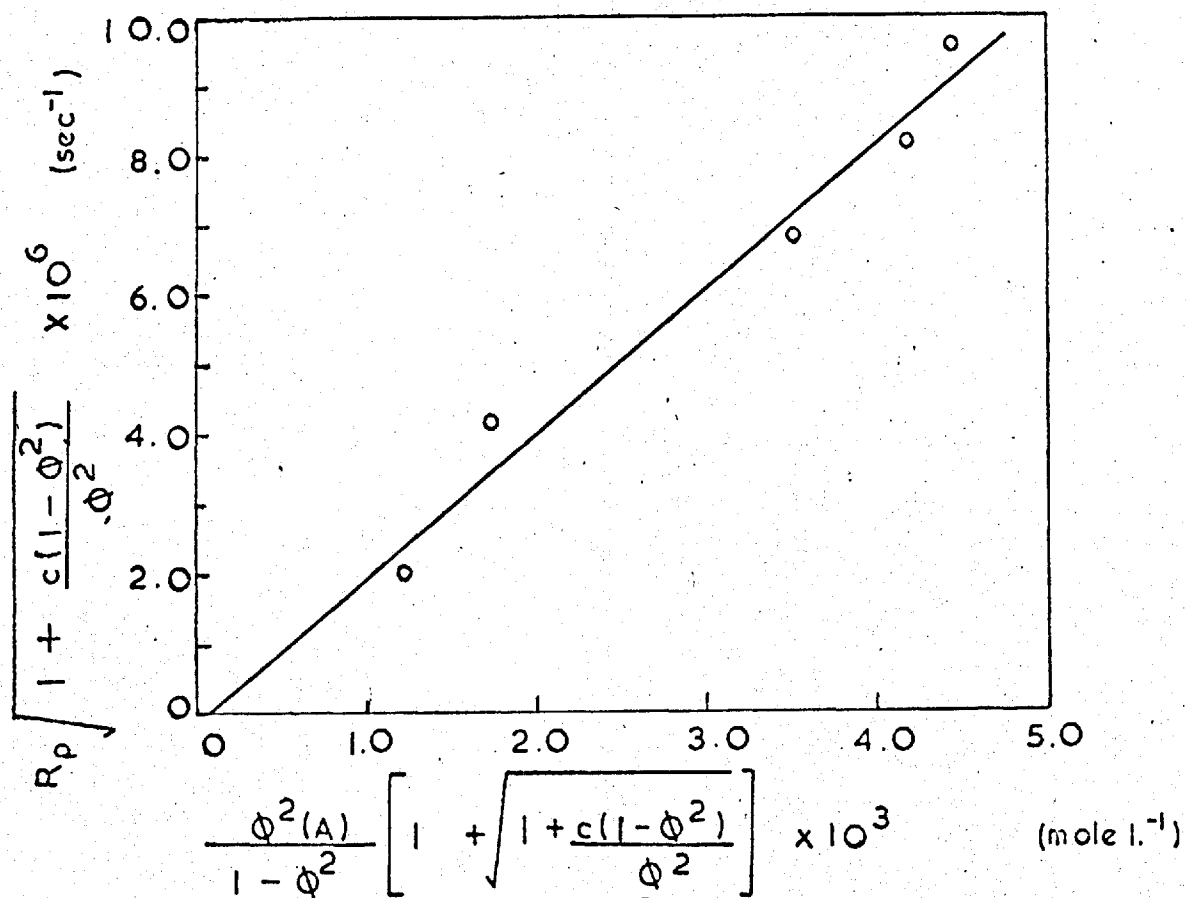
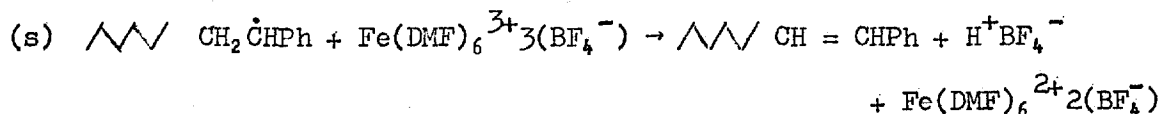


Fig. 29.

Kice plot of retardation results with complex A alone. At 60°C., [styrene] = 2.490 mole/l.; [DMF] = 8.792 mole/l.; value of c chosen = 1.0×10^{-6} .

in Fig.29. The slope of the line is $2.07 \times 10^{-3} \text{ l.mole}^{-1}\text{sec}^{-1}$, and using values⁶⁵ of k_p and $2 k_t$ equal to $176 \text{ l.mole}^{-1}\text{sec}^{-1}$, and $7.2 \times 10^7 \text{ l.mole}^{-1}\text{sec}^{-1}$; k_x was $847 \text{ l.mole}^{-1}\text{sec}^{-1}$. From the intercept, $\frac{k_o}{k_c}$ was 2.31×10^{-10} at 60°C .

The low value of $\frac{k_o}{k_c}$ indicates a low tendency of Z. species to attack monomer. The transfer constant for polystyryl radicals to DMF is only 4.0×10^{-4} at 60°C , and involves H atom abstraction from a CH_3 -group. Hence unless the reactivity of a DMF molecule is greatly increased when it is a ligand in the complex ion, another type of radical-A reaction must occur to explain the high value of k_x . This equation might be



5.10. Effect of Adding LiCl to Complex, $[\text{Fe}(\text{DMF})_6^{3+}](\text{BF}_4^-)_3$, A, on Rates of Polymerization

On progressively adding lithium chloride to mixtures of constant composition containing styrene, DMF, ALBN and complex, A, and measuring rates at 60°C , definite induction periods were observed, as indicated in Fig.30. A plot of τ evaluated from individual rate curves against concentration of lithium chloride added is shown in Fig.31 and the data are collected in Table 10. It was found experimentally that LiCl alone did not affect the reaction rate of the above system in absence of the complex, A, though Bamford et al.⁴⁴

observed some unexpected accelerative effects with LiCl in the polymerization of acrylonitrile.

All these results confirmed the spectroscopic evidence of formation of chloro-species on addition of Cl^- ions to systems containing $\text{Fe}(\text{DMF})_6^{3+}$ ions, fully discussed in Section 5.3, and also suggested that they are more reactive than $\text{Fe}(\text{DMF})_6^{3+}$ ions alone.

Table 10

Induction period τ as a function of added lithium chloride concentration.

At 60°C , $[\text{Styrene}] = 2.490 \text{ mole } \ell.^{-1}$; $[\text{DMF}] = 8.792 \text{ mole } \ell.^{-1}$;
 $[\text{A}] = 7.87 \times 10^{-3} \text{ mole } \ell.^{-1}$; $[\text{AIBN}]_0 = 7.62 \times 10^{-2} \text{ mole } \ell.^{-1}$

Molar ratio	LiCl : A	τ (min.)
0.25	: 1	62
0.40	: 1	74
0.50	: 1	96
1	: 1	120
1.5	: 1	122
2	: 1	128
3	: 1	128
4	: 1	121
5	: 1	124
6	: 1	97
7	: 1	95
8	: 1	92
9	: 1	92
10	: 1	92
Anhydrous FeCl_3 , $[\text{FeCl}_3]_0 = 7.87 \times 10^{-3} \text{ mole } \ell.^{-1}$		131

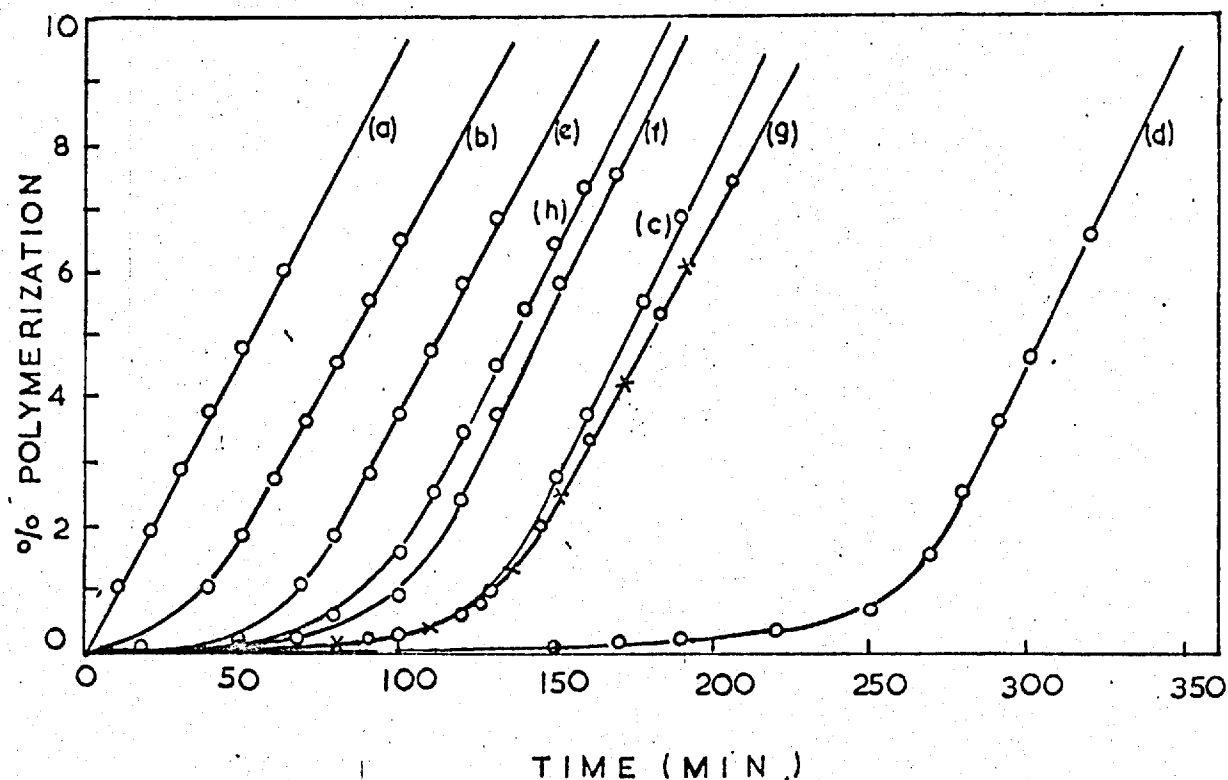


Fig. 30. Polymerization of styrene in DMF solution at 60°C initiated by AIBN in the presence of various iron(III) species: (a) no added iron(III) compound. (b) $[\text{FeCl}_3]_0 = 2.62 \times 10^{-3}$ mole/l.; (c) $[\text{FeCl}_3]_0 = 7.87 \times 10^{-3}$ mole/l.; (d) $[\text{FeCl}_3]_0 = 1.58 \times 10^{-2}$ mole/l.; (e) molar ratio LiCl: A = 0.25:1, $[A] = 7.87 \times 10^{-3}$ mole/l.; (f) molar ratio LiCl: A = 1:1, $[A] = 7.87 \times 10^{-3}$ mole/l.; (g) (O) results for a molar ratio LiCl: A = 2:1; (X) results for a molar ratio of LiCl: A = 3:1, $[A] = 7.87 \times 10^{-3}$ mole/l.; (h) molar ratio LiCl: A = 10:1, $[A] = 7.87 \times 10^{-3}$ mole/l. At 60°C., $[\text{styrene}] = 2.490$ mole/l.; $[\text{DMF}] = 8.792$ mole/l.; $[\text{AIBN}] = 7.62 \times 10^{-2}$ mole/l.

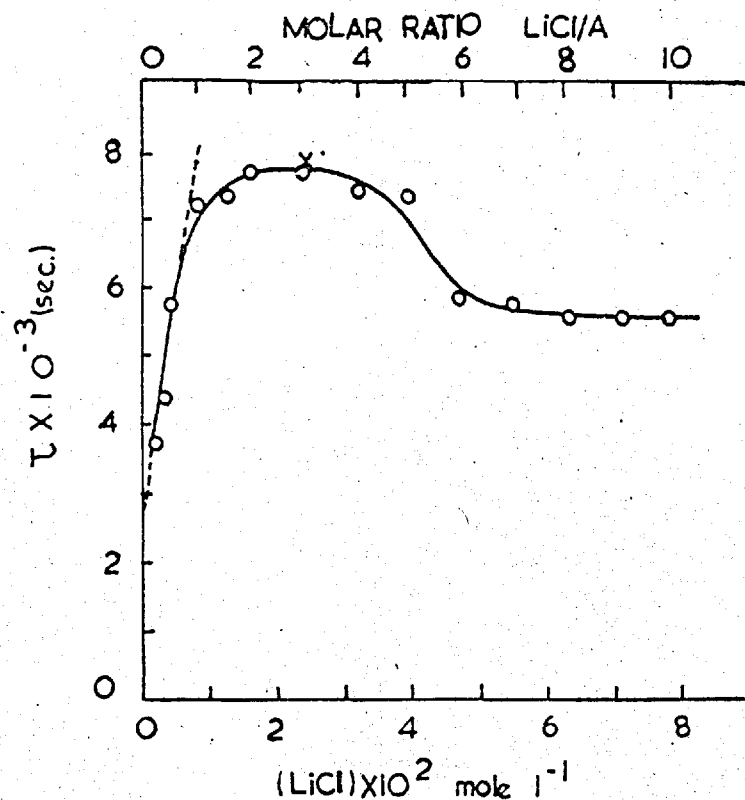


Fig. 31. Induction period τ as a function of added lithium chloride concentration. At 60°C., [styrene] = 2.490 mole/l.; [DMF] = 8.792 mole/l.; [A] = 7.87×10^{-3} mole/l.; [AIBN] = 7.62×10^{-2} mole/l.

5.10.1. Analysis of Results up to a Molar Ratio of LiCl : A of 1:1

Evaluation of k_6

Spectroscopic evidence⁸³ suggested that up to a 1:1 molar ratio of LiCl to A, $\text{Fe}(\text{DMF})_5\text{Cl}^{2+}$ ions were progressively formed by the equilibrium reaction (n), which has a high equilibrium constant (Section 5.3). Since no chlorine could be found by microanalysis in the low molecular weight polymers formed during induction periods, the predominant inhibition reaction may be written:

(t) $\text{CH}_2\dot{\text{C}}\text{HPh} + \text{Fe}(\text{DMF})_5\text{Cl}^{2+} \rightarrow \text{CH}=\text{CHPh} + \text{Fe}(\text{DMF})_5^{2+} + \text{H}^+\text{Cl}^-$

and presumably the $\text{Fe}(\text{DMF})_5^{2+}$ ion rapidly acquires another DMF molecule to become $\text{Fe}(\text{DMF})_6^{2+}$.

In this case, the total τ value will depend on the initial equilibrium concentration of $\text{Fe}(\text{DMF})_5\text{Cl}^{2+}$ ions and also on the concentration of $\text{Fe}(\text{DMF})_5\text{Cl}^{2+}$ ions formed by equilibrium (n) as Cl^- ions are liberated in (t). If $(\text{A})_0$ and $(\text{Cl}^-)_0$ are the initial concentrations of A and Cl^- , then the initial concentrations of $\text{Fe}(\text{DMF})_6^{3+}$ and $\text{Fe}(\text{DMF})_5\text{Cl}^{2+}$ are $(\text{A})_0 - (\text{Cl}^-)_0$ and $(\text{Cl}^-)_0$, respectively.

By analogy with eqn (27);

$$\tau = \frac{k' \{ (\text{A})_0 - (\text{Cl}^-)_0 \}}{I} + \frac{(\text{Cl}^-)_0}{I} = \frac{k'(\text{A})_0}{I} + (\text{Cl}^-)_0 \left\{ \frac{1}{I} - \frac{k'}{I} \right\} \quad (64)$$

where the first term on the right hand side of eqn (64) allows for the conversion of $\text{Fe}(\text{DMF})_6^{3+}$ to $\text{Fe}(\text{DMF})_5\text{Cl}^{2+}$, and k' is an arbitrary constant.

In accordance with this prediction, Fig.31 gave an initially linear plot of τ against $(Cl^-)_0$ up to a molar ratio of LiCl/A of 1:1. The slope was $5.748 \times 10^5 \text{ sec. l.mole}^{-1}$ and intercept, 2847.6 sec, and these values gave a rate of initiation, I , equal to $1.07 \times 10^{-6} \text{ mole l.}^{-1} \text{ sec}^{-1}$. This is reasonable since using $[\overline{In}]$ equal to $7.31 \times 10^{-2} \text{ mole l.}^{-1}$, over the range considered and k_d equal to $1.2 \times 10^{-5} \text{ sec}^{-1}$, the initiator efficiency was found to be 0.62.

Again, when both A and added LiCl had a concentration of $7.873 \times 10^{-3} \text{ mole l.}^{-1}$ at 60°C , the value of τ was 7200 sec. Writing

$$\tau = \frac{[\text{Fe}(\text{DMF})_5\text{Cl}^{2+}]_0}{I} = \frac{[Cl^-]_0}{I} \quad (65)$$

and using the above mentioned value of k_d and $[\overline{In}]$, the value of f was 0.61. This value of f is in good agreement with other literature values, although the dependence on the value of k_d used is clear.

A detailed analysis of the rate curve measured with a 1:1 molar ratio of LiCl/A was then made, and a plot of ϕ_t vs $k_6[R\cdot]_S t + A^*$ is shown in Fig.32, where it was assumed that only $\text{Fe}(\text{DMF})_5\text{Cl}^{2+}$ ions were present and k_6 referred to reaction (t).

Reasonable agreement was found between the experimental and theoretical plot when $k_6[R\cdot]_S$ was $4.00 \times 10^3 \text{ sec}^{-1}$ and A^* was -29.6 (Fig.32). k_6 was also calculated by Bengough's methods (Fig.33 and 34) with ϕ values lying between 0.15 and 0.8. The methods are fully discussed in Sections 2.1.3.2 and 2.1.3.3. A summary of the different values obtained is given in Table 11. The values of k_6 obtained by three different methods agreed well (Table 19) and the mean value of k_6 was $4.53 \times 10^4 \text{ l.mole}^{-1} \text{ sec}^{-1}$ at 60°C .

Table 11

Data used in the calculation of k_6 at 60°C .

$$[\text{styrene}] = 2.49 \text{ mole } \ell^{-1}$$

$$[\text{DMF}] = 8.792 \text{ mole } \ell^{-1}$$

$$[\text{AlBN}]_0 = 7.618 \times 10^{-2} \text{ mole } \ell^{-1}$$

$$[\text{Fe}(\text{DMF})_6](\text{BF}_4)_3 = 7.873 \times 10^{-3} \text{ mole } \ell^{-1}$$

$\text{LiCl} : \text{Complex} = 1:1$

Maximum rate = $0.102\% \text{ min}^{-1}$ at 60°C .

Reaction time (t) (Sec.)	Reduced rate $\frac{\text{Rate at } t}{\text{Max. rate}} = \phi_t$	$k_6 [\text{R}\cdot]_s t + A^*$ assuming $k_6 [\text{R}\cdot]_s = 4 \times 10^{-3}$ and $A^* = -29.6$	$\frac{1}{\phi_t} + \frac{\ln(1+\phi_t)}{(1-\phi_t)}$	$\log(1-F)$	$\log \frac{(1-\phi_t^2)}{\phi_t}$
4200	0.0186	- 12.8			
4800	0.049	- 9.8			
5400	0.119	- 8.0			
6000	0.1568	- 5.6	- 6.0571	$\bar{1}.9991$	0.7936
6300	0.1872	- 4.4	- 5.0045	$\bar{1}.9989$	0.7120
6600	0.3128	- 3.2	- 2.5498	$\bar{1}.9985$	0.4602
6960	0.3461	- 2.0	- 2.1673	$\bar{1}.9974$	0.4053
7200	0.6196	- 0.08	- 0.1651	$\bar{1}.9967$	-0.0024
7500	0.7618	+ 0.4	+ 0.6886	$\bar{1}.9952$	-0.2589
7800	0.8971	+ 1.6			
8100	1	+ 2.8			

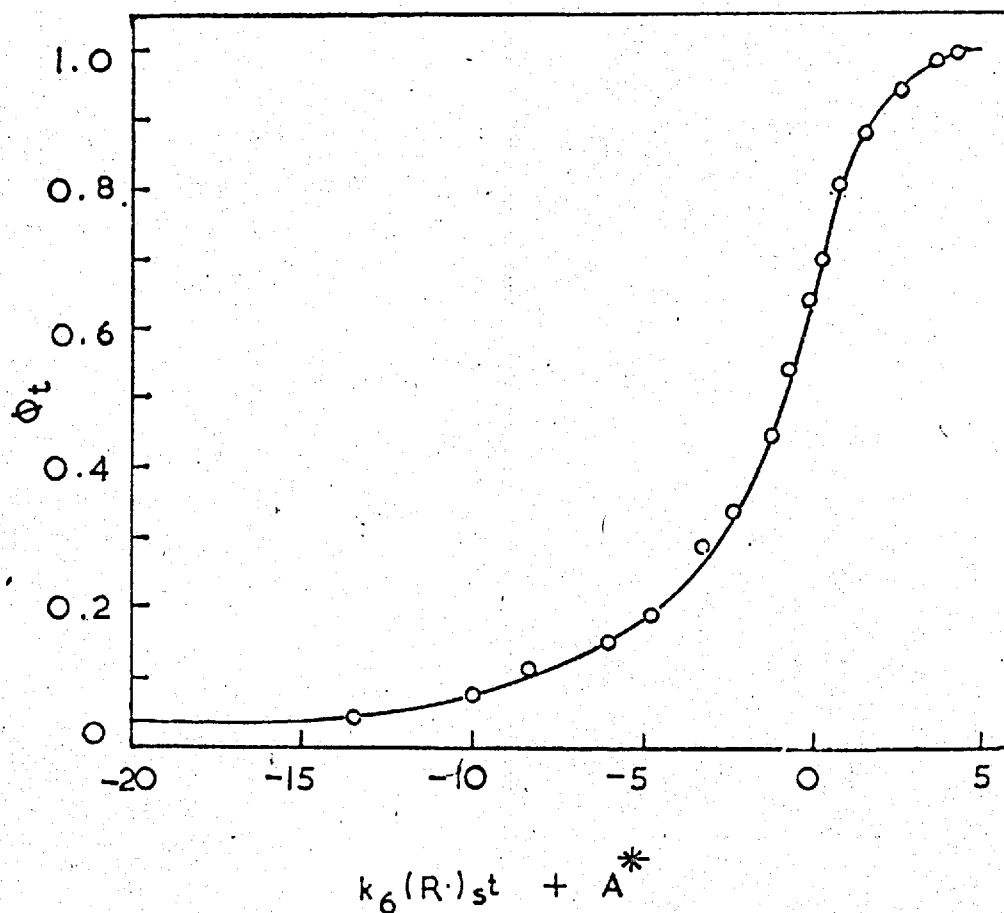


Fig.32. Reduced rate ϕ_t as a function of reaction time t : (O) experimental points; (—) calculated curve. Molar ratio of LiCl: A = 1:1; at 60°C.; [styrene] = 2.490 mole/l.; [DMF] = 8.792 mole/l.; [AIBN] = 7.62×10^{-2} mole/l.; [A] = 7.87×10^{-3} mole/l.; [LiCl] = 7.87×10^{-3} mole/l.

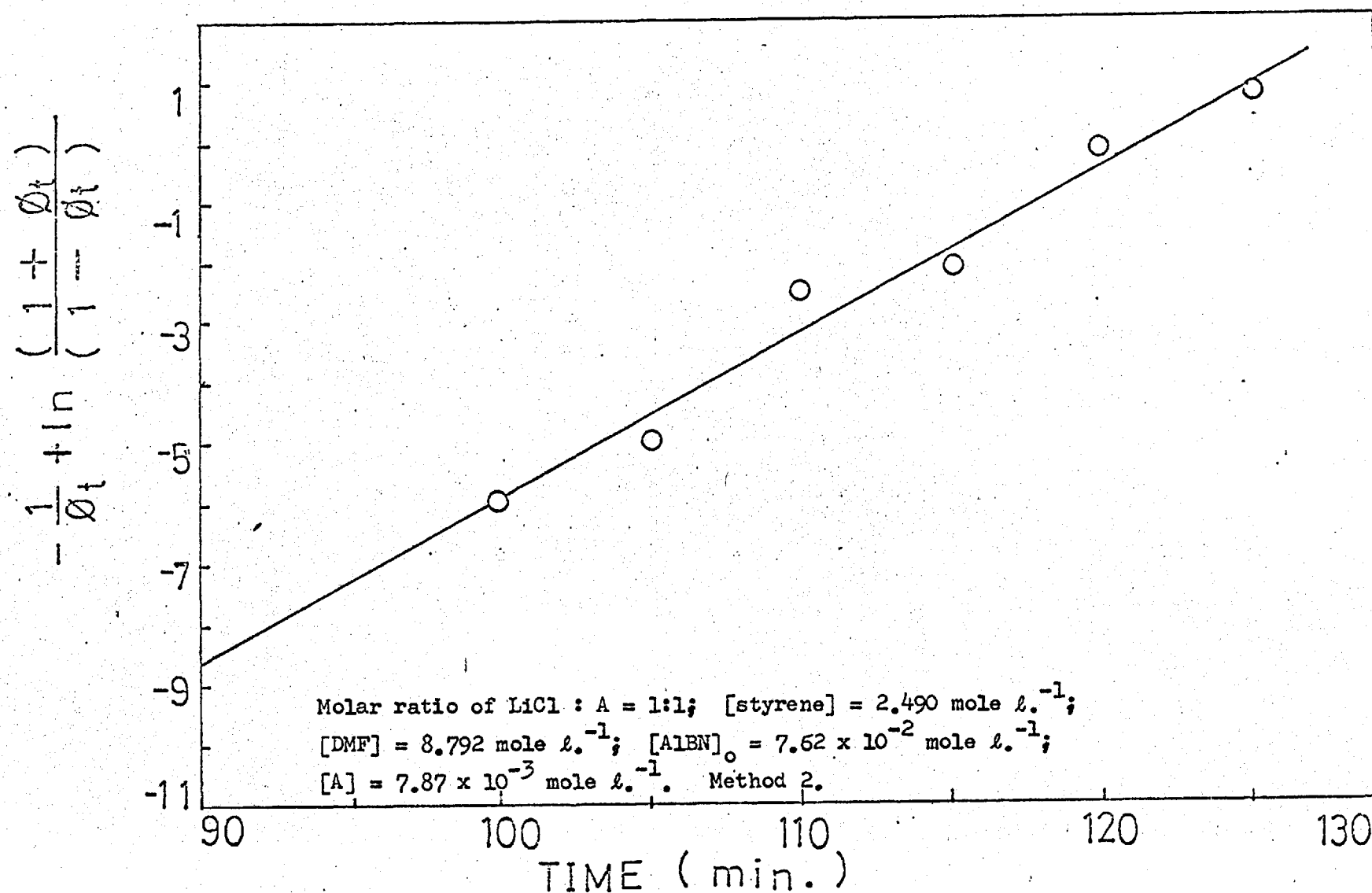


Fig.33. Analysis of the results for the polymerization of styrene initiated by α, α' -azobisisobutyronitrile, AlBN, at 60°C, and inhibited by $Fe(DMF)_5Cl^{2+}$, prepared in situ.

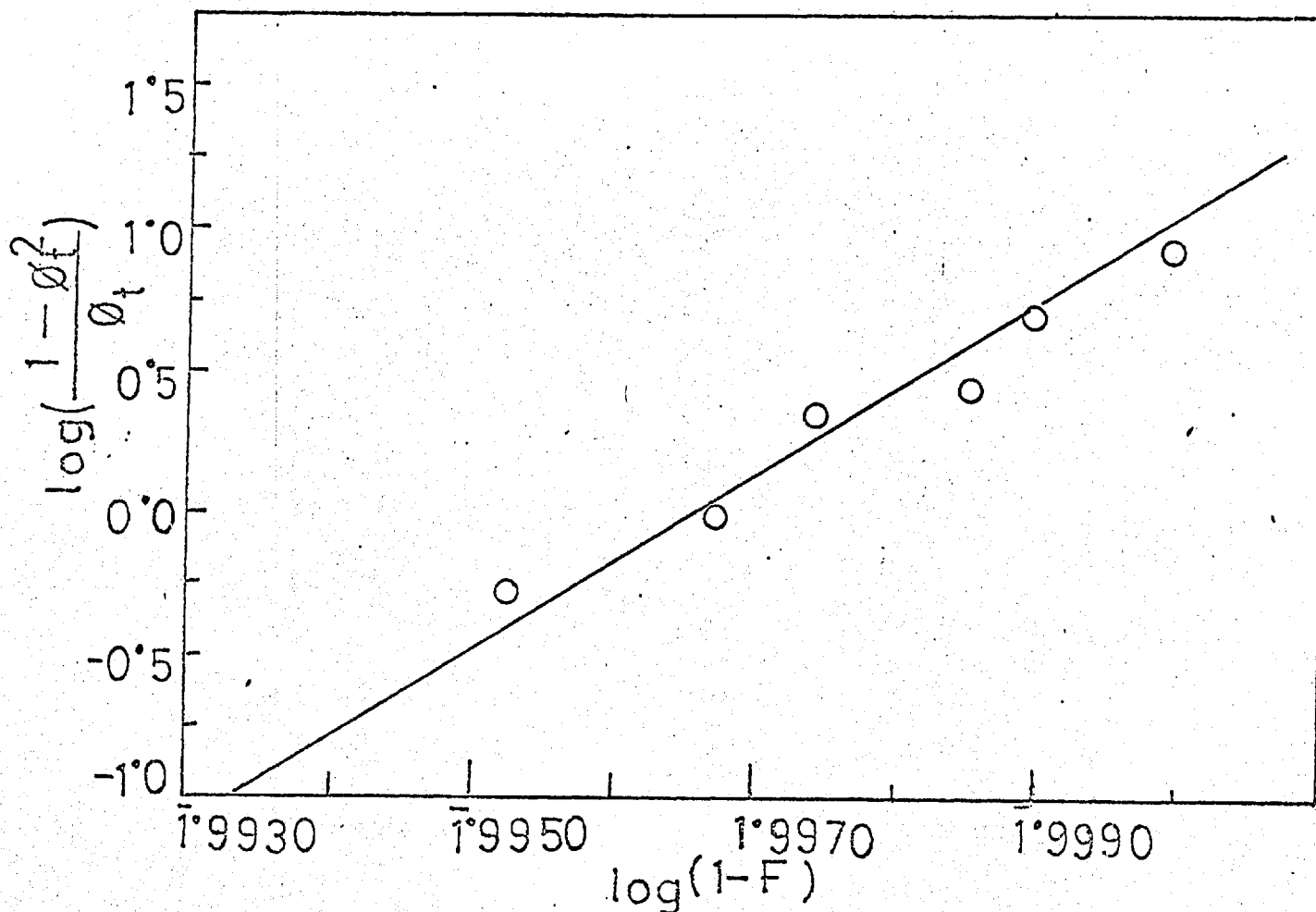
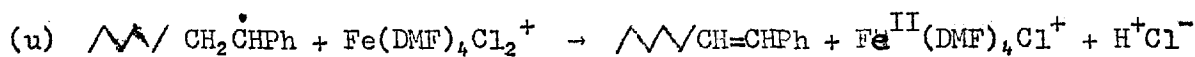


Fig.34. Analysis of the results for the polymerization of styrene initiated by ALBN and inhibited by $\text{Fe}(\text{DMF})_5\text{Cl}$ at 60°C . $\text{Fe}(\text{DMF})_5\text{Cl}$ was prepared in situ by using a molar ratio of $\text{LiCl:A} = 1:1$. $[\text{Styrene}] = 2.490 \text{ mole } \ell.^{-1}$; $[\text{DMF}] = 8.792 \text{ mole } \ell.^{-1}$; $[\text{ALBN}]_0 = 7.62 \times 10^{-2} \text{ mole } \ell.^{-1}$; $[\text{A}] = 7.87 \times 10^{-3} \text{ mole } \ell.^{-1}$. Method 3.

5.10.2. Evaluation of k_7

Spectroscopic evidence⁸³ suggested that when the molar ratio of LiCl/A was greater than 1:1 in the polymerizing system, the equilibrium (o) was established and the induction periods were possibly due to mechanisms (t) and (u).



with the iron(II) complex becoming rapidly solvated with DMF.

The equilibrium constant of (o) was estimated to be 5×10^4 from the spectroscopic results and so for a molar ratio of LiCl/A of 2:1, virtually all the Fe(III) ions were expected to exist as $\text{Fe}(\text{DMF})_4\text{Cl}_2^+$.

Hence,

$$\tau = \frac{[\text{Fe}(\text{DMF})_4\text{Cl}_2^+]_0}{I} \quad (66)$$

The experimental τ value gave a value of I of $1.03 \times 10^{-6} \text{ mole } \ell^{-1} \text{ sec}^{-1}$ and an f value 0.61.

Reasonable agreement was found between the experimental and theoretical plot when $k_7(R\cdot)_s = 5.2 \times 10^{-3} \text{ sec}^{-1}$, and $A^* = -38$ (Fig.35). k_7 was also calculated by Bengough's plot (Fig.36 and 37). A summary of the different values obtained is given in Table 12. The values of k_7 obtained by the three different methods agreed well (Table 19) and the mean value of k_7 hence calculated was $6.40 \times 10^4 \ell \cdot \text{mole}^{-1} \text{ sec}^{-1}$ at 60°C .

Table 12

Data used in the calculation of k_7 at 60°C

[Styrene] = 2.49 mole L^{-1}

[DMF] = 8.792 mole L^{-1}

[AlBN]₀ = 7.618×10^{-2} mole L^{-1}

$[\text{Fe}(\text{DMF})_6](\text{BF}_4)_3 = 7.873 \times 10^{-3}$ mole L^{-1}

LiCl : Complex = 2 : 1

Maximum rate = $0.084\% \text{ min.}^{-1}$ at 60°C

Reaction time (t) (sec.)	Reduced rate, $\frac{\text{Rate at } t}{\text{Max. rate}} = \phi_t$	$k_7 [\text{R}\cdot]_s t + A^*$ assuming $k_7 [\text{R}\cdot]_s = 5.2 \times 10^{-3}$ and $A^* = -38$	$-\frac{1}{\phi_t} + \frac{1}{(1+\phi_t)}$ $\ln \frac{1}{(1-\phi_t)}$	$\log(1-F)$	$\log \frac{(1-\phi_t^2)}{\phi_t}$
2100	0.0179	-27.08			
2400	0.0250	-25.52			
3000	0.0357	-22.40			
3600	0.0429	-19.28			
4200	0.0500	-16.16			
4800	0.0619	-13.04			
5400	0.0744	-9.92			
5700	0.0764	-8.36			
6000	0.1033	-6.80			
6300	0.1809	-5.24	-5.1620	$\bar{1}.9989$	0.7281
6600	0.2381	-3.68	-3.7142	$\bar{1}.9986$	0.5972
6900	0.3572	-2.12	-2.0520	$\bar{1}.9980$	0.3878
7200	0.5798	-0.56	-0.3457	$\bar{1}.9976$	0.2967
7500	0.7500	+1.00	+0.6130	$\bar{1}.9963$	-0.2341
7800	0.8690	+1.78			
8400	1	+5.68			

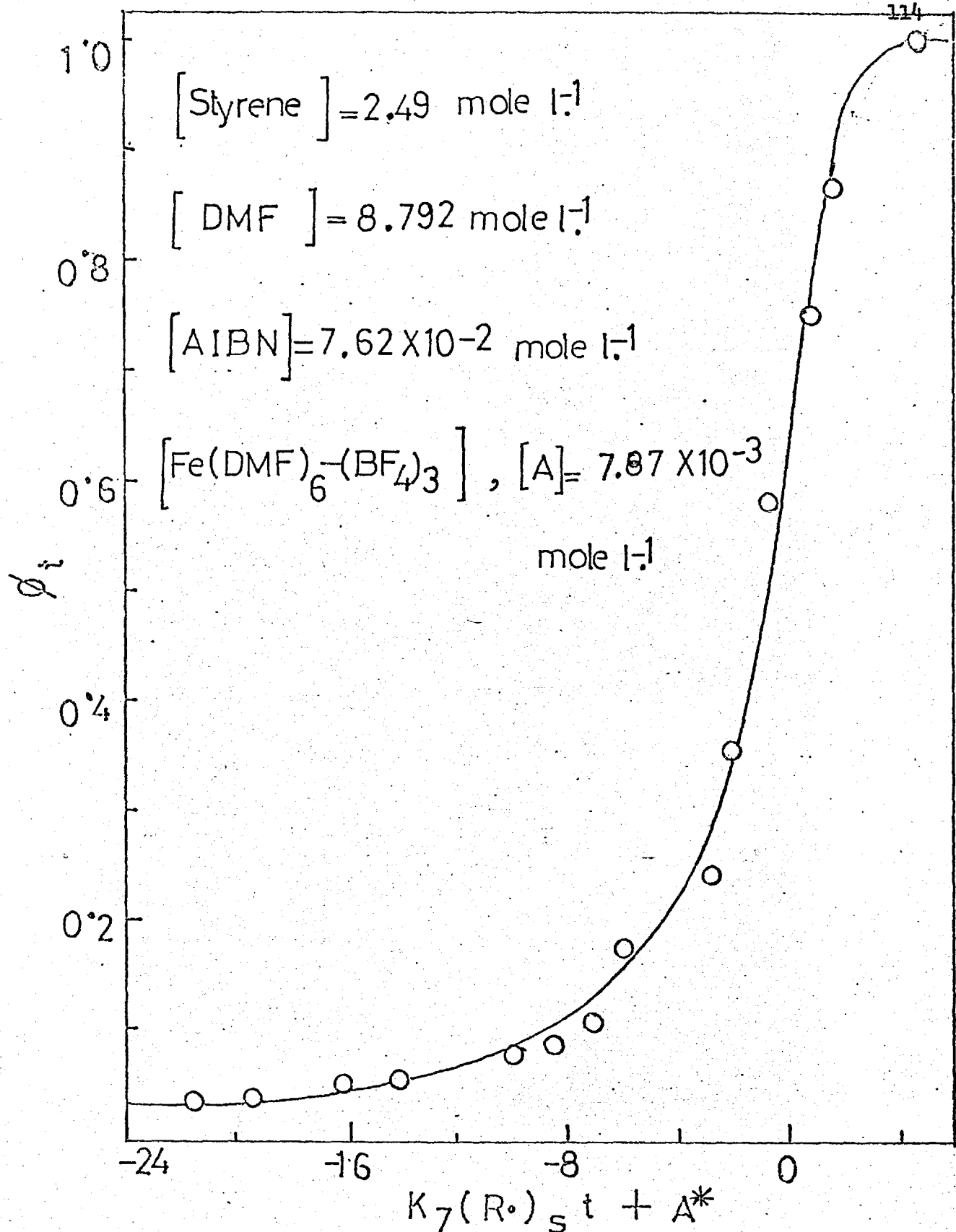


Fig.35. Reduced rate ϕ_t as a function of time, t : (O) experimental points, (-) calculated curve. Molar ratio of $\text{LiCl} : \text{A} = 2:1$. Temperature = 60°C . Method 1.

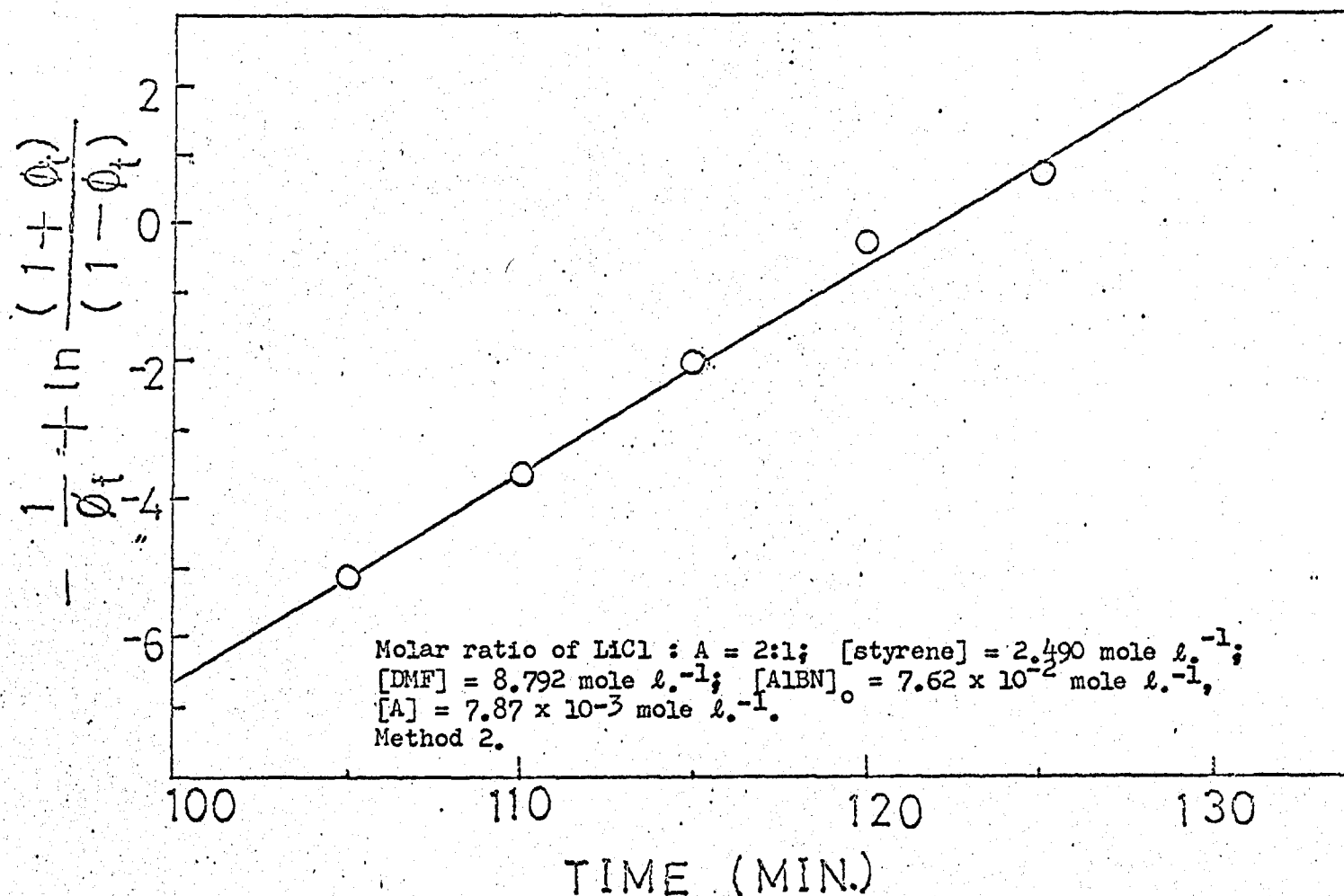


Fig.36. Analysis of the results for the polymerization of styrene initiated by AlBN at 60°C., and inhibited by $\text{Fe}(\text{DMF})_4\text{Cl}_2^+$ prepared in situ.

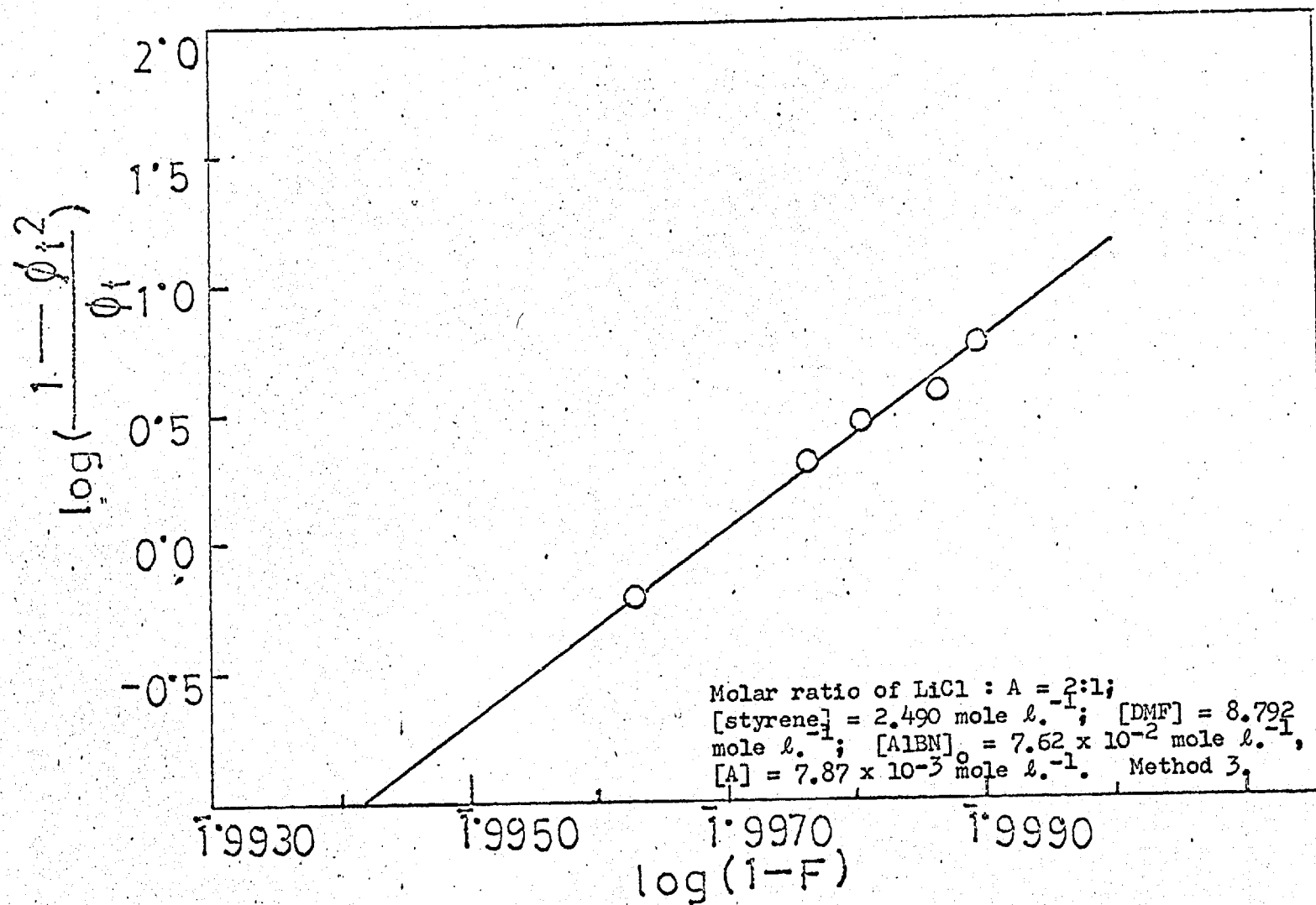


Fig.37. Analysis of the results for the polymerization of styrene initiated by AIBN at 60°C., and inhibited by Fe(DMF)₄Cl₂ prepared in situ.

5.10.3. Evaluation of k_8

Spectroscopic results⁸³ suggested that all iron(III) species from complex A with LiCl/A molar ratios in excess of 6:1 existed as FeCl_4^- in the polymerizing system at 60°C. The equilibrium constant, K_3 , for (p) was estimated to be about 10^8 .

A detailed analysis of the rate curve (Table 13) measured with a 10:1 molar ratio of LiCl/A was then made and a plot of ϕ_t vs $k_8[\text{R}\cdot]_s t + A^*$ is shown in Fig.38, where it was assumed that only FeCl_4^- ions were present and k_8 referred to reaction (v).



Reasonable agreement was found between the experimental and theoretical plots when $k_8(\text{R}\cdot)_s$ was $3 \times 10^{-3} \text{ sec}^{-1}$, and A^* was -16.9. k_8 was also calculated by Bengough's methods (Fig.39 and 41) with ϕ_t values lying between 0.15 and 0.8. The values of k_8 obtained by three different methods agreed reasonably well (Table 19) and the mean value of k_8 hence calculated was $2.96 \times 10^{-4} \text{ l.mole}^{-1} \text{ sec}^{-1}$ at 60°C.

However, the measured values of τ for LiCl/A molar ratio greater than 6:1, although virtually constant with increase of (LiCl), seemed somewhat lower than suggested by the usual treatment, and gave an f value of 0.8. The rate of production of iron(II) species was therefore followed spectroscopically in a polymerization experiment with a molar ratio of LiCl/A equal to 10:1. The experimental details are discussed in Section 4.7. The experiment indicated a linear rate of production of iron(II) species of $1.11 \times 10^{-7} \text{ mole l.}^{-1} \text{ sec}^{-1}$ and the

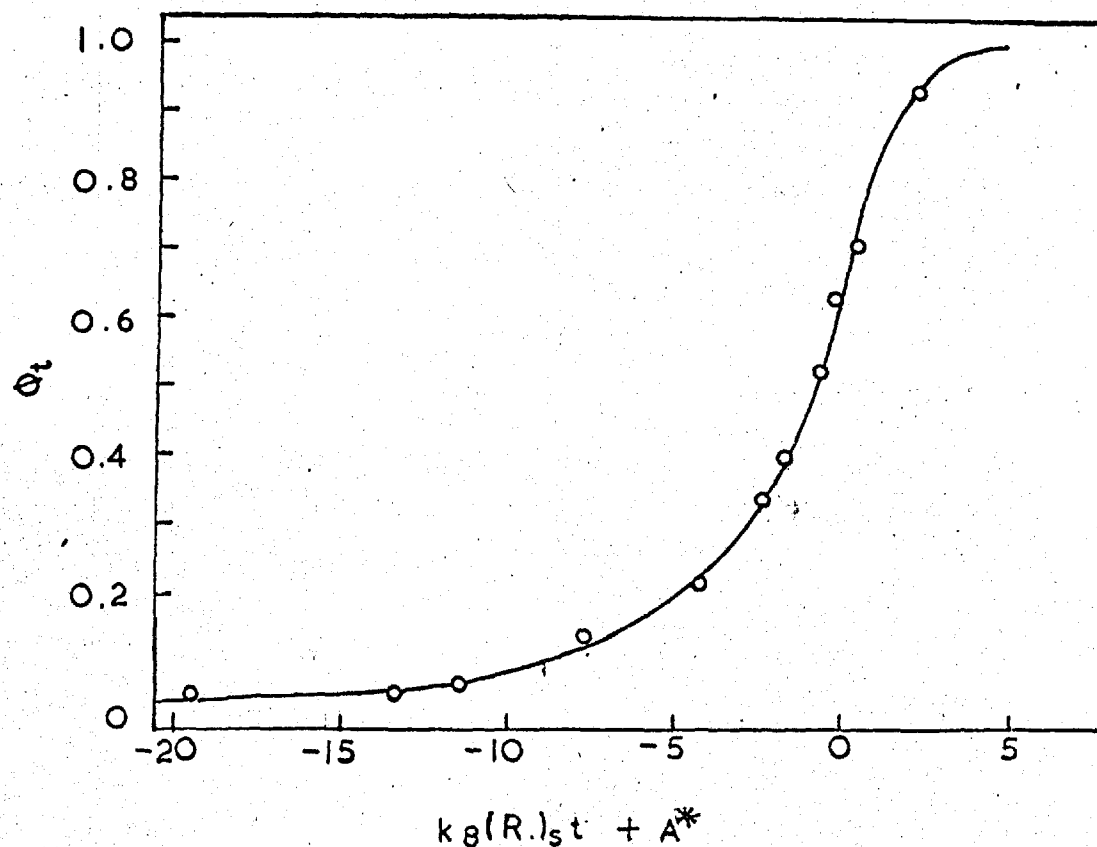


Fig.38. Reduced rate ϕ_t as a function of reaction time t : (O) experimental points; (—) calculated curve. Molar ratio of LiCl:A = 10:1; at 60°C.; [styrene] = 2.490 mole/l.; [DMF] = 8.792 mole/l.; [AIBN] = 7.62×10^{-2} mole/l.; [A] = 7.87×10^{-3} mole/l.; [LiCl] = 7.87×10^{-2} mole/l.

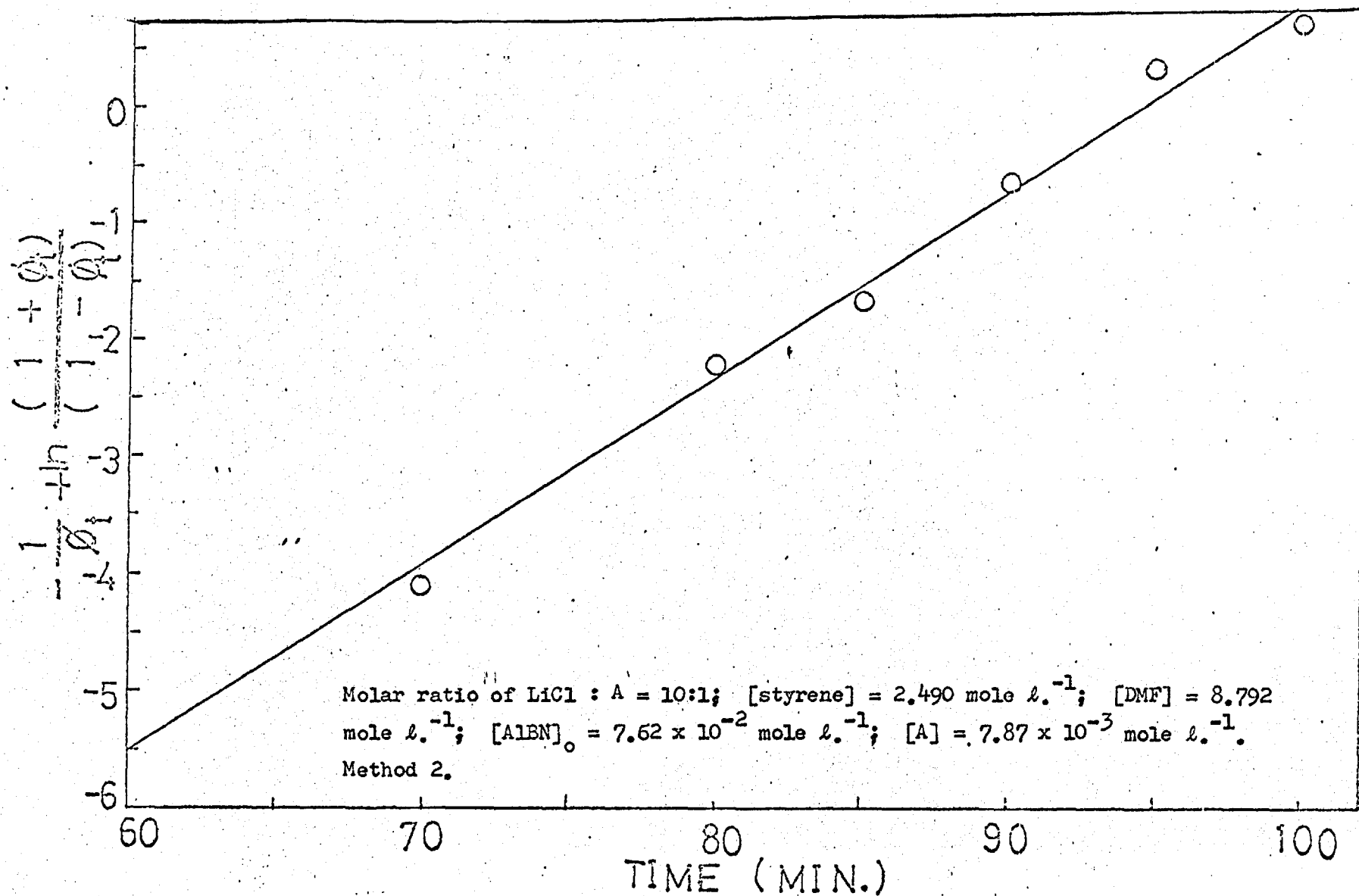


Fig.39. Analysis of the results for the polymerization of styrene initiated by AlBN at 60°C., and inhibited by FeCl₄⁻ prepared in situ.

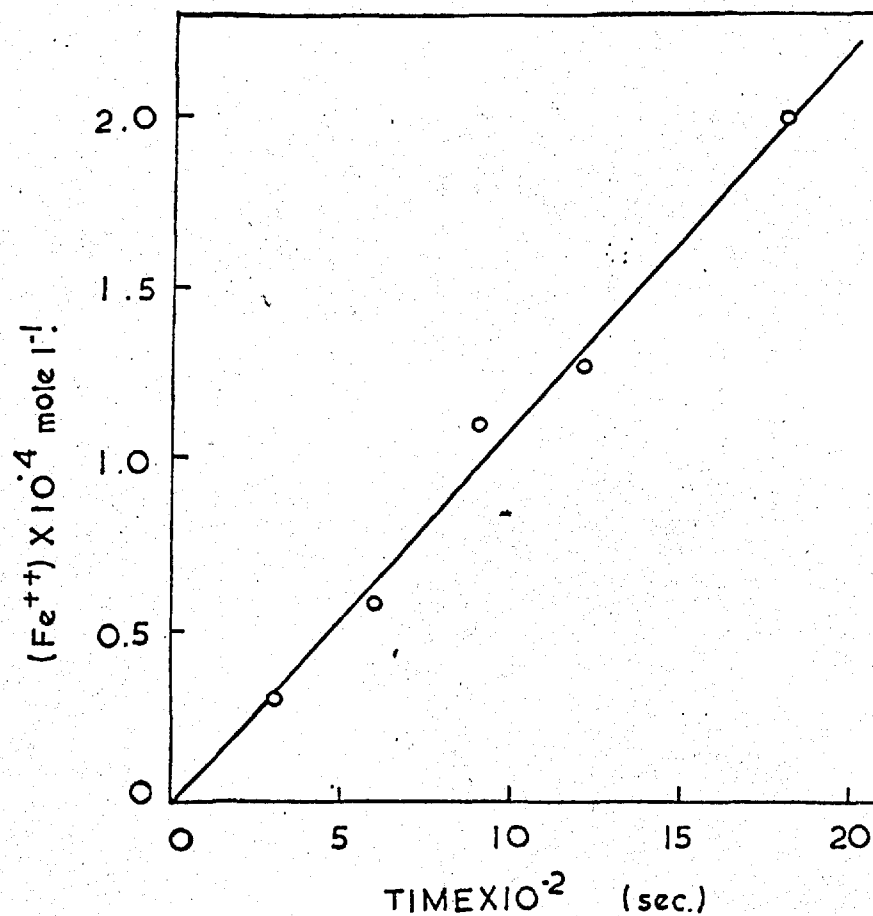


Fig. 40. Concentration of ferrous ions produced during an inhibition period as a function of time. At 60°C .; [styrene] = 2.490 mole/l.; [DMF] = 8.792 mole/l.; [AIBN] = 7.62×10^{-3} mole/l.; [A] = 4.40×10^{-4} mole/l.; [LiCl] = 4.40×10^{-3} mole/l.

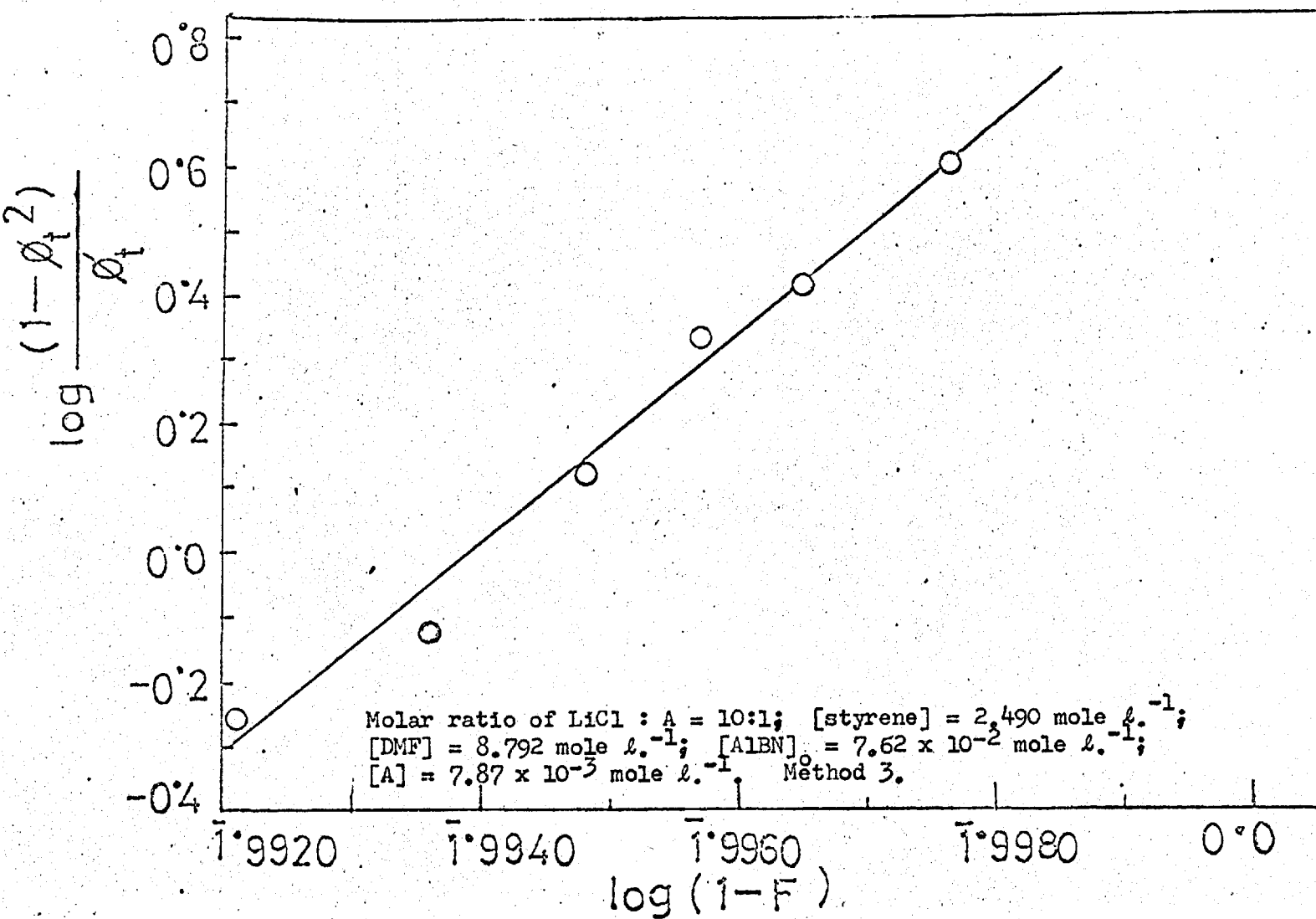


Fig. 41. Analysis of the results for polymerization of styrene initiated by AIBN at 60°C., and inhibited by FeCl_4^- prepared in situ.

results are shown graphically in Fig.40. Assuming that each polystyryl radical is captured by one FeCl_4^- ion during the induction period, simple theory suggests:

$$\frac{d(\text{Fe}^{\text{II}})}{dt} = I = 2 k_d f [\overline{\text{In}}]$$

For an average value of $[\overline{\text{In}}]$ equal to $7.52 \times 10^{-3} \text{ mole l.}^{-1}$ during the induction period, the corresponding value of f is 0.62 in agreement with previous results.

The reason for the discrepancy between f values calculated from τ measurement and those obtained by direct measurement of the rates of production of $\text{Fe}(\text{II})$ species remains uncertain.

5.10.4. The Kinetic Effects of Tetraethyl-ammonium-tetrachloroferrate, $(\text{C}_2\text{H}_5)_4\text{NFeCl}_4$, B, on the Polymerization of Styrene

Some of the results obtained with compound, B, in the polymerization of styrene are shown in Fig.42, and summarised in Table 14. Unfortunately, $(\text{C}_2\text{H}_5)_4\text{N}^+$ ions were found to affect the polymerization of styrene as is evident from curve (b) in Fig.42. Assuming $\tau \propto [(\text{C}_2\text{H}_5)_4\text{N}]^+$ attempts were made to correct the total τ value as shown in Table 14. The plots of $[\overline{\text{AlBN}}]_\tau$ against the concentration of B with constant $[\text{M}]$, $[\text{DMF}]$ and $[\overline{\text{In}}]_0$ (Fig.43) and $\frac{1}{\tau}$ against $[\overline{\text{AlBN}}]$ with $[\text{M}]$, $[\text{DMF}]$ and $[\text{B}]$ constant (Fig.44) gave reasonable straight lines with a mean f value of 0.66.

Table 13

Data used in the calculation of k_8

$$[\text{Styrene}] = 2.49 \text{ mole } \ell^{-1}$$

$$[\text{DMF}] = 8.792 \text{ mole } \ell^{-1}$$

$$[\text{AlBN}]_0 = 7.618 \times 10^{-2} \text{ mole } \ell^{-1}$$

$$[\text{Fe}(\text{DMF})_6](\text{BF}_4)_3 = 7.873 \times 10^{-3} \text{ mole } \ell^{-1}$$

LiCl : Complex = 10:1

Maximum rate = 0.102% min.⁻¹ at 60°C.

Reaction time (t) (sec.)	Reduced rate Rate at t = ϕ_t Max. rate	$k_8[\text{R}\cdot]_s t + A^*$ assuming $k_8[\text{R}\cdot]_s = 3 \times 10^{-3}$ and $A^* = -16.9$	$-\frac{1}{\phi} + \frac{1}{\phi_t}$ $\ln \frac{1+\phi_t}{1-\phi_t}$	$\log(1-F)$	$\log \frac{(1-\phi_t^2)}{\phi_t}$
1200	0.0392	-13.3			
1800	0.0617	-11.5			
2400	0.107	-9.7			
3000	0.147	-7.9			
3600	0.176	-6.1	-5.3262	1.9986	0.819
4200	0.219	-4.3	-4.1208	1.9976	0.6057
4800	0.343	-2.5	-2.2214	1.9965	0.4102
5100	0.392	-1.6	-1.7224	1.9957	0.3342
5400	0.539	-0.7	-0.6499	1.9948	0.1192
5700	0.696	-0.44	0.2819	1.9936	-0.1303
6000	0.762	1.1	0.6899	1.9921	-0.2594
6300	0.880	2.0			
6600		2.9			

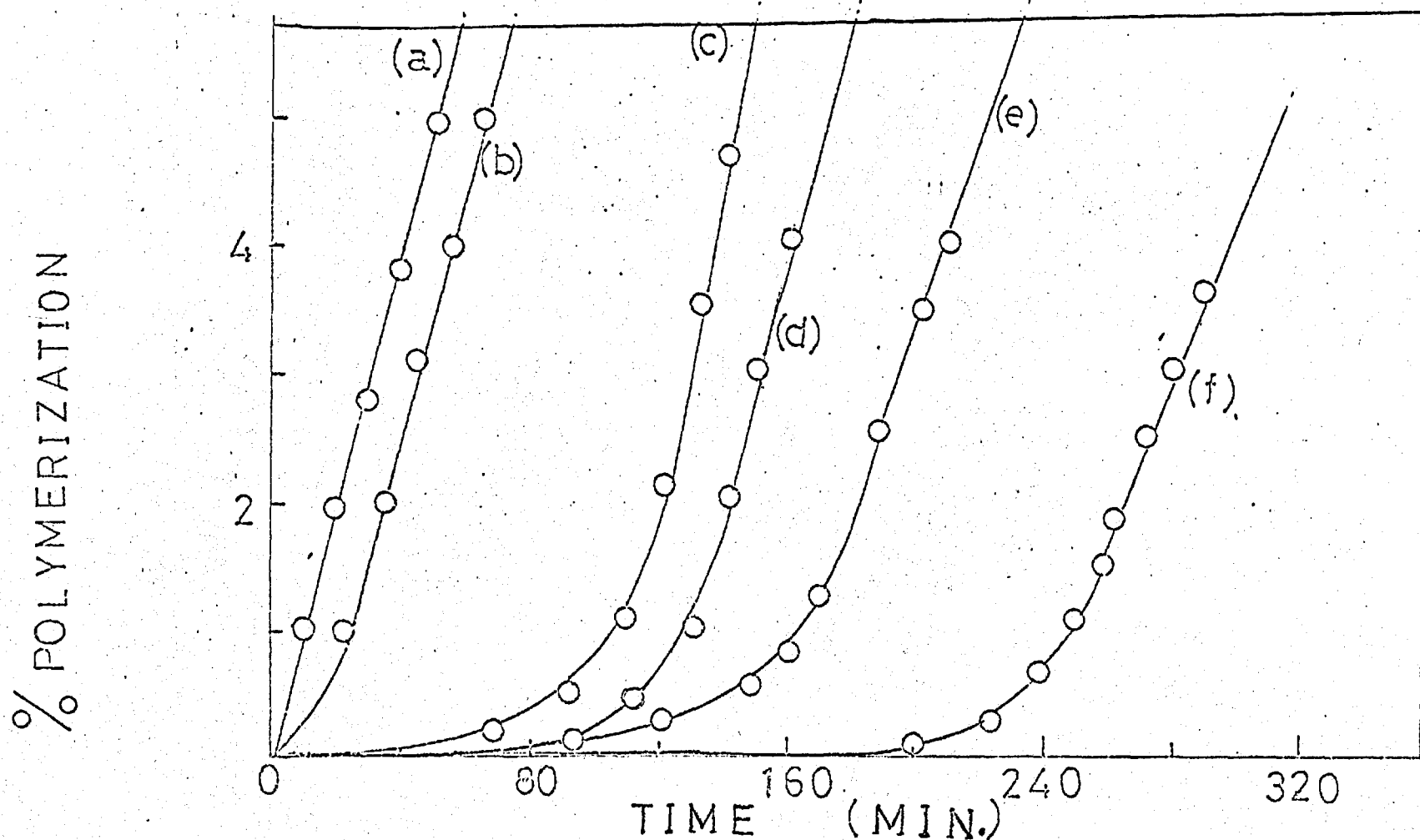


Fig.42. Polymerization of styrene in DMF solution at 60°C., initiated by AIBN in presence of $(C_2H_5)_4N FeCl_4$:
 (a) $[(C_2H_5)_4N FeCl_4] = 0.000$; (b) $[(C_2H_5)_4NCl] = 7.873 \text{ mole } l.^{-1}$; $[(C_2H_5)_4N FeCl_4] = 0.000$;
 $[AIBN] = 7.62 \times 10^{-2} \text{ mole } l.^{-1}$; for curves (c) to (f) $[(C_2H_5)_4NFeCl_4] = 7.873 \times 10^{-3} \text{ mole } l.^{-1}$
 and (AIBN) for (c) $10 \times 10^{-2} \text{ mole } l.^{-1}$; (d) $8 \times 10^{-2} \text{ mole } l.^{-1}$; (e) $6 \times 10^{-2} \text{ mole } l.^{-1}$;
 (f) $4 \times 10^{-2} \text{ mole } l.^{-1}$. At 60°C., $[styrene] = 2.490 \text{ mole } l.^{-1}$, $(DMF) = 8.792 \text{ mole } l.^{-1}$.

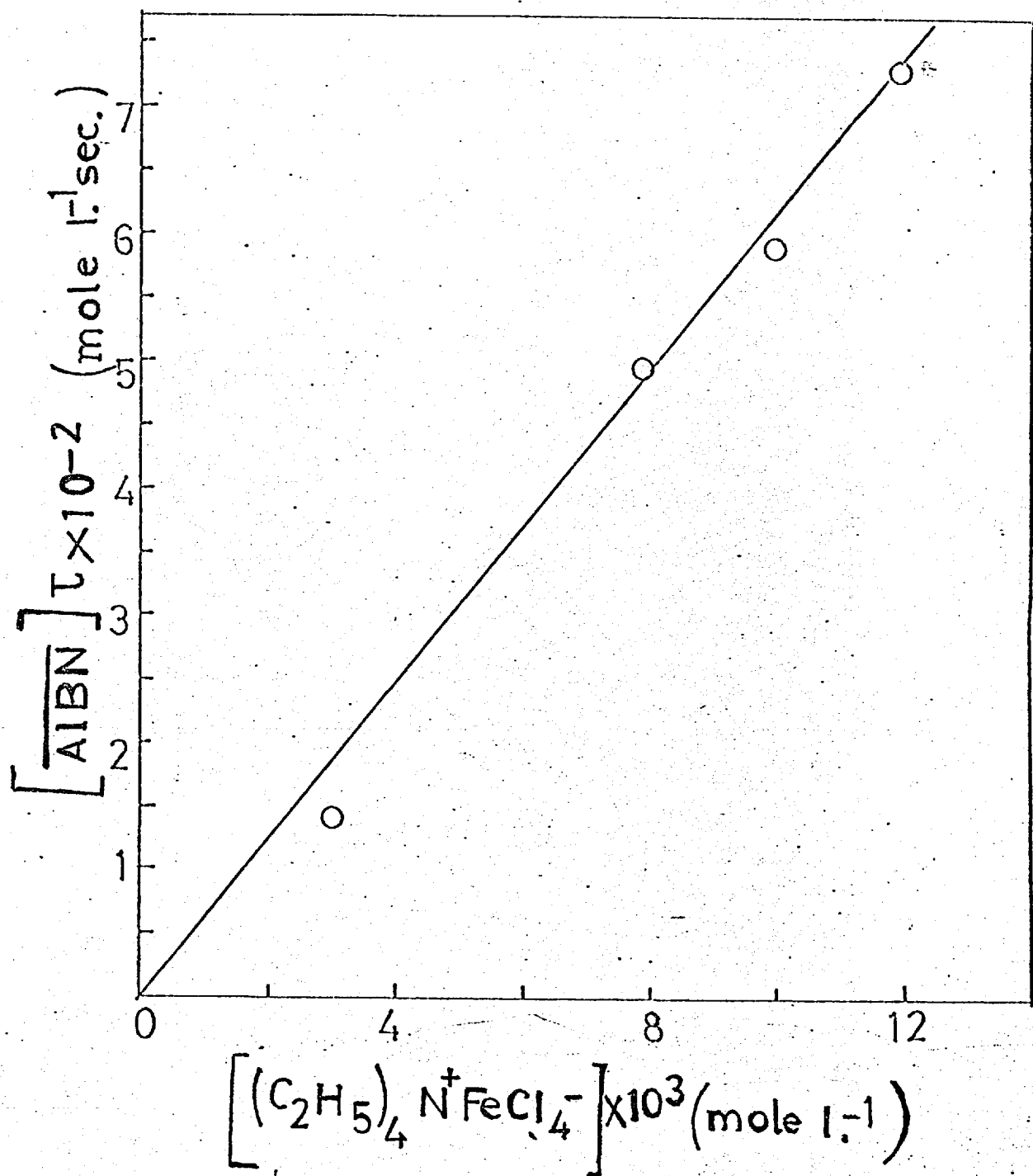


Fig. 43. Dependence of τ on the initial tetra-ethyl ammonium tetrachloroferrate concentration $[(\text{C}_2\text{H}_5)_4\text{N}^+\text{FeCl}_4^-]_0 : [\text{AIBN}]_0 = 7.618 \times 10^{-2}$ mole l.⁻¹; and $[\text{DMF}] = 8.792$ mole l.⁻¹ at 60°C.

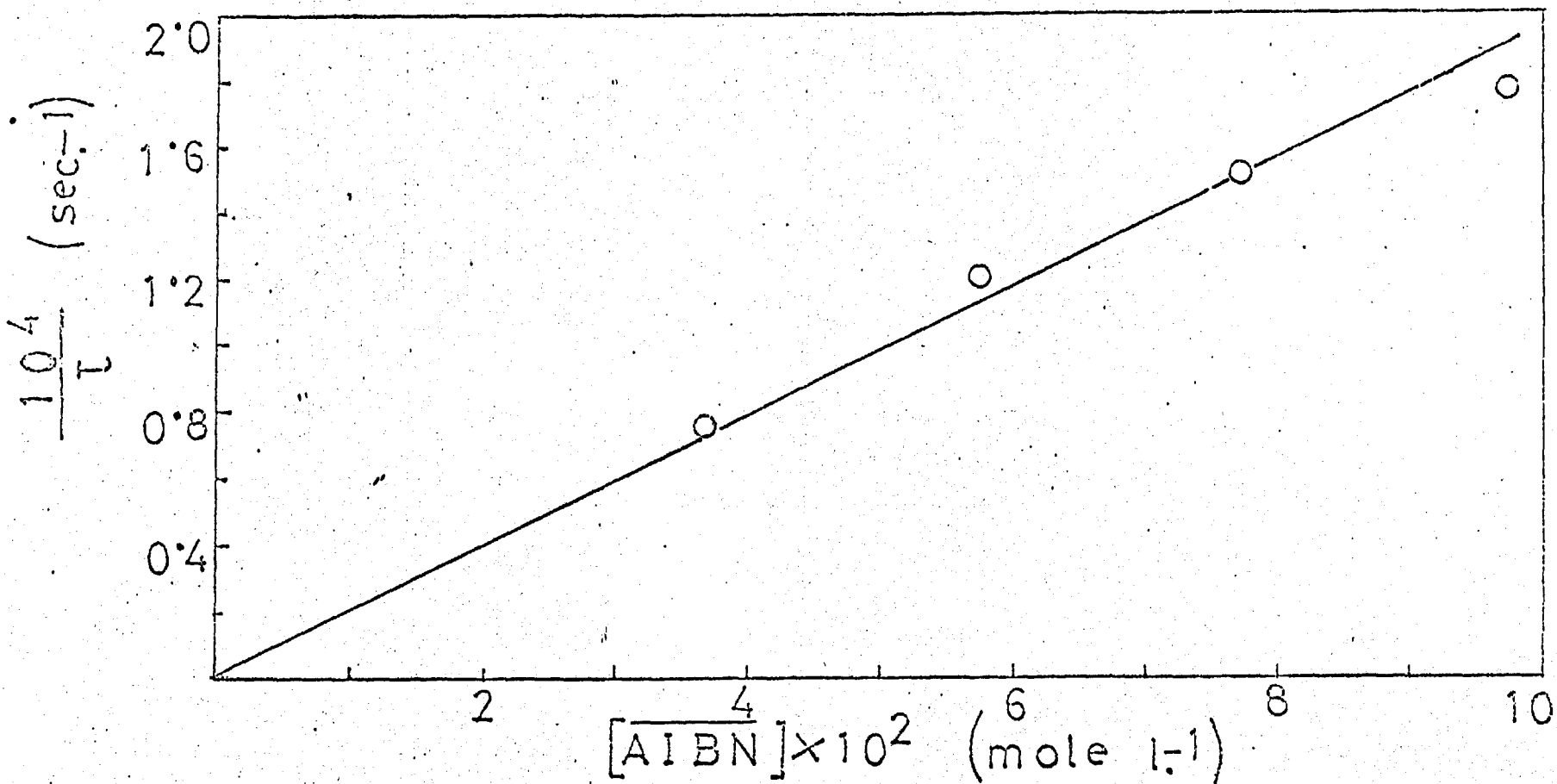


Fig. 44. Dependence of τ on the mean α, α' azobisisobutyronitrile concentration, $[\overline{AIBN}]$.
 $[\text{Styrene}] = 2.490 \text{ mole l}^{-1}$; $[(\text{C}_2\text{H}_5)_4\text{N FeCl}_4]_0 = 7.873 \times 10^{-3} \text{ mole l}^{-1}$;
 $[\text{DMF}] = 8.792 \text{ mole l}^{-1}$, at 60°C .

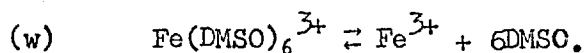
Table 14

Dependence of the Induction Period on mean $[\overline{\text{AlBN}}]$. $[\text{Styrene}] = 2.490 \text{ mole } \ell^{-1};$ $[(\text{C}_2\text{H}_5)_4\text{NFeCl}_4]_0 = 7.873 \times 10^{-3} \text{ mole } \ell^{-1};$ $[\text{DMF}] = 8.792 \text{ mole } \ell^{-1}. \quad \text{Temperature} = 60^\circ\text{C}.$

$[\overline{\text{AlBN}}] \times 10^2$ mole ℓ^{-1}	$\frac{[(\text{C}_2\text{H}_5)_4\text{N}^+]}{[\overline{\text{AlBN}}]}$ $\times 10^2$	$\tau_{\text{correction}}$ (sec.)	$\tau_{\text{expt.}}$ (sec.)	τ_{true} (sec.)	$\frac{10^4}{\tau_{\text{true}}}$ (sec.^{-1})
9.736	8.086	608.8	6330	5,772	1.7476
7.713	10.207	768.5	7440	6,671	1.4991
5.731	13.738	1,034.4	9420	8,386	1.1924
3.720	21.164	1,593.5	14820	13,226	0.7576

5.11. Rate Measurements using the Complex, $[\text{Fe}(\text{DMSO})_6]^{3+}(\text{BF}_4^-)_3$, D.5.11.1. Evaluation of k'_x

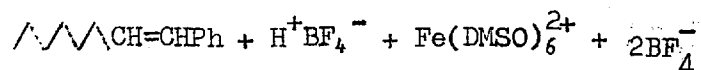
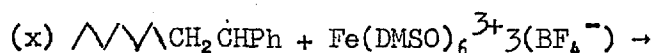
On polymerizing styrene at 60°C , in the presence of AlBN, DMSO and complex, D, retarded rates of polymerization were recorded dilatometrically (Fig.45). The rate results were analysed by the method of Kice,^{70,71} assuming that the equilibrium (w) was well over to the left hand side and the precipitated polystyrene had little effect on the reaction rate during the initial stages of the reaction.



According to the Kice equation, which is fully discussed in Section 2.12.2,

$$R_p \sqrt{1 + \frac{c(1-\phi^2)}{\phi^2}} = \frac{k_p k'_x}{2k_t} \frac{\phi^2 (D)}{(1-\phi^2)} \left\{ 1 + \sqrt{\frac{1 + c(1-\phi^2)}{\phi^2}} \right\} - \frac{k_o k_p}{k_c} (M) \quad (12)$$

A value of c equal to 1×10^{-6} gave the least deviation of the experimental points from a straight line and the results are collected in Table 15 and plotted in Fig. 46. The slope of the line is $0.5609 \times 10^{-3} \text{ l.mole}^{-1} \text{ sec}^{-1}$, and using values of k_p and $2k_t$ equal to $176 \text{ l.mole}^{-1} \text{ sec}^{-1}$, and $7.2 \times 10^7 \text{ l.mole}^{-1} \text{ sec}^{-1}$, k'_x was $229 \text{ l.mole}^{-1} \text{ sec}^{-1}$. From the intercept $\frac{k_o}{k_c}$ was 7.42×10^{-10} at 60°C . The low value of k_o/k_c indicated a low tendency of $Z\cdot$ species to attack monomer. The transfer constant is only 2.42×10^{-5} at 60°C , and probably involves a hydrogen atom abstraction from a CH_3 -group. Therefore, another type of radical-D reaction must occur to explain the relatively high value of k'_x . This equation might be:



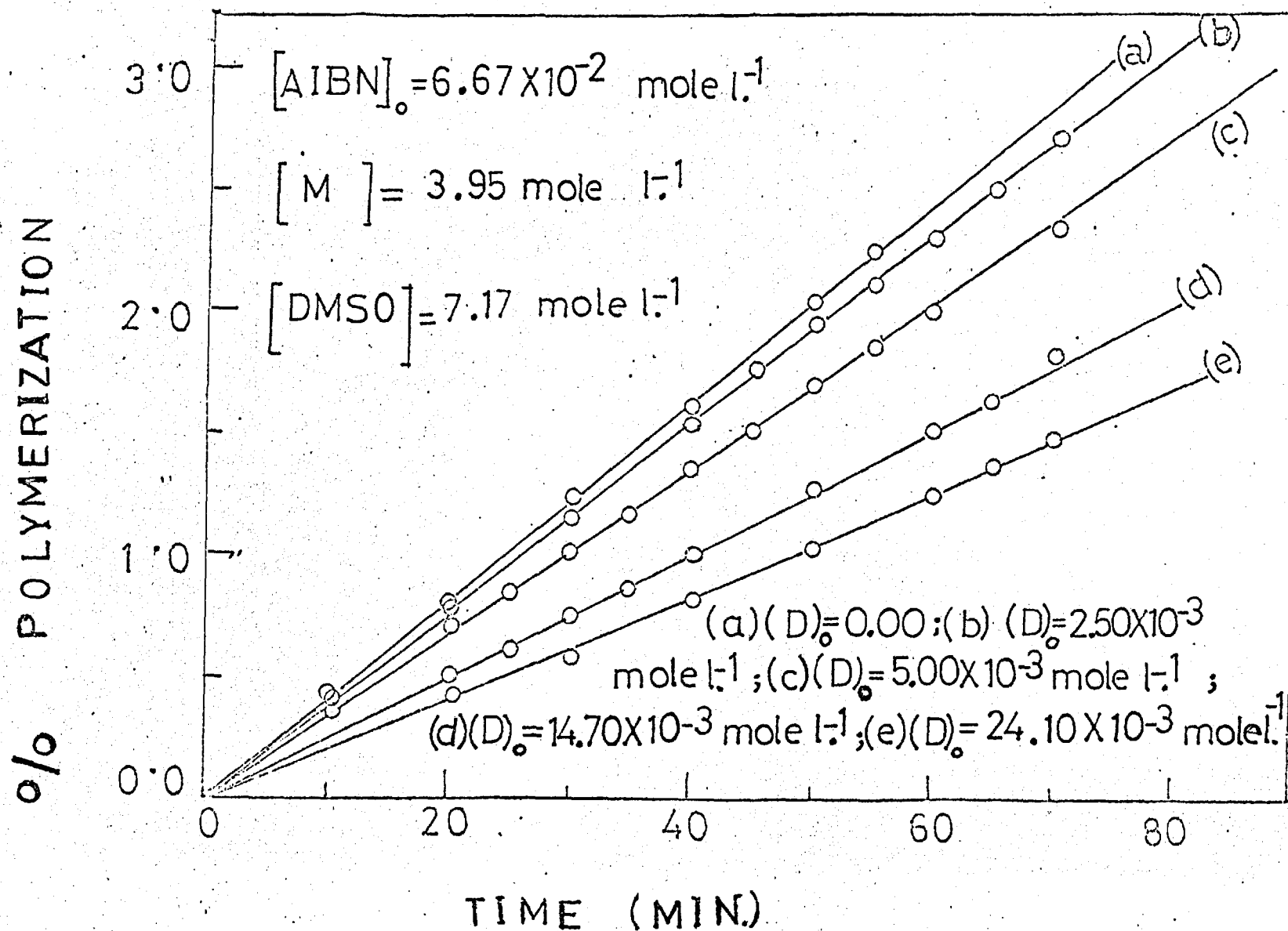


Fig.45. Effect of the complex, D, $[Fe(DMSO)_6](BF_4)_3$, on the polymerization of styrene initiated by AIBN in DMSO solution at $60^\circ C$.

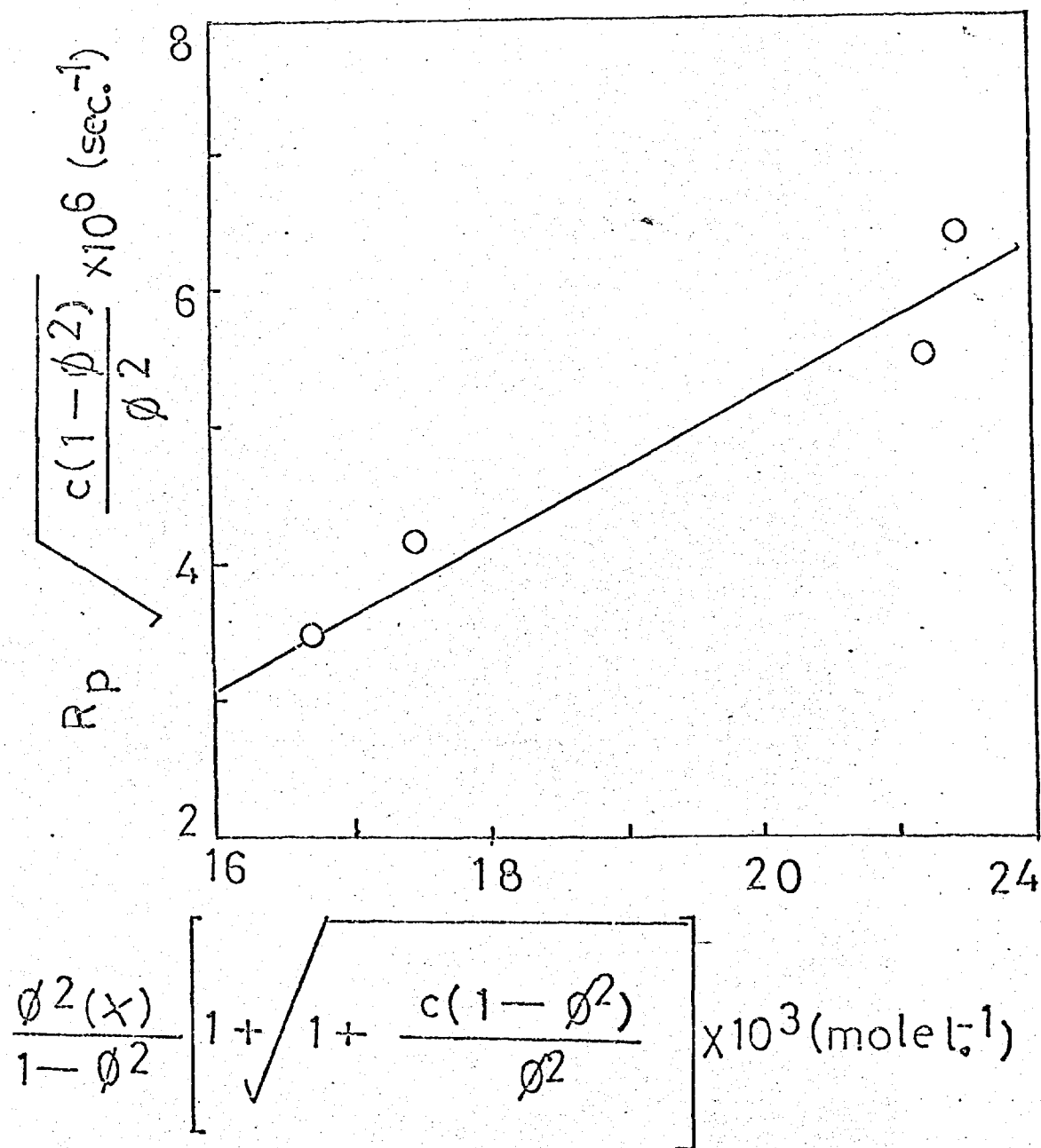


Fig. 46. Kice plot of retardation results with complex, D, alone.

At 60°C., $[AIBN]_0 = 6.67 \times 10^{-2} \text{ mole l.}^{-1}$; $[\text{styrene}] = 3.95 \text{ mole l.}^{-1}$; $[\text{DMSO}] = 7.17 \text{ mole l.}^{-1}$; value of c chosen = 1.0×10^{-6} .

Table 15

Effect of complex, D, on the polymerization of styrene initiated by AIBN in DMSO solution at 60°C.

$[M] = 3.95 \text{ mole } \ell.^{-1}$; $[DMSO] = 7.17 \text{ mole } \ell.^{-1}$.

Value of c chosen for best fit of experimental data to the theoretical line $= 1.0 \times 10^{-6}$

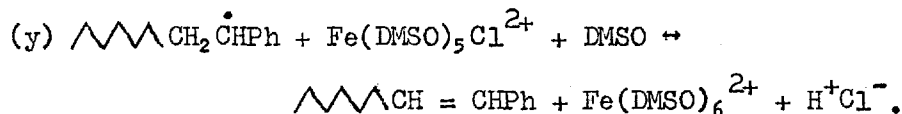
AIBN $\times 10^2$ (mole $\ell.^{-1}$)	Rate of polymerization $\times 10^5$ (mole $\ell.^{-1} \text{ sec.}^{-1}$)	Retarder concentration $[D] \times 10^3$ (mole $\ell.^{-1}$)	$\frac{\phi^2(D)}{(1-\phi^2)} \frac{1 + \frac{c(1-\phi^2)}{\phi^2}}{\times 10^3}$ (mole $\ell.^{-1}$)	$R_p \sqrt{\frac{1+c(1-\phi^2)}{\phi^2}}$ $\times 10^6$ (sec. $^{-1}$)
6.67	2.697	0.00	-	-
6.67	2.526	2.50	21.4300	6.390
6.67	2.223	5.00	21.1876	5.630
6.67	1.644	14.70	17.3842	4.163
6.67	1.368	24.10	16.6964	3.464

5.11.2. Effect of Adding LiCl to the Complex, $\text{Fe}(\text{DMSO})_6^{3+}(\text{BF}_4^-)_3$, D
on the Rates of Polymerization

Evaluation of k_p

On progressively adding LiCl to mixtures of constant composition containing styrene, DMSO and complex, D, and measuring rates at 60°C., definite induction periods were observed as indicated in Fig. 47. A plot of T evaluated from the individual rate curves against the concentration of lithium chloride added is shown in Fig. 48. It was

found that LiCl alone did not affect the reaction rate of the above system in the absence of complex, D. All these results confirmed the spectroscopic conclusion that all iron(III) species from complex, D, with a molar ratio of LiCl/D in excess of 6:1 existed as $\text{Fe}(\text{DMSO})_5\text{Cl}^{2+}$ in the polymerizing system at 60°C , and $\text{Fe}(\text{DMSO})_5\text{Cl}^{2+}$ ions are much more reactive towards polystyryl radicals than $\text{Fe}(\text{DMSO})_6^{3+}$ ions. The induction periods were possibly due to mechanism (y):



By analogy with eqn (27), we can write,

$$\tau = \frac{[\text{Fe}(\text{DMSO})_5\text{Cl}^{2+}]_0}{I} \quad (67)$$

assuming that only the monochloro species was present for a molar ratio of LiCl:D of 10:1. The assumption is quite reasonable as the equilibrium constant for the reaction (4) was estimated to be about 10^3 from the spectroscopic results.

Further experiments with constant $[\text{M}]$, $[\text{DMSO}]$ and $[\text{D}]$ and with a molar ratio of LiCl/D equal to 10:1, indicated that there was a linear relationship between τ^{-1} and $[\text{AlBN}]$ (Fig.49, Table 16) as expected from equation (67). Again, for a series of experiments in which $[\text{AlBN}]_0$ was maintained constant, but $[\text{Fe}(\text{DMSO})_5\text{Cl}^{2+}]$ prepared in situ was varied, there was a linear relationship between τ $[\text{AlBN}]$ and $[\text{Fe}(\text{DMSO})_5\text{Cl}^{2+}]$, Fig.50, Table 17, as expected from eqn (67). The f values obtained from these plots agreed reasonably well and the mean value was 0.61.

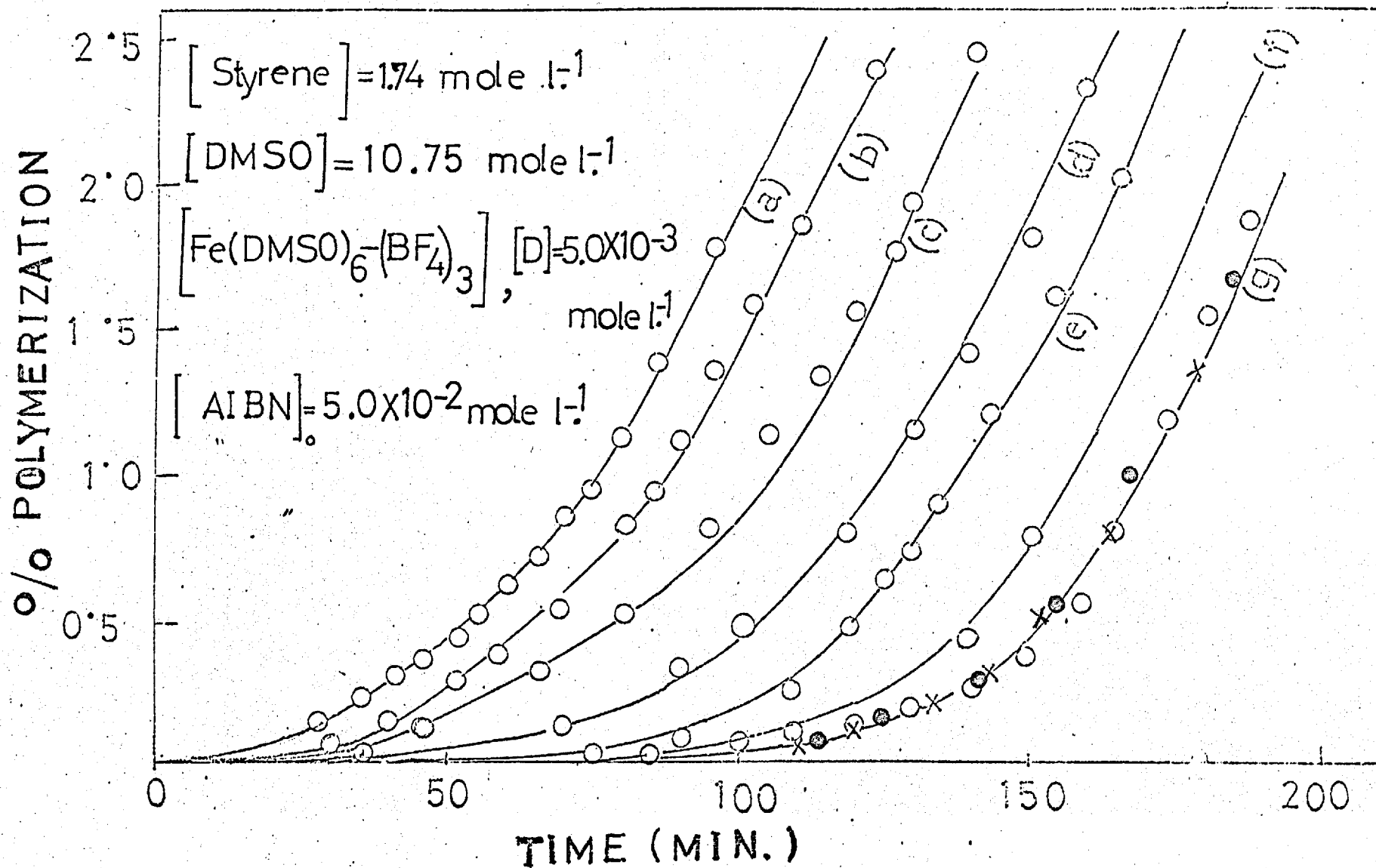


Fig.47. Polymerization of styrene in DMSO at 60°C., initiated by AIBN in presence of various iron(III) species: Molar ratio LiCl:D, (a) 1:1; (b) 1.5:1; (c) 2:1; (d) 2.6:1; (e) 3:1; (f) 4:1 and (g) 6:1 (X), 8:1 (●), 9.3:1 (○).

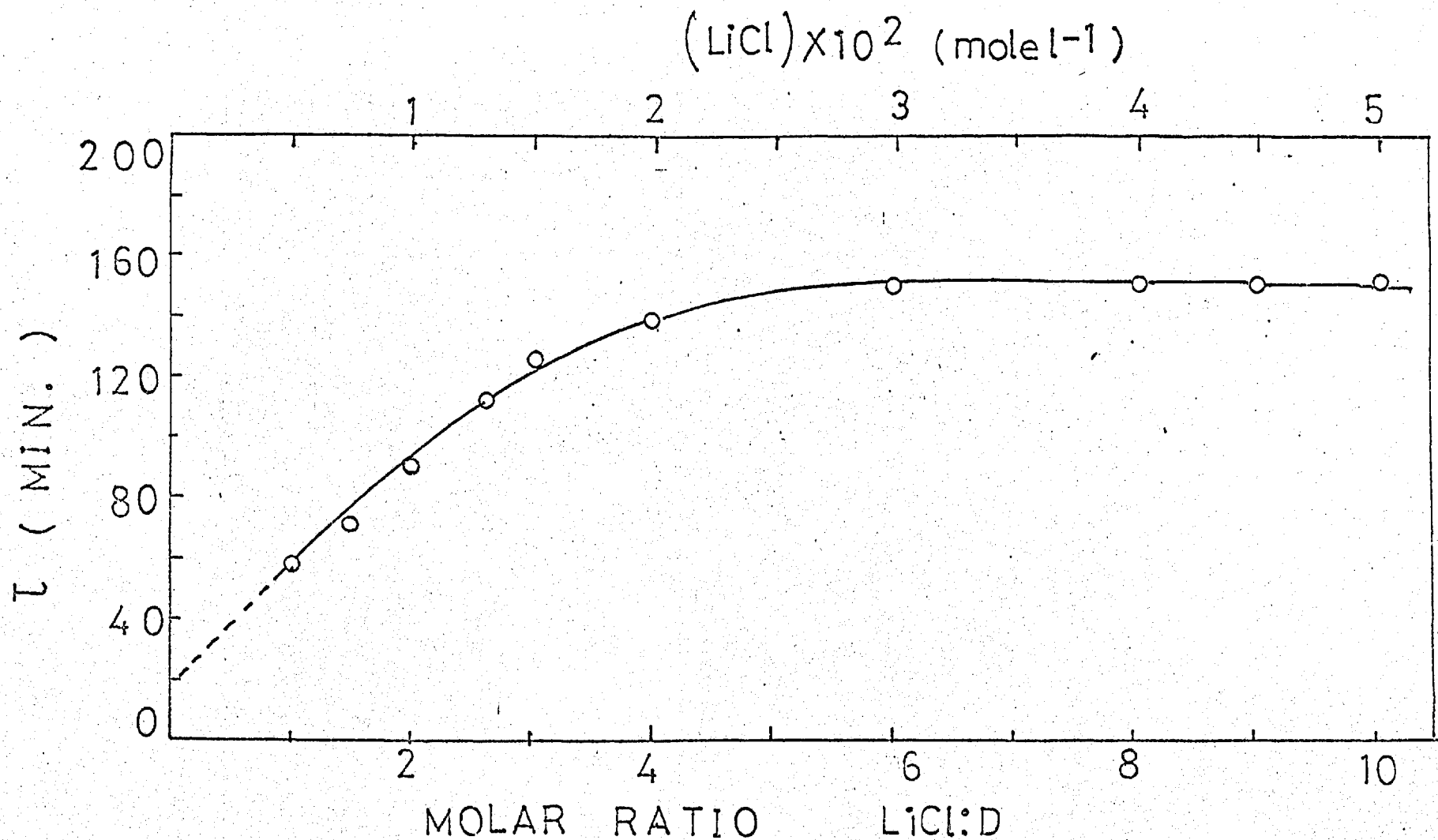


Fig.48. Value of τ as a function of added lithium chloride concentration. At 60°C , $[\text{styrene}] = 1.74 \text{ mole l.}^{-1}$; $[\text{DMSO}] = 10.75 \text{ mole l.}^{-1}$; $[\text{AIBN}]_0 = 5.0 \times 10^{-2} \text{ mole l.}^{-1}$; $[\text{Fe}(\text{DMSO})_6-(\text{BF}_4)_3], [\text{D}] = 5.0 \times 10^{-3} \text{ mole l.}^{-1}$.

Table 16

Dependence of the induction period, τ , on the mean azo-bis-isobutyronitrile concentration, $[\overline{\text{AIBN}}]$. $[\text{Styrene}] = 1.74 \text{ mole } \ell.^{-1}$;
 $[\text{DMSO}] = 10.75 \text{ mole } \ell.^{-1}$; $[\text{Fe}(\text{DMF})_6](\text{BF}_4)_3 = 5.0 \times 10^{-3} \text{ mole } \ell.^{-1}$;
 $\text{LiCl:A} = 10:1$. Temperature = 60.0°C .

$[\text{AIBN}] \times 10^2$ (mole $\ell.^{-1}$)	$[\overline{\text{AIBN}}] \times 10^2$ (mole $\ell.^{-1}$)	τ (secs)	$\frac{1}{\tau} \times 10^4(\text{sec}^{-1})$
5.00	4.5840	9120	1.096
6.25	6.0315	7260	1.377
7.50	7.0440	6480	1.543
10.00	9.5420	4800	2.083

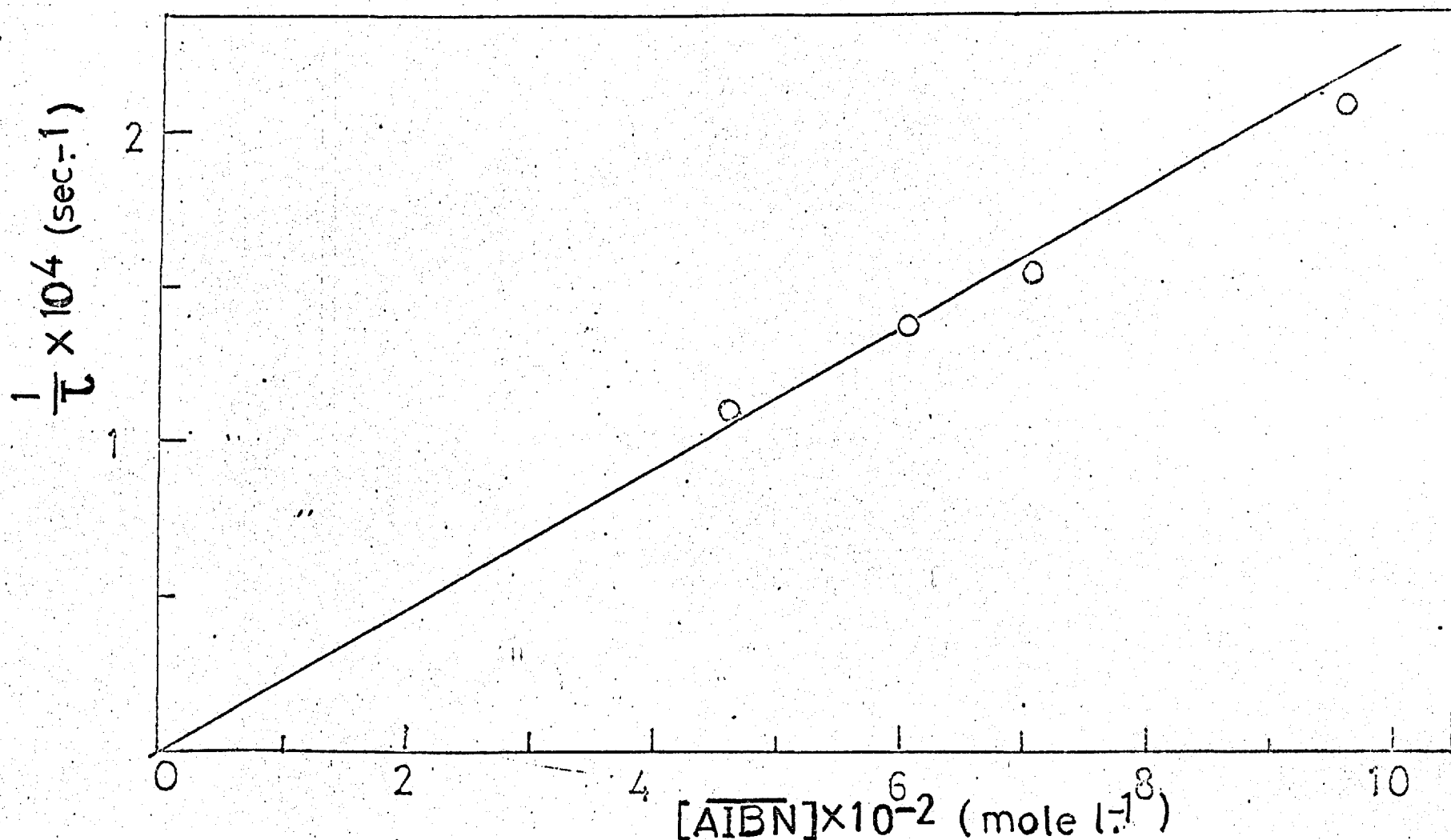


Fig.49. Dependence of τ on the mean initiator concentration, $[\text{AIBN}]$. $[\text{Styrene}] = 1.74 \text{ mole l.}^{-1}$; $[\text{DMSO}] = 10.75 \text{ mole l.}^{-1}$; $[\text{Fe}(\text{DMF})_6-(\text{BF}_4)_3]$, $[\text{A}] = 5.0 \times 10^{-3} \text{ mole l.}^{-1}$ $\text{LiCl} : \text{A} = 10:1$.

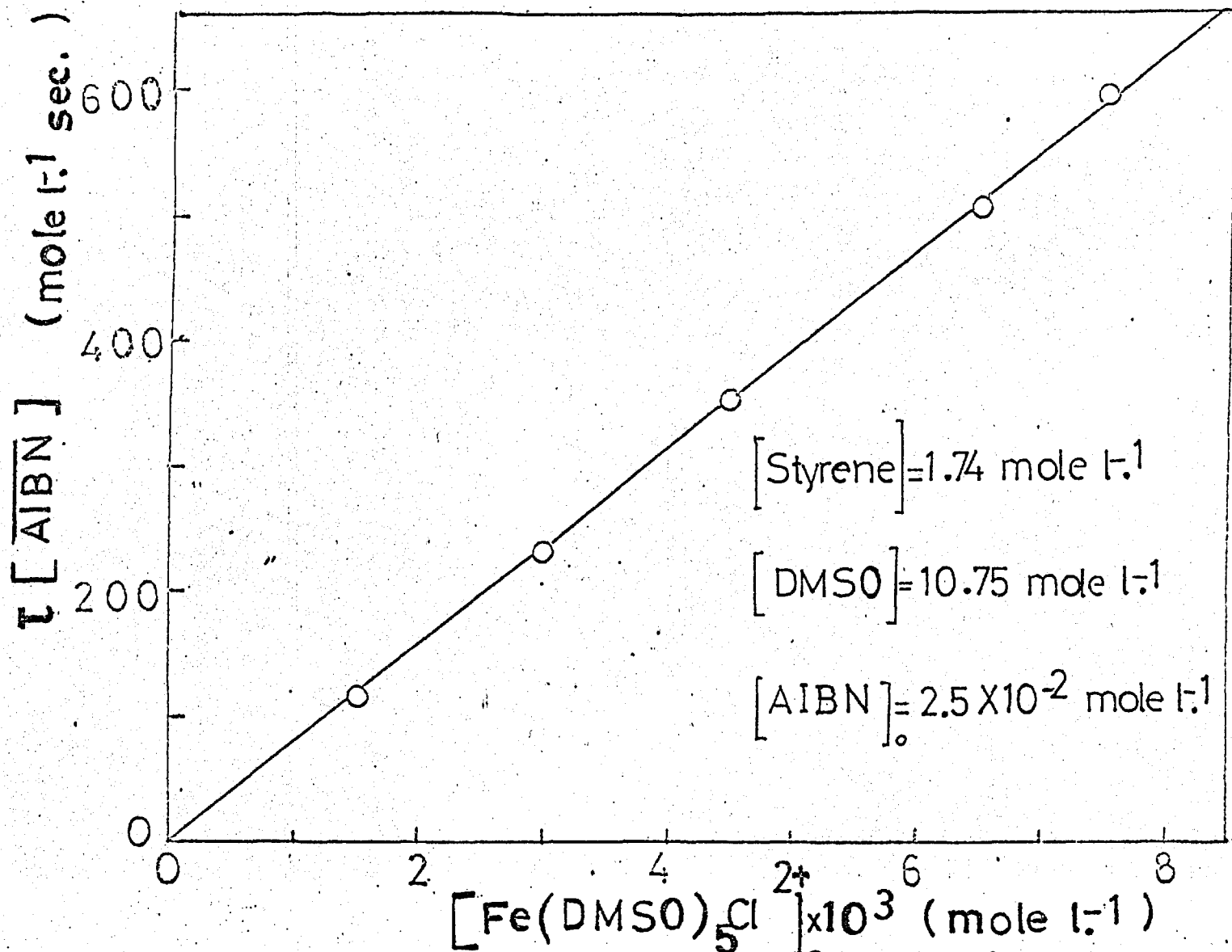


Fig.50. Dependence of τ on the initial concentration of $\text{Fe}(\text{DMSO})_5\text{Cl}^{2+}$ prepared in situ using a molar ratio of $\text{LiCl} : \text{D} = 10:1$.

Table 17

Dependence of induction period, τ , on initial $\text{Fe}(\text{DMSO})_5\text{Cl}^{2+}$ concentration. $[\text{Styrene}] = 1.74 \text{ mole l.}^{-1}$; $[\text{DMSO}] = 10.75 \text{ mole l.}^{-1}$; $[\text{AlBN}]_0 = 2.5 \times 10^{-2} \text{ mole l.}^{-1}$. $[\text{Fe}(\text{DMSO})_5\text{Cl}^{2+}]$ was prepared in situ using molar ratio $\text{LiCl:A} = 10:1$. A represents the complex $\text{Fe}(\text{DMF})_6^{3+} - (\text{BF}_4)_3$.

$[\text{AlBN}] \times 10^2$ (mole l.^{-1})	τ (sec.)	$\tau [\text{AlBN}]$ (sec. mole l.^{-1})	$[\text{Fe}(\text{DMSO})_5\text{Cl}^{2+}] \times 10^3$ (mole l.^{-1})
2.44	4824	117.7	1.500
2.39	9642	230.4	3.000
2.33	15,120	352.3	4.500
2.25	22,440	504.9	6.500
2.21	26,310	581.5	7.500

A detailed analysis of the rate curve (Table 18) measured with a 10:1 molar ratio of LiCl/D was then made and a plot of ϕ_t vs $k_g[\text{R}\cdot]_s t + A^*$ is shown in Fig. 51; (Table 18) it was assumed that only $[\text{Fe}(\text{DMSO})_5\text{Cl}^{2+}]$ were present and k_g referred to reaction (y). Reasonable agreement was found between the experimental and theoretical plots when $k_g(\text{R}\cdot)_s = 2.9 \times 10^{-3} \text{ sec.}^{-1}$, and $A^* = -27.2$. k_g was also calculated by Bengough's methods (Fig. 52 and 53 and Table 18) with ϕ_t values lying between 0.15 and 0.8. The values of k_g ,

obtained by these three different methods agreed reasonably well (Table 19) and the mean value of k_p was $7.18 \times 10^4 \text{ l.mole}^{-1} \text{ sec.}^{-1}$ at 60°C .

Table 18

Data used in the calculation of k_p at 60°C .

[Styrene] = $1.74 \text{ mole l.}^{-1}$ [DMSO] = $10.75 \text{ mole l.}^{-1}$

[AlBN] = $5 \times 10^{-2} \text{ mole l.}^{-1}$ $[\text{Fe}(\text{DMSO})_6](\text{BF}_4)_3 = 5 \times 10^{-3} \text{ mole l.}^{-1}$

LiCl : Complex = 9.3 : 1 Maximum rate = $0.0418\% \text{ min.}^{-1}$

Reaction time ($\bar{t}$) (sec.)	Reduced rate $\frac{\text{Rate at } t}{\text{Max. rate}} = \phi_t$	$k_p [\text{R}\cdot]_s t + A^*$ assuming $k_p [\text{R}\cdot]_s = 2.9 \times 10^{-3}$ $A^* = -27.2$	$-\frac{1}{\phi_t} + \ln \frac{(1+\phi_t)}{(1-\phi_t)}$	$\log (1-F)$	$\log \frac{(1-\phi_t)^2}{\phi_t}$
4800	0.0478	- 13.28			
5400	0.0598	- 11.54			
6000	0.0765	- 9.8			
6600	0.0909	- 8.06			
7200	0.1220	- 6.32			
7800	0.2129	- 4.58	- 4.2645	$\bar{1}.99905$	0.65167
8100	0.2560	- 3.71	- 3.3826	$\bar{1}.99896$	0.56229
8400	0.2895	- 2.84	- 2.8580	$\bar{1}.99874$	0.50038
8700	0.3469	- 1.97	- 2.1589	$\bar{1}.99848$	0.40397
9000	0.5622	- 1.1	- 0.5066	$\bar{1}.99804$	-0.08517
9300	0.6220	- 0.23	- 0.1496	$\bar{1}.99761$	-0.00612
9600	0.6938	+ 0.64	+ 0.2696	$\bar{1}.99695$	-0.12633
9900	0.8851	+ 1.51			
10200	1	+ 2.38			

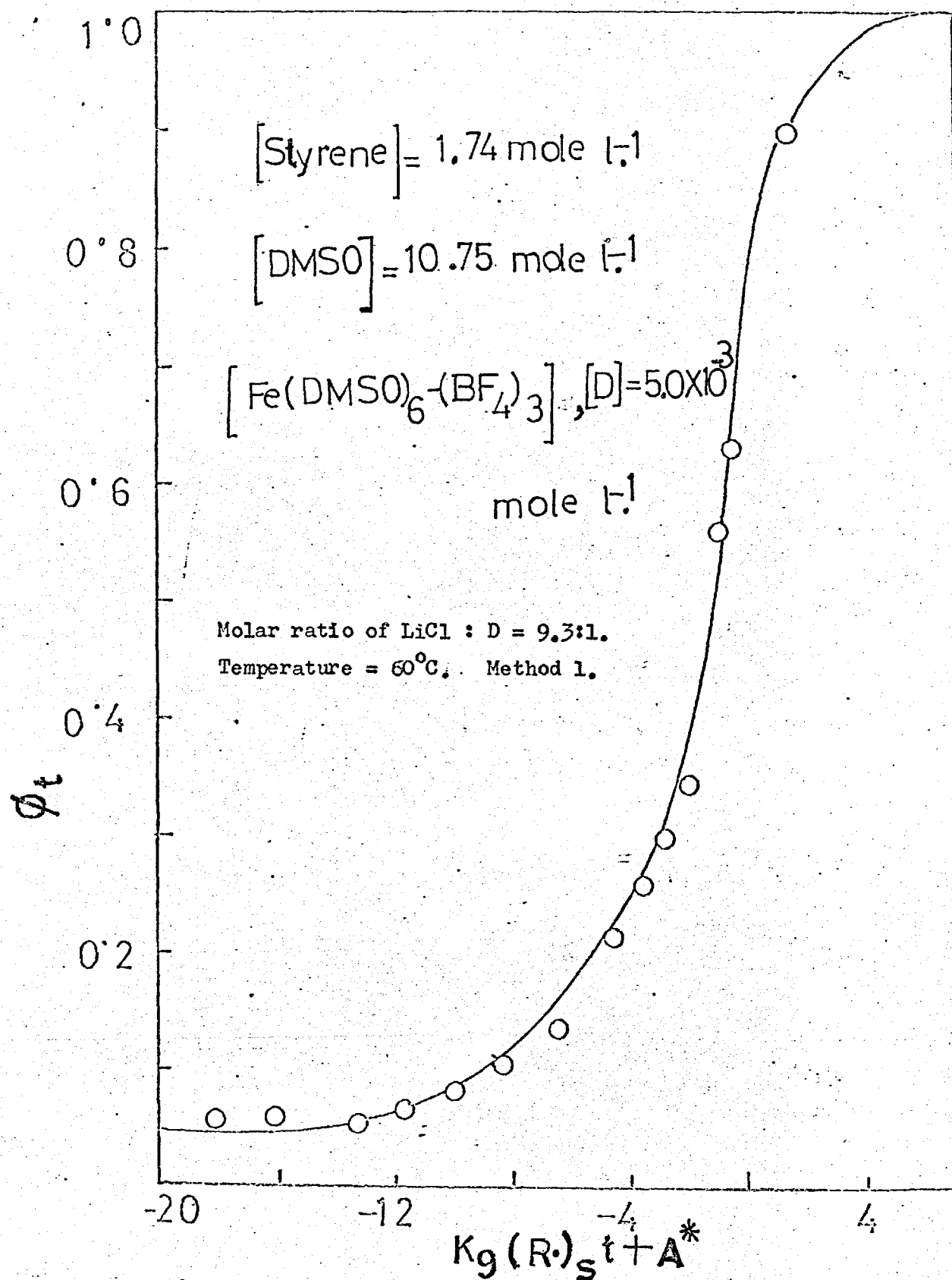


Fig.51. Reduced rate ϕ_t as a function of reaction time t :

(O) experimental points; (—) calculated curve.

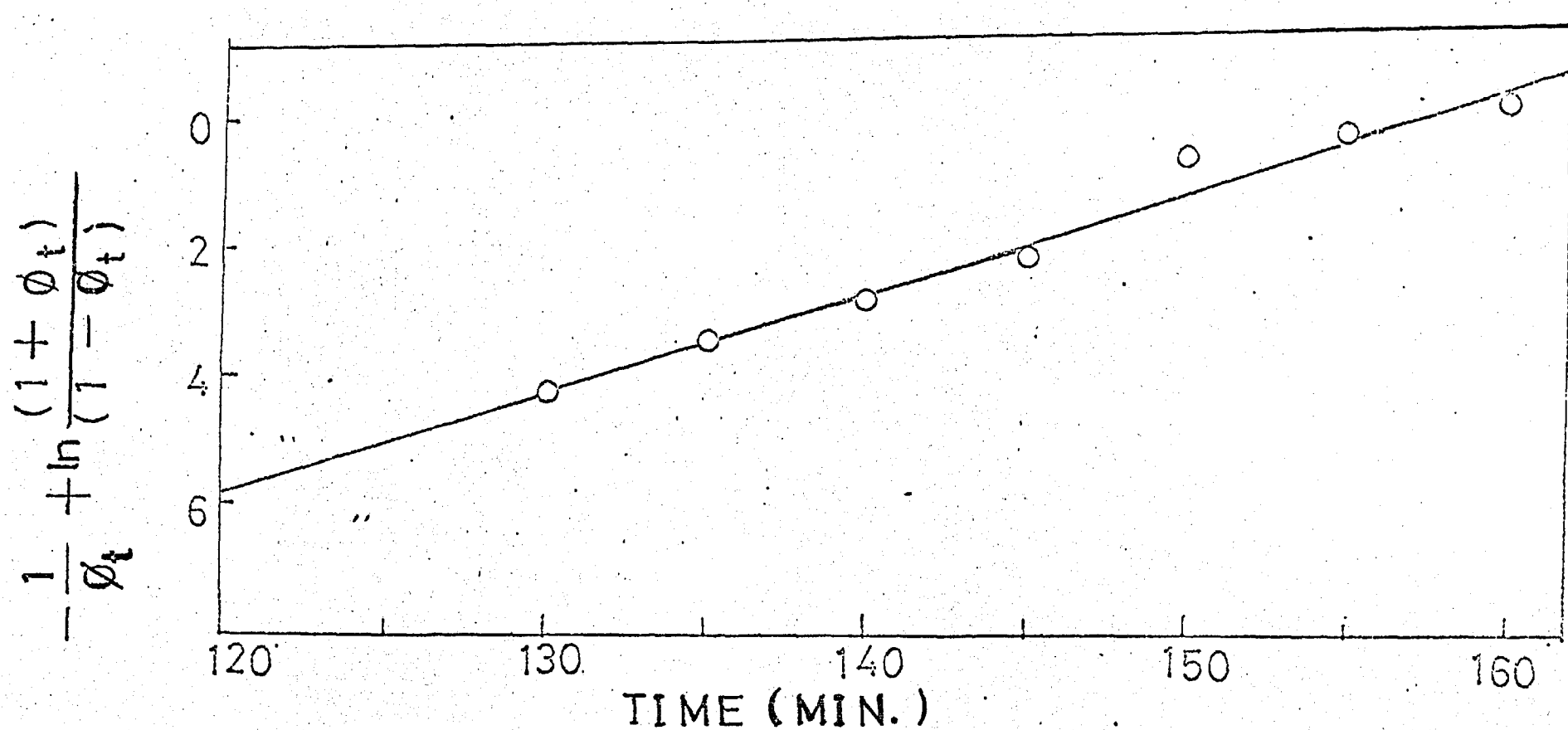


Fig.52. Analysis of the results for the polymerization of styrene initiated by AIBN at 60°C., and inhibited by $\text{Fe}(\text{DMSO})_5\text{Cl}^{2+}$ prepared in situ. Molar ratio of $\text{LiCl} : \text{D} = 9.3:1$; $[\text{Styrene}] = 1.74 \text{ mole l.}^{-1}$; $[\text{DMSO}] = 10.75 \text{ mole l.}^{-1}$; $[\text{D}] = 5.0 \times 10^{-3} \text{ mole l.}^{-1}$. Method 2.

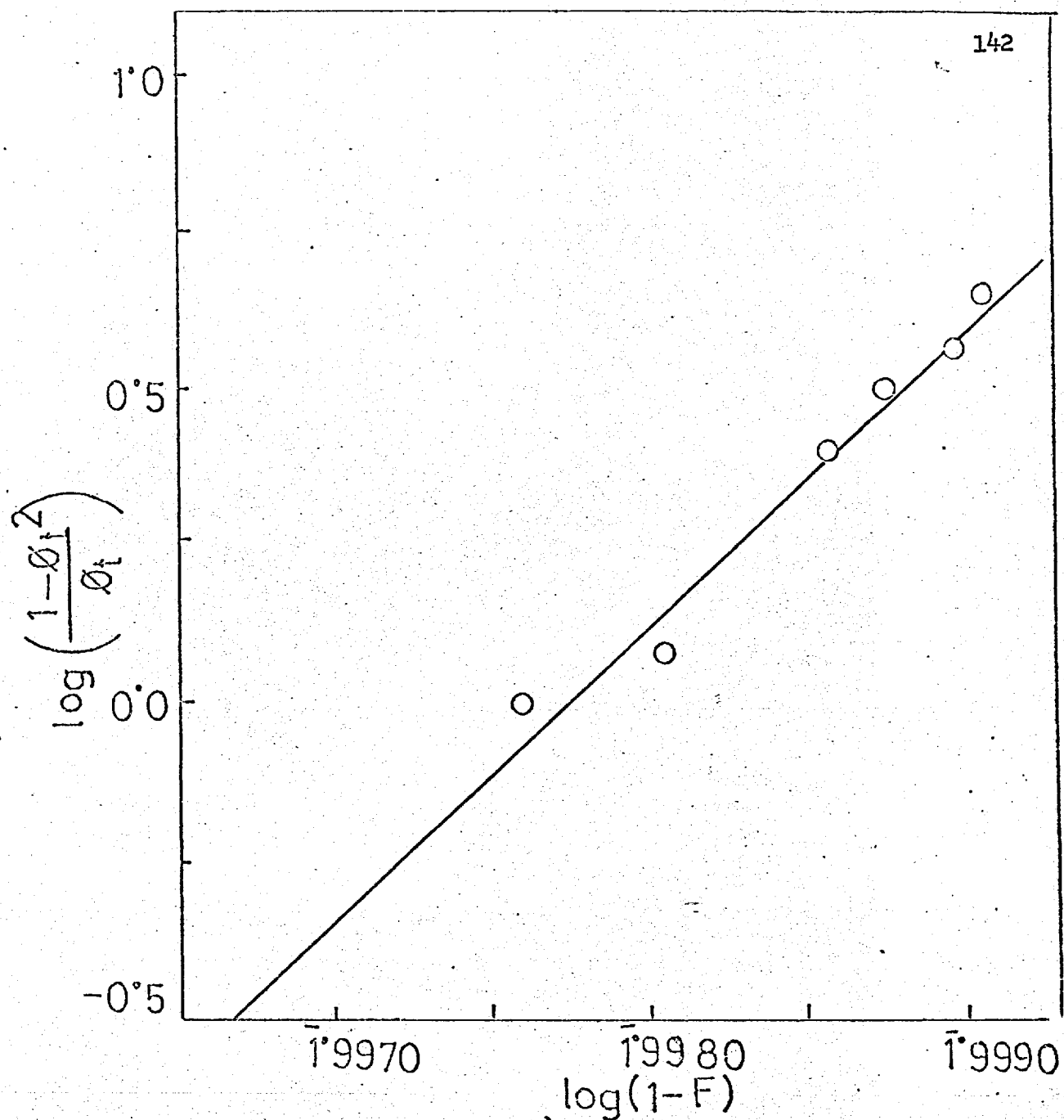


Fig.53. Analysis of the results for the polymerization of styrene initiated by AIBN at 60°C., and inhibited by $\text{Fe}(\text{DMSO})_5\text{Cl}^{2+}$ prepared in situ. Molar ratio of $\text{LiCl} : \text{D} = 9.3:1$.
 $[\text{Styrene}] = 1.74 \text{ mole l.}^{-1}$; $[\text{DMSO}] = 10.75 \text{ mole l.}^{-1}$;
 $[\text{D}] = 5.0 \times 10^{-3} \text{ mole l.}^{-1}$. Method 3.

Table 19

A comparison of the specific reaction rate constants of different chlorinated species of Fe(III) with polystyryl radicals, evaluated by three different methods.

Temperature = 60°C.

Fe(III) species	Symbol for specific reaction rate constant	Value of k, (l. mole ⁻¹ sec. ⁻¹ at 60°C			
		evaluated by ϕ_t vs. $k(R^\bullet)_s t + A^*$ plot	evaluated by ϕ_t vs. $-\frac{1}{\phi_t} + \ln \frac{\phi_t(1+\phi_t)}{(1-\phi_t)}$ plot	evaluated by $\log \frac{(1-\phi_t^2)}{\phi_t}$ vs. $\log(1-F)$ plot	Mean specific reaction rate constant
Fe(DMF) ₅ Cl ²⁺	k ₆	4.15x10 ⁴	4.79x10 ⁴	4.65 x 10 ⁴	4.53x10 ⁴
Fe(DMF) ₄ Cl ₂ ⁺	k ₇	6.55x10 ⁴	6.25x10 ⁴	6.39 x 10 ⁴	6.40x10 ⁴
FeCl ₄ ⁻	k ₈	3.14x10 ⁴	2.84x10 ⁴	2.90 x 10 ⁴	2.96x10 ⁴
Fe(DMSO) ₅ Cl ²⁺	k ₉	7.33x10 ⁴	6.74x10 ⁴	7.47 x 10 ⁴	7.18x10 ⁴

5.12. Effect of Adding Fluoride, Bromide and Sulphate Ions to the Complex, [Fe(DMF)₆]³⁺ (BF₄⁻)₃, A, on Rates of Polymerization of Styrene

The equilibrium constants for the formation of different fluoro-complexes from Fe³⁺ in aqueous solution⁹¹ are very high. So attempts were made to prepare these complexes in situ in DMF/styrene from [Fe(DMF)₆]³⁺(BF₄⁻)₃. Unfortunately, LiF, NaF and NH₄F were not

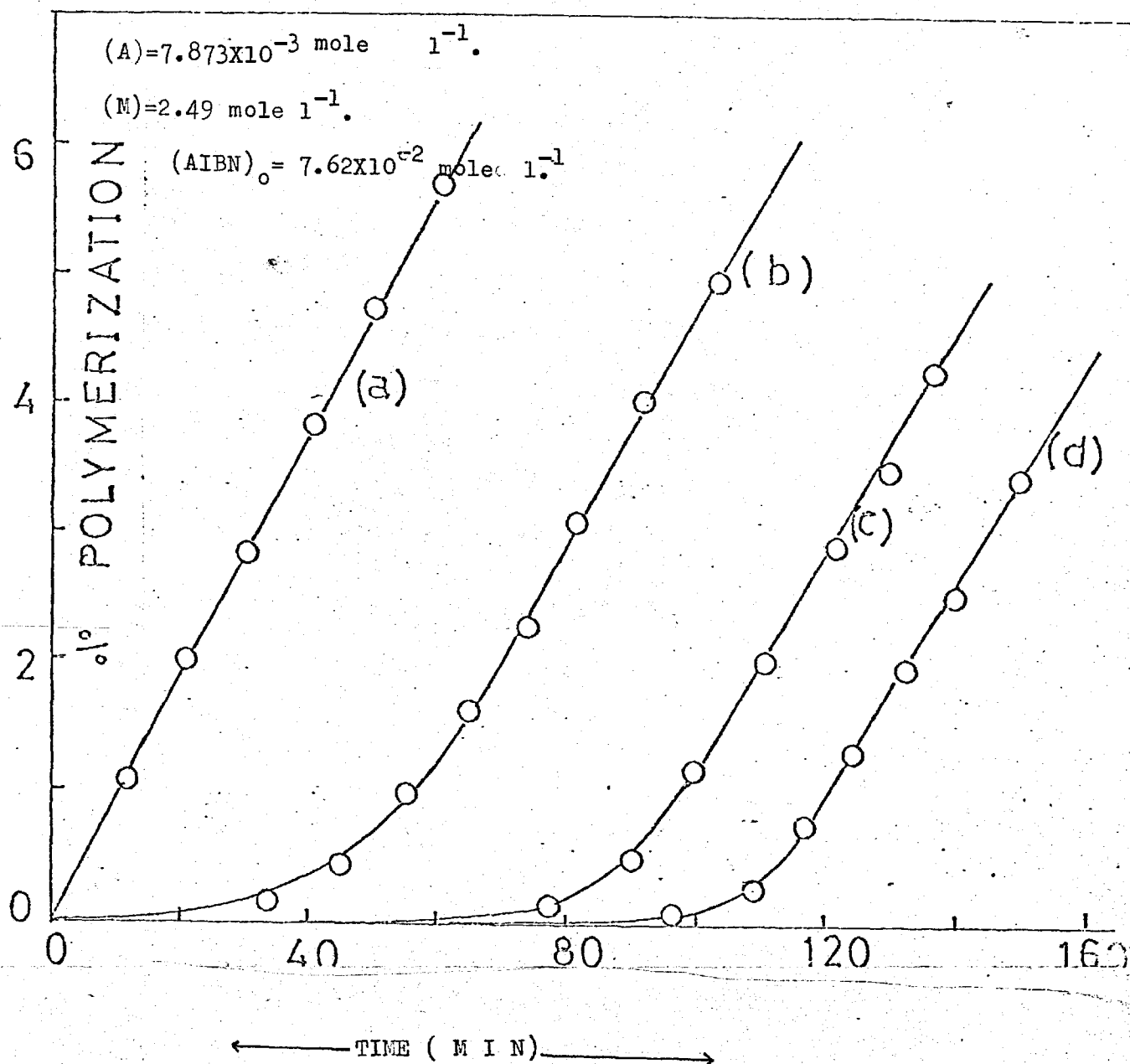
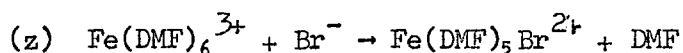


Fig. 54. Polymerization of styrene in DMF at 60°C .
 initiated by AIBN in the presence of various Fe(III)
 species: (a) no added iron compounds. From (b) to
 (d); Complex, $(A) = 7.873 \times 10^{-3} \text{ mole l}^{-1}$; ;
 (b) $(\text{LiBr}) : (A) = 0.25 : 1$ (c) $(\text{LiBr}) : (A) = 0.5 : 1$
 (d) $(\text{LiBr}) : (A) = 1 : 1$.

sufficiently soluble in DMF for fluoro-complexes to be detected.

The effect of lithium bromide, LiBr, was found promising. Some preliminary experiments done with lithium bromide at 60°C, with a constant composition of [DMF], [styrene], [AlBN] and [A] are shown in Fig.54. Assuming that $\text{Fe}(\text{DMF})_5\text{Br}^{2+}$ ions were progressively formed on adding LiBr by the equilibrium (z),



and that when both A and LiBr had a concentration of 7.873×10^{-3} mole ℓ^{-1} at 60°C, all the $\text{Fe}(\text{DMF})_6^{3+}$ ions were converted into $\text{Fe}(\text{DMF})_5\text{Br}^{2+}$ we can write,

$$\tau = \frac{[\text{Fe}(\text{DMF})_5\text{Br}^{2+}]_0}{I} = \frac{[\text{Br}^-]_0}{I} \quad (68)$$

The value of τ was 6900 seconds and using $k_d = 1.2 \times 10^{-5} \text{ sec.}^{-1}$,^{67,89} f was 0.63, which agreed well with other literature values.

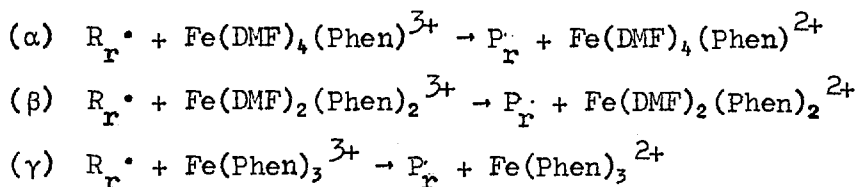
Lithium sulphate, Li_2SO_4 , was sparingly soluble in DMF, while H_2SO_4 , though soluble in DMF, had a small accelerative effect on the polymerization of styrene initiated by AlBN in the presence of the complex A (Fig.55).

5.13. Effect of Adding 1,10 Phenanthroline Monohydrate to the Complex,

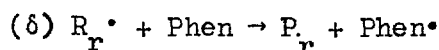
A, $[\text{Fe}(\text{DMF})_6]^{3+}(\text{3BF}_4^-)$, on Rates of Polymerization of Styrene

The results of adding phenanthroline, phen, to the complex, A, in the polymerization of styrene, initiated by AlBN, are shown in Fig.55.

The fact that a slight inhibition period was produced (curve d) with a phenanthroline/A molar ratio of 1:1 may be attributed to the reactions of the type:



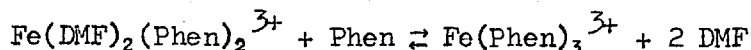
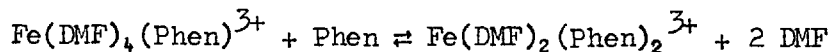
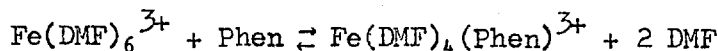
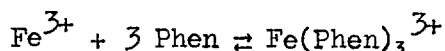
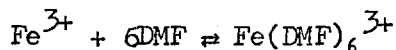
Since phenanthroline itself was shown to have a negligible effect (curve a) on the rate of polymerization of styrene in DMF initiated by ALBN in absence of ferric substances, transfer to phenanthroline itself, that is,



is probably not a significant reaction in the system.

The existence of the complex ion $[Fe(Phen)_3]^{3+}$ has been established 95,96,97 conclusively, while that of the other two phenanthroline-substituted ions is a matter of controversy.

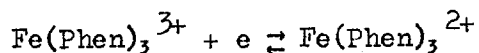
On increasing the concentration of phenanthroline to reach a phenanthroline:A molar ratio of 3:1, a long inhibition period was followed by a final retarded rate (curve e). The results are difficult to explain, but can be rationalized by assuming that on increasing the concentration of phenanthroline, ions of the type $Fe(Phen)_3^{3+}$ are produced, presumably by a set of stepwise equilibria;



The species $Fe(Phen)_3^{3+}$ is presumably a relatively reactive species, having a comparable reactivity to that of the chloro iron(III) complex

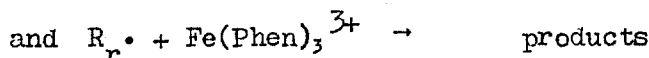
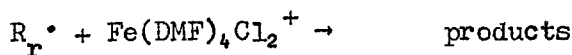
ions and giving rise to an induction period, while the ions with fewer phenanthroline molecules as ligands have a lesser reactivity and may persist in the polymerizing system to cause the final retarded rate.

The postulated high reactivity of Fe(Phen)_3^{3+} ions in the polymer radical-ion electron transfer is in agreement with the high positive standard reduction potential, E^0 , of the couple,^{5(a)}



and the consequent negative value of the standard free energy, ΔF^0 in the forward direction. Again, very high rates of electron exchange have been observed for the $\text{Fe(Phen)}_3^{2+} - \text{Fe(Phen)}_3^{3+}$ system, giving a velocity constant greater than $10^5 \text{ l. mole}^{-1} \text{ sec.}^{-1}$, at 0°C .⁴

On the other hand, when phenanthroline is added to ferric chloride in a DMF/styrene mixture in the presence of AIBN, the phenanthroline produced very little effect. Presumably this is due to the fact that velocity constants for the reactions,



are approximately of the same order. The final rate of polymerization for a system containing ferric chloride and phenanthroline was not significantly retarded since the ions $\text{Fe(DMF)}_4(\text{Phen})^{3+}$ and $\text{Fe(DMF)}_2(\text{Phen})_2$ with lower reactivity were less likely to be formed. The mechanism of the polymer radical - Fe(Phen)_3^{3+} ion reaction remains uncertain, but there is a possibility that electron transfer occurs by conduction through the phenanthroline ligands.

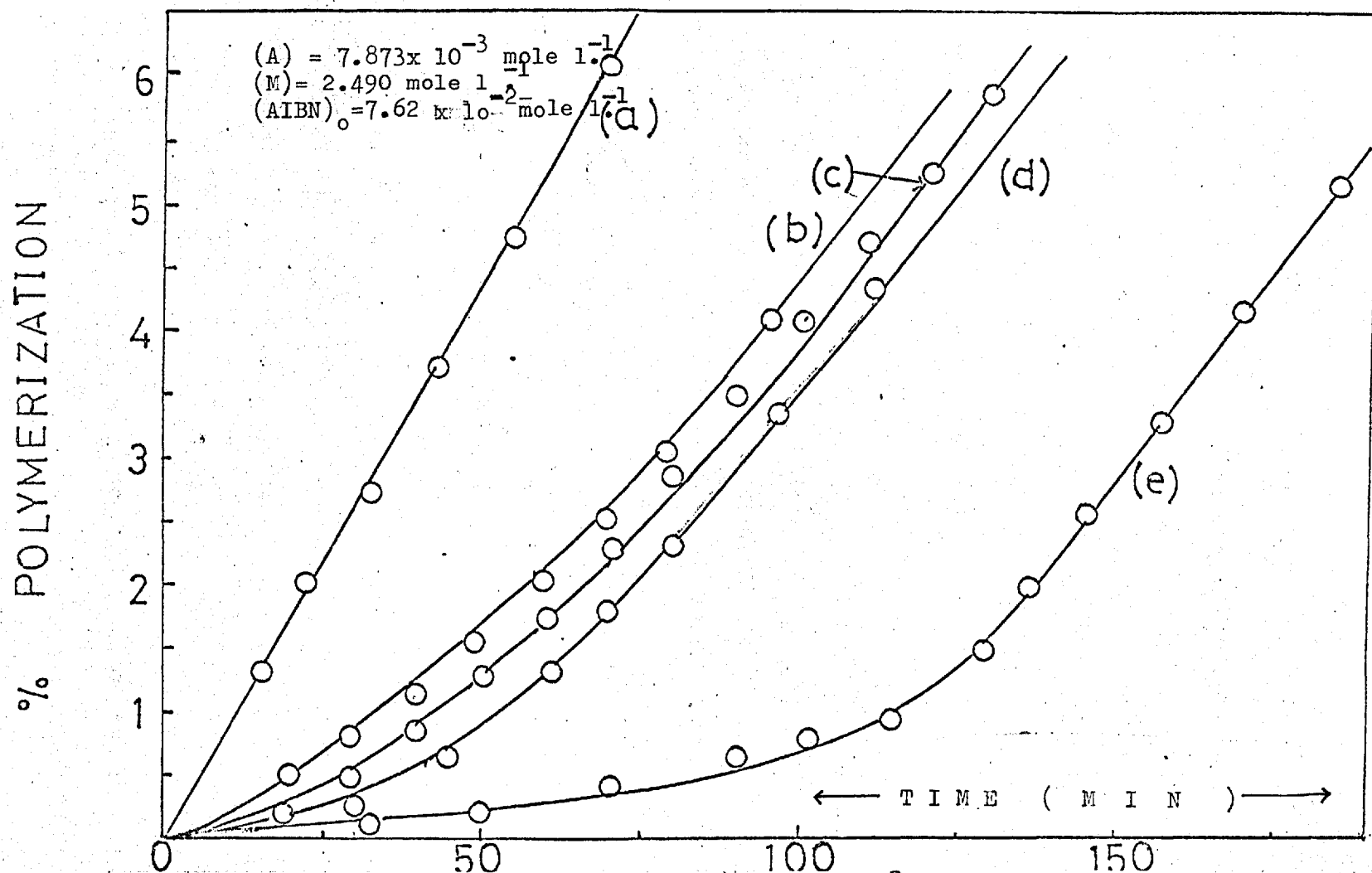


Fig.55. Polymerization of styrene in DMF at 60°C., initiated by AIBN and inhibited or retarded by various iron(III) species: (a) no added iron compound, 1,10 Phenanthroline, $(Phen) = 0.4542 \times 10^{-1} \text{ mole l}^{-1}$; (b) Molar ratio $SO_4^{2-} : A = 2.2:1$; (c) only the complex, $A, [Fe(DMF)_6](BF_4)_3$; (d) molar ratio, $Phen : A = 1:1$; (e) Molar ratio, $Phen : A = 3:1$.

5.14. Note on the Nature and Absorption Spectra of the Complexes used

For convenience only, some of the ionic species have been represented as inner sphere complexes rather than outer sphere complexes. In spite of the lack of conclusive evidence, spectroscopic and kinetic data suggest that the term "ion pair" is certainly not adequate to describe such complexes. This point has been extensively reviewed by Beck⁹⁹, recently.

The absorption spectra of ferric complexes discussed in this thesis are due to d - d transitions coupled with partial charge transfer to the cation.^{97, 98} In the charge transfer complexes such as the bromo and chloro ones, the anion is the electron donor¹⁰⁰ to the central metal ion, while in phenanthroline complexes the conjugated ligand is the donor of the electron.⁹⁷

5.15. Comparison of Velocity Constants

The velocity constant, k_x , for polystyryl radical attack on $\text{Fe}(\text{DMF})_6^{3+}$ of $847 \text{ l.mole}^{-1} \text{ sec.}^{-1}$, is much less than the corresponding mean values for iron(III) chloro-complexes, $\text{Fe}(\text{DMF})_5\text{Cl}^{2+}$, $\text{Fe}(\text{DMF})_4\text{Cl}_2^+$ and FeCl_4^- of $4.65^{53} \times 10^4$, $6.39^{40} \times 10^4$ and $2.96 \times 10^4 \text{ l.mole}^{-1} \text{ sec.}^{-1}$, respectively. Similarly, the velocity constant, k'_x , for polystyryl radical attack on $\text{Fe}(\text{DMSO})_6^{3+}$, of $229 \text{ l.mole}^{-1} \text{ sec.}^{-1}$, is much less than the value for the corresponding iron(III) monochloro species, of $7.47^{18} \times 10^4 \text{ l.mole}^{-1} \text{ sec.}^{-1}$. The presence of chloride ions in the complexes of iron(III), facilitates the electron transfer process in a way that is relatively unaffected by either the number of

chloride ions present, even if a statistical correction is applied, by the net charge carried by the ion, or by the geometry of the complex, octahedral, $\{ \text{Fe}(\text{DMF})_5\text{Cl}^{2+}, \text{Fe}(\text{DMF})_4\text{Cl}_2^+ \text{ and } \text{Fe}(\text{DMSO})_5\text{Cl}^+ \}$ or tetrahedral $\{ \text{FeCl}_4^- \}$.

Again, initial results indicated that the presence of a bromide ion in $\text{Fe}(\text{DMF})_5\text{Br}^{2+}$ facilitates electron transfer with respect to a polystyryl radical. Some of the photochemical behaviour of $\text{Fe}(\text{III})(\text{H}_2\text{O})_5\text{Br}^{2+}$ in water also confirms the effect of bromide ions in facilitating electron transfer¹⁰¹.

The accelerative effect of chloride ions^{2,102-104}, and other ions^{4,5,105} with respect to electron transfer between iron(III) and iron(II) species is well established in aqueous^{2,4,5,102,104} and in non-aqueous^{92,103} solutions. The Cl^- ion might facilitate electron transfer between two metal ions by a bridge mechanism or may act as a "conductor" for the transfer of the electron. Precise mechanisms remain uncertain, however.

For a few other radical-iron(III) reactions, accelerative effects of ions within the complex have also been observed. Thus, the velocity constants for termination of polyacrylamide radicals in aqueous solutions at 25°C, with $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ and $\text{Fe}(\text{H}_2\text{O})_5\text{Cl}^{2+}$ have values of $2.8 \times 10^3 \text{ l.mole}^{-1} \text{ sec.}^{-1}$ ³⁷, and $18.9 \times 10^4 \text{ l.mole}^{-1} \text{ sec.}^{-1}$ ⁴⁰, respectively. The high reactivity of the inner sphere complex, $\text{Fe}(\text{H}_2\text{O})_4\text{SO}_4^+$ towards the polyacrylamide radical in water has also been noted.⁴⁰

The velocity constant, k_x , for polystyryl radical attack on $\text{Fe}(\text{DMF})_6^{3+}$ was found to be greater than of corresponding value, k'_x , for $\text{Fe}(\text{DMSO})_6^{3+}$. Infrared spectroscopy suggested that the $\text{Fe}(\text{III})$ ion in the complex, A, is coordinated through the oxygen atoms⁸³ of the ligands as in the complex $[\text{Fe}(\text{DMA})_6](\text{ClO}_4)_3$, reported by Drago.⁸² The $\text{Fe}(\text{III})$ ion in the complex, D, is also likely to be co-ordinated through oxygen atoms since $\text{Fe}(\text{DMSO})_6^{2+}$ is reported to be a strongly oxygen-bonded complex.¹⁰⁶ So the nature of co-ordination in both the complexes is essentially the same, although the strengths of the ligand-ion bonds, which might involve σ and π -bonding are different. Thus, the compound, D, $[\text{Fe}(\text{DMSO})_6](\text{BF}_4)_3$ could be prepared merely by dissolving A, $[\text{Fe}(\text{DMF})_6](\text{BF}_4)_3$ in DMSO. This suggested that the ligands in complex D are more strongly held than in A. Further, a molar ratio of 1:1 of $\text{LiCl}:\text{A}$ was sufficient to convert all the $\text{Fe}(\text{DMF})_6^{3+}$ ions into $\text{Fe}(\text{DMF})_5\text{Cl}^{2+}$ but at least a 6:1 molar ratio of $\text{LiCl}:\text{D}$ was required for complete conversion of $\text{Fe}(\text{DMSO})_6^{3+}$ into $\text{Fe}(\text{DMSO})_5\text{Cl}^{2+}$ ions. This confirms the greater strength of a $\text{DMSO}-\text{Fe}(\text{III})$ ion bond compared with a $\text{DMF}-\text{Fe}(\text{III})$ ion bond.

Collinson et al.³⁷ suggested that the oxidation of a polymer radical involves the utilization of one of the vacant d orbitals of the cation. They envisaged that the radical approached the cation in order to achieve sufficient overlap of the p orbital of the carbon and a d orbital of the cation in the transition state so that rapid electron transfer could take place. The release of an electron by the radical enabled it to expel a proton.

The DMSO ligands in forming relatively strong bonds with the central iron(III) cation, presumably increase the electron charge density around this cation, more than would the corresponding DMF ligands. The polystyryl radical is more reactive towards the $\text{Fe}(\text{DMF})_6^{3+}$ species for which the central ion has unfilled d orbitals and a lower electron cloud density immediately around it, than towards the $\text{Fe}(\text{DMSO})_6^{3+}$ species.

The velocity constants, k_6 , for polystyryl radical attack on $\text{Fe}(\text{DMF})_5\text{Cl}^{2+}$ and k_7 for $\text{Fe}(\text{DMSO})_5\text{Cl}^{2+}$ were 6.40×10^4 and $7.18 \times 10^4 \text{ l.mole}^{-1}\text{sec.}^{-1}$, respectively. This suggests that for these ions, the ligand shape, size and nature of bonding are relatively unimportant and that a Cl^- ion probably conducts an electron from the radical to the central metal ion by a similar mechanism.

VI. CONCLUSIONS

The iron(III) chloro-complexes existing in solution in pure dimethyl formamide (DMF), pure dimethyl sulphoxide (DMSO), styrene/DMF and styrene/DMSO mixtures at 20°C and 60°C, have been identified. Identification has been achieved by the use of spectroscopic techniques, together with the use of model compounds such as hexakis (N,N-dimethyl formamide)iron(III) tetrafluoroborate, $[\text{Fe}(\text{DMF})_6](\text{BF}_4)_3$, hexakis (dimethyl sulphoxide)iron(III) tetrafluoroborate, $[\text{Fe}(\text{DMSO})_6](\text{BF}_4)_3$, and tetraethylammonium tetrachloroferrate(III), $(\text{C}_2\text{H}_5)_4\text{NFeCl}_4$, in the presence of varying amounts of lithium chloride. By these methods, the ions $\text{Fe}(\text{DMF})_6^{3+}$, $\text{Fe}(\text{DMF})_5\text{Cl}^{2+}$, $\text{Fe}(\text{DMF})_4\text{Cl}_2^+$, FeCl_4^- , have been identified in the presence of DMF, and the ions $\text{Fe}(\text{DMSO})_6^{3+}$ and $\text{Fe}(\text{DMSO})_5\text{Cl}^{2+}$ have been observed in the presence of DMSO.

The kinetics of the solution polymerization of styrene in DMSO initiated by α,α' -azobisisobutyronitrile (AIBN) at 60°C have been studied gravimetrically and dilatometrically. Number-average molecular weights, $\bar{M}_n$, of various isolated polymer samples have been measured by osmometry and viscometry, and the transfer constant, C_s , for DMSO at 60°C was found to be 2.42×10^{-5} . Similar types of rate measurements have also been made using the solvent, N,N-dimethylformamide.

Kinetic studies of the polymerization of styrene initiated by AIBN at 60°C in either DMF or DMSO, and in the presence of ferric compounds together with additives such as lithium chloride, lithium

bromide, sulphuric acid and phenanthroline have been made.

The presence of $\text{Fe}(\text{DMF})_6^{3+}$ or $\text{Fe}(\text{DMSO})_6^{3+}$ ions in the polymerizing systems caused retardation, but iron chloro-complexes produced well defined induction periods. Mean velocity constants at 60°C ., for polystyryl radicals towards $\text{Fe}(\text{DMF})_6^{3+}$, $\text{Fe}(\text{DMSO})_6^{3+}$, $\text{Fe}(\text{DMF})_5\text{Cl}^{2+}$, $\text{Fe}(\text{DMF})_4\text{Cl}_2^+$, FeCl_4^- and $\text{Fe}(\text{DMSO})_5\text{Cl}^{2+}$ were 847, 229, 4.65×10^4 , 6.79×10^4 , 2.96×10^4 and 7.47×10^4 $\text{l.mole}^{-1} \text{sec}^{-1}$, respectively. Iron(III) bromo- and phenanthroline-complexes also produced well-defined induction periods. Values of the initiator efficiency, f , for most systems investigated, ranged from 0.59 to 0.62. The decomposition of AlBN in DMSO was followed spectroscopically at 60°C and the first order decomposition rate constant, k_d for AlBN was found to be $0.94 \times 10^{-5} \text{sec}^{-1}$, at 60°C .

The detailed mechanism of these polystyryl radical-iron(III) complex electron transfer reactions still remains uncertain. In particular, the problem remains of whether the process occurs by an inner or an outer-sphere mechanism. It would appear profitable in the future to study the kinetic effect of other additives in such polymerizing systems. For example, the electron transfer reaction between a polystyryl radical and the ion $\text{FeS}_5\text{X}^{2+}$ could be studied, where S represents a ligand such as DMF or DMSO and X is an ion such as a halide ion or the azide ion, N_3^- . If a bridged type of transition complex is involved, and the polarizability of the ligand is important, electron transfer, and hence

the magnitude of the corresponding velocity constants would be expected to follow the series $I^- > Br^- > Cl^- > F^-$. A relatively large velocity constant for the azide substituted ion would also be expected due to the mobile electronic structure of the ligand. Experiments at different temperatures are also needed for the determination of activation energies.

Preliminary results also suggest that further studies of electron transfer between polyvinyl radicals and iron(III) complexes with conjugated ligands such as phenanthroline and bipyridine would be of interest.

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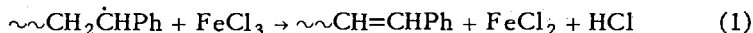
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I ABBREVIATIONS

N,N Dimethyl Formamide		DMF
Dimethyl Sulphoxide		DMSO
α, α' -azobisisobutyronitrile		AlBN
Hexakis N,N Dimethyl Formamide Iron(III) Tetrafluoroborate,		
$[\text{Fe}(\text{DMF})_6](\text{BF}_4)_3$		A
Tetraethyl Ammonium	.	
Tetrachloro Ferrate(III),		
$(\text{C}_2\text{H}_5)_4\text{NFeCl}_4$		B
Hexakis Dimethyl Sulphoxide Iron(III) Tetrafluoroborate,		
$[\text{Fe}(\text{DMSO})_6](\text{BF}_4)_3$		D
1,10 Phenanthroline		Phen

IRON(III)-CHLORO COMPLEXES IN N,N-DIMETHYLFORMAMIDE/ STYRENE SYSTEMS

The interaction of polyvinyl radicals with compounds of various transition elements has received increasing attention recently. For example, the polymerization of styrene initiated by 1,1'-azobisisobutyronitrile (AIBN) in solution in N,N-dimethylformamide (DMF) in the presence of low concentrations of ferric chloride has been studied (1-3), since under appropriate conditions the ferric chloride acts as an "ideal" retarder. Under these circumstances, polystyryl radicals react with ferric chloride to give products incapable of further reaction and kinetic analysis is simplified (1). The reaction is represented usually by a one-electron transfer reaction:



However, eq. (1) is expected to be an oversimplification since various complex ionic species are known to be formed when ferric chloride is dissolved in other solvents (4), including N,N-dimethylacetamide (5).

This paper reports the ultraviolet spectroscopic identification of the ionic species on dissolving small quantities of ferric chloride in DMF and DMF/styrene mixtures at 20 and 60°C. Spectral analysis has been achieved by studying the spectra of solutions containing the model compound hexakis(N,N-dimethylformamide) iron(III) tetrafluoroborate, $\text{Fe}(\text{DMF})_6-(\text{BF}_4)_3$, (A), in the presence of varying amounts of lithium chloride, and also of solutions containing the model compound, tetraethylammonium tetrachloroferrate(III), $(\text{C}_2\text{H}_5)_4\text{N}-\text{FeCl}_4$, (B). The tetrafluoroborate salt (A) was chosen for study since the BF_4^- ion shows little tendency to complex.

The compound (A) was prepared by the reaction of anhydrous iron(III) chloride and anhydrous silver tetrafluoroborate in DMF, by a method based on that described for the synthesis of hexakis(N,N-dimethylacetamide) iron(III) perchlorate (5). The yellow crystalline compound (A) was recrystallized from a DMF/ethyl alcohol mixture and stored in the dark until required.

Anal. Calcd. for $\text{C}_{18}\text{H}_{42}\text{N}_6\text{O}_6\text{F}_{12}\text{B}_3\text{Fe}$: C, 28.64%; H, 5.61%; N, 11.13%. Found: C, 28.76%; H, 5.82%; N, 11.26%.

The compound (B) was synthesized by a procedure previously described (5).

The infrared spectrum of a solution of (A) in methylene chloride was recorded together with a spectrum of DMF in methylene chloride. The C=O stretching vibration in the complex occurred at 1639.3 cm^{-1} com-

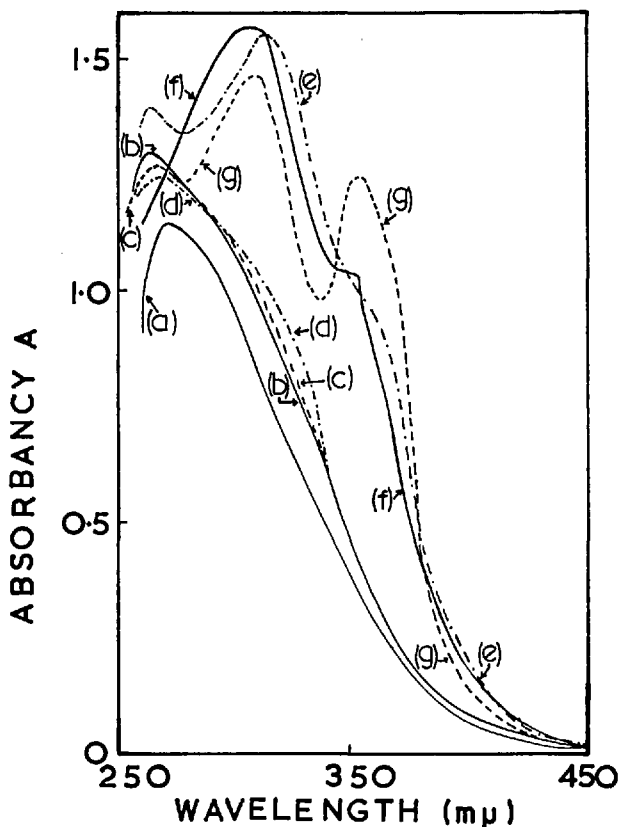


Fig. 1. Ultraviolet spectra of the complex (A), $\text{Fe}(\text{DMF})_6-(\text{BF}_4)_3$, with added LiCl in DMF at 20°C . [Total Fe(III) concentration is 2.2×10^{-4} mole l^{-1}]: (a) complex (A) alone; LiCl/(A) molar ratios are 0.25:1 in (b); 0.50:1 in (c); 1:1 in (d); 2:1 in (e); 3:1 in (f); and 4:1 in (g).

pared with a value of 1694.9 cm^{-1} for the free ligand. This suggests that the Fe(III) ion in the complex is co-ordinated to oxygen atoms of the ligand. Other absorption bands of free ligand and complex overlapped.

Ultraviolet absorption spectra were recorded with a Unicam SP800 or SP500 spectrometer using matched 10-mm. quartz cells against DMF or DMF/styrene mixtures, containing lithium chloride when appropriate.

The cells were thermostatted at 60°C ., and all solutions were protected against stray light to avoid reduction of any species from the iron(III) to the iron(II) state. The spectroscopic results were unaffected by the addition of traces of water to the solutions studied, and were not markedly time-dependent, indicating that the various equilibria were rapidly attained.

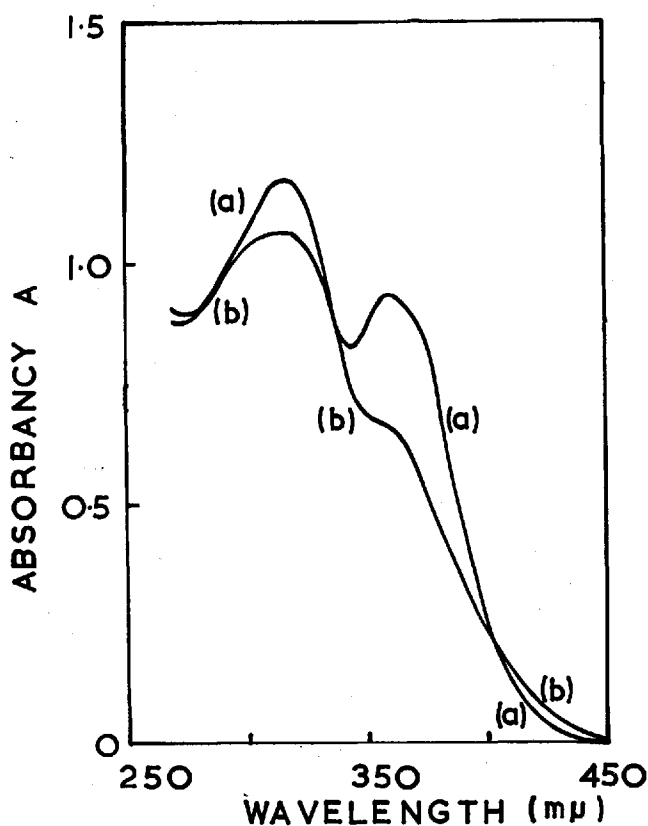


Fig. 2. Ultraviolet spectra in DMF at 20°C. [Total Fe(III) concentration is 1.37×10^{-4} mole l^{-1}]: (a) tetraethylammonium tetrachloroferrate(III); (b) iron(III) chloride.

The DMF and styrene were purified as described in the literature (6) and both solvents were dried over calcium hydride before use.

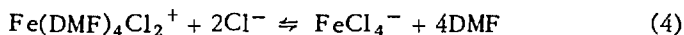
The spectra of $\text{Fe}(\text{DMF})_6-(\text{BF}_4)_3$ in DMF solutions containing different concentrations of added lithium chloride are shown in Figure 1. Assuming the usual co-ordination number of six for all cationic iron(III) species, curve (a) may be associated with the presence of $\text{Fe}(\text{DMF})_6^{3+}$ ions. Adding lithium chloride to give a $\text{LiCl}/(\text{A})$ molar ratio of 0.25 produces an increase in absorption over the entire wavelength range [curve (b)] attributed to the formation of $\text{Fe}(\text{DMF})_5\text{Cl}^{2+}$. The formula $\text{Fe}(\text{DMF})_5\text{Cl}^{2+}$ is used for simplicity here, and does not necessarily imply inner-sphere complexing, but could also refer to outer-sphere complexes of the type $\text{Fe}(\text{DMF})_6^{3+}$, Cl^- .



The intensity of absorption at about 265 $m\mu$ subsequently decreases progressively on increasing the LiCl/(A) molar ratio to 0.5 and 1.0 [curves (c) and (d)], and the absorption intensity at 320 $m\mu$ increases. These changes are due to the disappearance of $\text{Fe}(\text{DMF})_5\text{Cl}^{2+}$ ions and formation of $\text{Fe}(\text{DMF})_4\text{Cl}_2^+$ species, which by analogy with other results involving $\text{Fe}(\text{DMA})_4\text{Cl}_2^+$ are expected to absorb most strongly at about 320 $m\mu$ (5).



A relatively large increase in absorption over all wavelengths occurs for a LiCl/(A) molar ratio of 2:1 [curve (e)], presumably due to the increased concentration of $\text{Fe}(\text{DMF})_4\text{Cl}_2^+$ ions, and a hump also appears in the region 340–360 $m\mu$. For a LiCl/(A) molar ratio of 3:1 the intensity at 265 $m\mu$ again decreases, there is a peak at 305 $m\mu$, and the absorption at about 350 $m\mu$ is increased. [curve (f)]. There is strong independent evidence (4) that an absorption in the region of 360 $m\mu$ is due to FeCl_4^- ions which are presumably formed in this instance by the process:



This was confirmed also by recording the spectrum of the model compound (B), $(\text{C}_2\text{H}_5)_4\text{N}-\text{FeCl}_4$, in DMF at 20°C. as shown in Figure 2 [curve (a)]. The intensity of the strong peak at 360 $m\mu$ due to compound (B) was unaffected on adding lithium chloride to the solution, to give a molar ratio of LiCl/(B) of 3:1, indicating the stability of FeCl_4^- under these conditions. Again, in agreement with this rationalization, the absorbancy at 360 $m\mu$ increases markedly on increasing the LiCl/(A) molar ratio to 4:1 as shown in Figure 1 [curve (g)]. The intensity of the peak at 360 $m\mu$ thereafter only increased by 1.4% on increasing the LiCl/(A) molar ratio to 9:1, indicating that most of the iron(III) species beyond a 4:1 molar ratio existed as FeCl_4^- .

The results suggest that the equilibrium constant for the formation of the monochloro-iron(III) complex is smaller than that for the formation of the dichloro complex. The spectrum of anhydrous iron(III) chloride dissolved in DMF is shown in Figure 2 [curve (b)], and allowing for the difference in concentrations, the spectrum is almost identical with the spectrum obtained by dissolving (A) in DMF with a LiCl/(A) molar ratio of 3:1 [curve (f) of Fig. 1]. It is therefore concluded that when iron(III) chloride is dissolved at low concentrations in DMF at 20°C. the principal species present are $\text{Fe}(\text{DMF})_4\text{Cl}_2^+$ and FeCl_4^- ions, together with small concentrations of $\text{Fe}(\text{DMF})_5\text{Cl}^{2+}$ ions. These results are similar to those previously reported (5) for the solvent N,N-dimethylacetamide which has a dielectric constant similar to that of DMF (7). The above

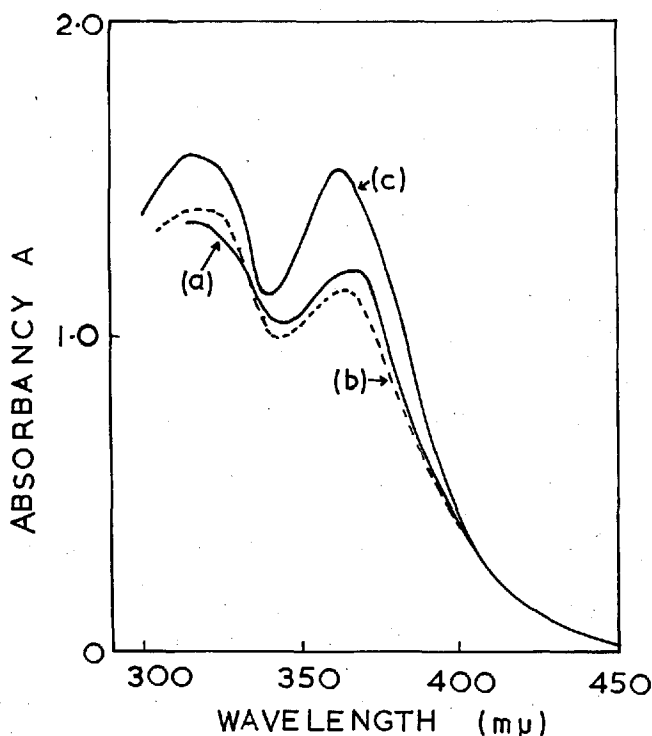
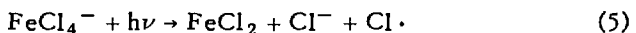


Fig. 3. Ultraviolet spectra in a DMF/styrene mixture at 60°C. [DMF] = 8.79 mole l.⁻¹; [styrene] = 2.49 mole l.⁻¹ [Total Fe(III) concentration is 2.2×10^{-4} mole l.⁻¹]: (a) iron(III) chloride; (b) LiCl/(A) molar ratio is 3:1; (c) tetraethylammonium tetrachloroferrate(III).

conclusions for the solvent DMF were also shown to be valid at 60°C.

Similar spectroscopic studies were made with DMF/styrene mixtures at 20 and 60°C., with concentrations of styrene similar to those employed in many kinetic studies (1). In these mixed solvent systems, at both temperatures, there was a tendency for the FeCl_4^- ions to be present to a greater extent than in pure DMF alone, the other principal ionic species again being $\text{Fe}(\text{DMF})_4\text{Cl}_2^+$. Figure 3 shows some of the spectral results at 60°C. Again, in the mixed solvent system, there is a close similarity between the spectrum of iron(III) chloride and that of LiCl-complex (A) in a 3:1 molar ratio.

Solutions of (A) in DMF both in the presence and absence of added lithium chloride undergo reduction from the Fe(III) to Fe(II) condition in visible or ultraviolet light. In vinyl monomer/DMF mixtures, one of the main processes undergone by iron(III) chloride when photolysed at about 4350 Å. is likely to be:



as has recently been suggested (8).

Further experiments will be performed in the future in an attempt to assess the relative reactivity of the various chloro complexes towards polystyryl radicals.

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APPENDIX II

Effects of Iron(III) Chloro-complexes on the Polymerization of

Styrene

by

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Synopsis

The polymerization of styrene initiated by 2,2'-azobisisobutyronitrile has been studied in N,N-dimethylformamide solution at 60°C in the presence of hexakis(N,N-dimethylformamide) iron(III) tetrafluoroborate alone, and also in the presence of added lithium chloride. The presence of $\text{Fe}(\text{DMF})_6^{3+}$ ions in the polymerizing systems caused retardation, but iron(III) chloro-complexes produced well-defined inhibition periods. Velocity constants at 60°C for polystyryl radicals towards $\text{Fe}(\text{DMF})_6^{3+}$, $\text{Fe}(\text{DMF})_5\text{Cl}^{2+}$, $\text{Fe}(\text{DMF})_4\text{Cl}_2^+$ and FeCl_4^- ions were calculated to be 847, 4.15×10^4 , 6.55×10^4 and 3.14×10^4 l.mole⁻¹ sec.⁻¹, respectively. Values of the initiator efficiency, f, for most systems investigated, ranged from 0.59 to 0.62.

Introduction

In recent years there has been increasing interest in the kinetics of reactions between polyvinyl radicals and transition metal salts in non-aqueous solutions. Under appropriate conditions,

ferric chloride in N,N-dimethylformamide (DMF) solution acts as an 'ideal retarder' in the polymerization of styrene since growing polystyryl radicals then react to give products incapable of further reaction¹⁻³. In such circumstances kinetic analysis is simplified and rates of initiation may be determined by the induction period technique or by measurements of the rate of formation of ferrous ions. Both techniques applied to styrene polymerization give results in good agreement⁴.

However, the precise nature of the polymer radical-substrate reaction has remained obscure, though it was realised that various complex ions of iron(III) might exist in monomer/DMF solutions^{1,2,5}. Recently, the complex ions produced when ferric chloride is dissolved in DMF and DMF/styrene solutions have been identified⁶. This paper reports the evaluation of the various kinetic constants at 60°C for the reaction of polystyryl radicals with individual iron(III) complex ions.

EXPERIMENTAL

Materials

The initiator 2,2'-azobisisobutyronitrile, (AIBN), N,N-dimethylformamide⁸, (DMF), and styrene⁹ were purified as described previously. The monomer and DMF were finally dried over calcium hydride, and the monomer was stored at -78°C under oxygen-free nitrogen until required.

The method of preparation and purification of hexakis(N,N-dimethylformamide) iron(III) tetrafluoroborate, $\text{Fe}(\text{DMF})_6 - (\text{BF}_4)_3$, A, has already been described⁶.

Laboratory reagent lithium chloride (B.D.H.) and anhydrous ferric chloride (Hopkin and Williams) were used directly in certain experiments. 1,10-Phenanthroline hydrate (Hopkin and Williams) was recrystallised from absolute A.R. ethyl alcohol and dried in vacuo before use in polymerization experiments; but was used as the monohydrate for estimating concentrations of ferrous ions in DMF/styrene mixtures spectrophotometrically. 1,10-Phenanthroline - ferrous perchlorate (Hopkin and Williams) was used to calibrate the spectrophotometric determination of iron(II) ions.

Procedure

Rates of polymerization were measured dilatometrically in the usual way⁷, care being taken to degas the reactants thoroughly before sealing off the dilatometers. In some experiments dilatometers with a bulb capacity of about 30 ml., and a capillary of 1.0 mm diameter were used to increase the accuracy of measuring reduced rates of polymerization.

Ultra-violet absorption spectra were recorded with a Unicam SP800 or SP500 spectrometer using matched quartz cells against DMF/styrene mixtures containing lithium chloride when appropriate.

Some determinations of iron(II) species produced in polymerizing styrene/DMF mixtures in the presence of AIBN and added iron(III) complexes were made by ceric titrations, after diluting the systems with excess DMF. However, the spectrophotometric determination, based on the formation of the tris- orthophenanthroline complex of

iron(II) was more successful. Polymerizations were then performed in small reaction tubes at 60°C, and at the end of a known time, a tube was cooled rapidly, cracked open and a 6:1 ratio of 1,10-phenanthroline based on the initial iron(III) concentration was added. Absorbancy readings for the solutions were measured at 518 mμ, at room temperature. The method was calibrated using 1,10-phenanthroline ferrous perchlorate dissolved in similar DMF/styrene mixtures in the presence of lithium chloride.

Beer's Law was obeyed up to a concentration of 1.8×10^{-4} mole ℓ^{-1} of ferrous ions with a molar absorptivity, ϵ , of 10,490 $\ell \cdot \text{mole}^{-1} \text{cm}^{-1}$.

RESULTS AND DISCUSSION

Measurements using ferric chloride alone

Some experiments were performed using ALBN to initiate the polymerization of styrene in DMF at 60°C in the presence and absence of anhydrous ferric chloride.

Polystyryl radicals react with the species produced when ferric chloride is dissolved in DMF/styrene so readily that well-defined induction periods are produced, at the end of which the rate rapidly attains that expected in the absence of ferric chloride. Typical results, in excellent agreement with those of Bamford et al.¹, are shown in Fig.1.

A simple kinetic scheme has been used to explain the results^{1,10}, assuming that ferric chloride exists as a single entity:

(a) Initiation:(b) Propagation:(c) Termination by ferric chloride:(d) Mutual termination of polystyryl radicals:

where In represents the initiator, AlBN, $\text{R}_c^\bullet$ is a radical produced by direct decomposition of AlBN, $\text{R}_1^\bullet$, $\text{R}_r^\bullet$ and $\text{R}_s^\bullet$ are all growing radicals, and M and P represent monomer and dead polymer molecules, respectively.

A stationary state treatment leads to the equation:

$$-\frac{1}{\phi_t} + \ln \frac{1 + \phi_t}{1 - \phi_t} = k_s (\text{R}^\bullet)_s t + A^* \quad (1)$$

where ϕ_t is the reduced rate, equal to the ratio of the rate at any time t in the presence of ferric chloride to the final maximum rate, $(\text{R}^\bullet)_s$ is the final maximum radical concentration when all of the ferric chloride has disappeared, and A is an integration constant.

Furthermore, if τ is defined as the time when the rate of polymerization has attained a value 0.648 of the final maximum value,

$$\tau = \frac{(\text{FeCl}_3)_0}{\text{I}} \quad (2)$$

where $(\text{FeCl}_3)_0$ is the initial concentration of ferric chloride at time $t = 0$. The rate of initiation, I , in any experiment may be expressed by the equation:

$$I = 2k_d f(\bar{I}n) \quad (3)$$

where $(\bar{I}n)$ is the mean initiator concentration and f is the initiator efficiency.

Further experiments with ferric chloride at 60°C indicated that with constant (M) , (DMF) and $(\text{FeCl}_3)_0$, there was a linear relationship between τ^{-1} and $(\bar{I}n)$. Again, for a series of experiments in which $(I_n)_0$ was maintained constant but $(\text{FeCl}_3)_0$ was varied, there was a linear relationship between $(\bar{I}n)\tau$ and $(\text{FeCl}_3)_0$. Both these relationships may be predicted from equations (2) and (3) and assuming a value of k_d of $1.2 \times 10^{-5} \text{ sec.}^{-1}$,^{11,12} a mean value of f of 0.60 was obtained.

Expansion of the kinetic scheme

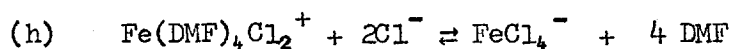
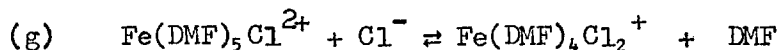
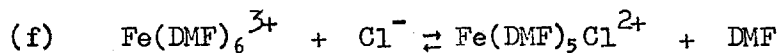
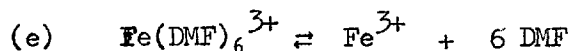
However, the above treatment is only approximate, since it has been shown⁶ that when iron(III) chloride is dissolved at low concentrations in DMF/styrene mixtures at 60°C , the principal ionic species present are $\text{Fe}(\text{DMF})_4\text{Cl}_2^+$ and FeCl_4^- .

A generalized kinetic scheme for systems containing arbitrary concentrations of iron(III) and chloride ions has, therefore, to include reactions of polymer radicals with $\text{Fe}(\text{DMF})_6^{3+}$, $\text{Fe}(\text{DMF})_5\text{Cl}^{2+}$, $\text{Fe}(\text{DMF})_4\text{Cl}_2^+$ and FeCl_4^- , with corresponding velocity constants k_x , k_6 , k_7 and k_8 , respectively. For convenience in writing only, some

of the ionic species have been represented as inner-sphere, rather than outer-sphere complexes.

The precise significance of the previous value of f is thus difficult to assess. For similar reasons, a detailed analysis of the ϕ_t -time t data by the method of Bamford et al.¹ was not made using the results obtained with ferric chloride alone.

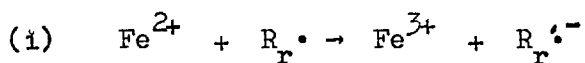
It was confirmed spectroscopically that iron(II) species were produced, at least in part, by polystyryl radical attack on all of the iron(III) species studied. The value of k_x was determined by experiments involving the complex $\text{Fe}(\text{DMF})_6 - (\text{BF}_4)_3$, A, while k_6 , k_7 and k_8 were evaluated by the study of polymerizing styrene systems containing A and added lithium chloride. Various ionic equilibria of the following type also have to be considered:^{6,13}



It was checked that addition of lithium chloride alone, over the concentration range used in later experiments, produced no retardation or inhibition of the polymerization of styrene in DMF initiated by AIBN at 60°C.

Some rate measurements were also performed when 1,10-phenanthroline was added in varying amounts to the polymerizing styrene systems in the presence of anhydrous ferric chloride. Values of

τ at 60°C were essentially identical to those observed in the absence of 1,10-phenanthroline. Since the latter functions predominantly by complexing with ferrous ions produced by iron(III) - radical interaction, it appears that a polystyryl radical is insufficiently electrophilic to accept an electron from an iron(II) species, and cause regeneration of an iron(III) ion:



Rate Measurements using Complex A; Evaluation of k_x

The tetrafluoroborate salt, A, $\text{Fe}(\text{DMF})_6-(\text{BF}_4)_3$, was selected for study since the BF_4^- ion shows little tendency to complex, and $\text{Fe}(\text{DMF})_6^{3+}$ ions are formed in DMF/styrene mixtures⁶.

On polymerisation of styrene at 60°C in the presence of ALBN, DMF and A, retarded rates of polymerization were recorded dilatometrically. The rate results were analysed by the method of Kice^{14,15}, assuming that the equilibrium (e) was well over to the left-hand side. This kinetic scheme includes the steps of initiation, propagation and mutual termination of polymer radicals and also:

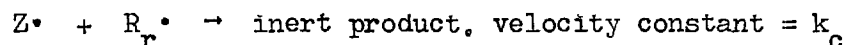
(j) Transfer

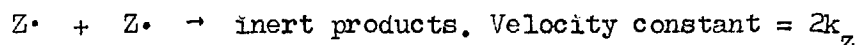


(k) Copolymerization



(l) Cross-termination



(m) Mutual termination of Z• radicals

where Z• represents any species formed by reaction between a polymer radical and complex A, which, a priori, might be a radical.

If ϕ is defined as the ratio of the retarded rate of polymerization to the rate in the absence of retarder A, c is a constant equal to $(4k_t k_z / k_c^2)$, R_p is the fractional rate of polymerization, $-d[\ln(M)]/dt$, in sec.^{-1} , and experiments are conducted at constant (M) and (DMF):

$$R_p \sqrt{1 + \frac{c(1 - \phi^2)}{\phi^2}} = \frac{k_p k_x}{2k_t} \cdot \frac{\phi^2(A)}{(1 - \phi^2)} \left\{ 1 + \sqrt{1 + \frac{c(1 - \phi^2)}{\phi^2}} \right\} - \frac{k_c k_p}{k_c} \quad (M) \quad (4)$$

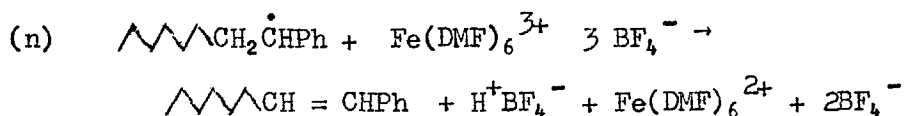
Thus a plot of the left hand side of equation (4) against

$$\frac{\phi^2(A)}{1 - \phi^2} \left\{ 1 + \sqrt{1 + \frac{c(1 - \phi^2)}{\phi^2}} \right\} \text{ at constant (M) should give a slope of } (k_p k_x / 2k_t) \text{ and an intercept on the vertical axis of } - \frac{k_o k_p}{k_c} \cdot (M)$$

A value of c of 1×10^{-6} was chosen to give the least deviation of the experimental points from a straight line and the results are collected in Table I and plotted in Fig.2.

The slope of the line in Fig.2 is $2.07 \times 10^{-3} \text{ l.mole}^{-1} \text{sec.}^{-1}$, and using values¹⁶ of k_p and $2k_t$ equal to 176 and $7.2 \times 10^7 \text{ l.mole}^{-1} \text{sec.}^{-1}$, respectively, k_x was $847 \text{ l.mole}^{-1} \text{sec.}^{-1}$. From the intercept, (k_o/k_c) was 2.31×10^{-10} , at 60°C .

The low value of (k_o/k_c) indicates a low tendency of $Z^\bullet$ species to attack monomer. The transfer constant for polystyryl radicals to DMF is only 4.0×10^{-4} at 60°C , and involves H-atom abstraction from a CH_2 -group⁸. Hence, unless the reactivity of a DMF molecule is greatly increased when it is a ligand in the complex ion, another type of radical - A reaction must also occur to explain the relatively high value of k_x . This might be:



for which the products are completely inert.

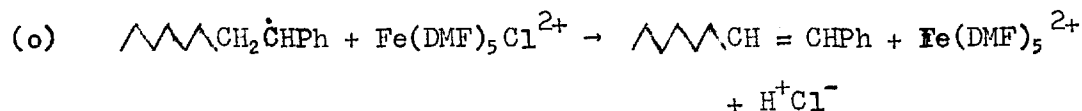
Effect of adding LiCl to A on Rates of Polymerization

On progressively adding lithium chloride to mixtures of constant composition containing styrene, DMF, ALBN and complex A, and measuring rates at 60°C , definite induction periods were observed, as indicated in Fig.1. A plot of τ evaluated from individual rate curves, against concentration of lithium chloride added is shown in Fig.3, and this suggests that the various iron(III) - chloro complexes are all much more reactive towards polystyryl radicals than $\text{Fe}(\text{DMF})_6^{3+}$ ions.

The rate curves for molar ratios of LiCl to A of 2:1 and 3:1 were almost identical, but curve (g) of Fig.1 was not identical with that for ferric chloride at an equal concentration of iron(III), as might have been expected, although the τ -values differed by only three minutes, (Fig.3).

Analysis of Results up to a Molar Ratio of (LiCl)/(A) of 1:1

Spectroscopic evidence⁶ suggests that up to a 1:1 molar ratio of LiCl to A, $\text{Fe}(\text{DMF})_4\text{Cl}^{2+}$ ions are progressively formed by the equilibrium reaction (f), which has a relatively high equilibrium constant. Since no chlorine could be found by microanalysis in low molecular weight polymers formed during induction periods, the predominant inhibition reaction may be written:



and presumably the $\text{Fe}(\text{DMF})_5^{2+}$ ion rapidly acquires another DMF molecule to become $\text{Fe}(\text{DMF})_6^{2+}$.

In this case, the total τ -value will depend on the initial equilibrium concentration of $\text{Fe}(\text{DMF})_5\text{Cl}^{2+}$ ions and also on the concentration of $\text{Fe}(\text{DMF})_5\text{Cl}^{2+}$ ions formed by equilibrium (f) as Cl^- ions are liberated in (o). If $(A)_0$ and $(\text{Cl}^-)_0$ are the initial concentrations of A and LiCl, and the equilibrium constant in (f) is high, the initial concentrations of $\text{Fe}(\text{DMF})_6^{3+}$ and $\text{Fe}(\text{DMF})_5\text{Cl}^{2+}$ are, $(A)_0 - (\text{Cl}^-)_0$ and $(\text{Cl}^-)_0$, respectively.

By analogy with equation (2),

$$\tau = \frac{k' \left\{ (A)_p - (\text{Cl}^-)_0 \right\}}{I} + \frac{(\text{Cl}^-)_0}{I} = \frac{k'(A)_0}{I} + (\text{Cl}^-)_0 \left\{ \frac{1}{I} - \frac{k'}{I} \right\} \quad (5)$$

where the first term on the right hand side of (5) allows for the conversion of $\text{Fe}(\text{DMF})_6^{3+}$ to $\text{Fe}(\text{DMF})_5\text{Cl}^{2+}$, and k' is an arbitrary constant.

Table I

Effect of Complex A on the Polymerization of Styrene Initiated by AIBN in DMF Solution at 60°C

(M) = 2.490 mole ℓ^{-1} ; (DMF) = 8.792 mole ℓ^{-1} . Value of c chosen

$= 1.0 \times 10^{-6}$

(AIBN) $\times 10^2$ (mole ℓ^{-1})	Rate of Poly- merization $\times 10^5$ (mole $\ell^{-1} \text{ sec}^{-1}$)	Retarder Concentration (A) $\times 10^3$ (mole ℓ^{-1})	$\frac{\phi^2(A)}{1-\phi^2} \left[1 + \sqrt{\frac{1+c(1-\phi^2)}{\phi^2}} \right]$ $\times 10^3$ (mole ℓ^{-1})	$R_p \sqrt{\frac{1+c(1-\phi^2)}{\phi^2}} \times 10^6$ (sec^{-1})
7.618	3.979	0.000	-	-
7.618	2.390	3.936	4.443	9.598
7.618	2.035	5.904	4.183	8.173
7.618	1.701	7.873	3.521	6.831
7.618	1.037	11.909	1.736	4.165
1.404	1.859	0.000	-	-
1.404	0.500	7.873	1.228	2.008

In accordance with this prediction, Fig.3 gave an initially linear plot of τ against $(Cl^-)_0$ up to a molar ratio of LiCl/A of 1:1. The slope was $5.748 \times 10^5 \text{ sec. l. mole}^{-1}$ and intercept 2847.6 sec, and these values give a rate of initiation, I , equal to $1.07 \times 10^{-6} \text{ mole l.}^{-1} \text{ sec.}^{-1}$. This is reasonable, since using $[\bar{In}]$ equal to $7.31 \times 10^{-2} \text{ mole l.}^{-1}$ over the range considered, and k_d equal to $1.2 \times 10^{-5} \text{ sec.}^{-1}$, the initiator efficiency f is 0.62.

Again when both A and added LiCl have a concentration of $7.873 \times 10^{-3} \text{ mole l.}^{-1}$ at 60°C , the value of τ was 7,200 sec. Writing,

$$\tau = \frac{[Fe(DMF)_5Cl^{2+}]_0}{I} = \frac{(Cl^-)_0}{I} \quad (6)$$

and using the above-mentioned values of k_d and $(\bar{In})$, the value of f is 0.61. These values of f are in good agreement with other literature values¹⁷, although the dependence on the value of k_d used is clear.

A detailed analysis of the rate curve measured with a 1:1 molar ratio of LiCl/A was then made, and a plot of ϕ_t vs $k_6 (R^\bullet)_s t + A^*$ is shown in Fig.4, where it is assumed that only $Fe(DMF)_5Cl^{2+}$ ions are present, and k_6 refers to reaction (o). Agreement between the experimental and theoretical plot was reasonable when $k_6 (R^\bullet)_s$ was $4.00 \times 10^{-3} \text{ sec.}^{-1}$.

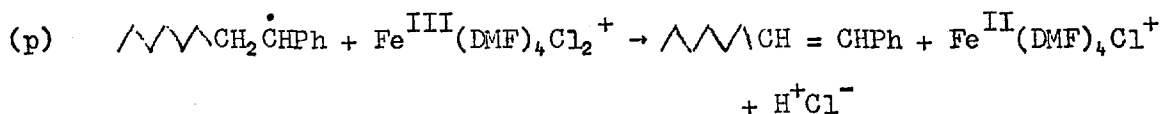
Now,

$$\frac{k_6}{k_p} = \frac{k_6 (R^\bullet)_s (M)}{R_{ps}} \quad (7)$$

where R_{ps} represents the maximum rate of polymerization for the system. Using the experimental values of R_{ps} and (M) of 4.23×10^{-5} mole ℓ^{-1} sec. $^{-1}$ and 2.49 mole ℓ^{-1} , respectively, and using k_p equal to $176 \ell \cdot \text{mole}^{-1} \text{sec}^{-1}$, the value of k_6 is $4.15 \times 10^4 \ell \cdot \text{mole}^{-1} \text{sec}^{-1}$ at 60°C .

Evaluation of k_7

Spectroscopic evidence⁶ suggested that on adding lithium chloride to polymerizing systems in excess of a 1:1 molar ratio of $\text{LiCl}:\text{A}$, the equilibrium (g) is involved, and induction periods are possibly due to mechanisms (o) and (p):



with the iron(II) complex becoming rapidly solvated with DMF.

The equilibrium constant in (g) is high⁶, so that for a 2:1 molar ratio of LiCl to A , all of the iron(III) ions exist as $\text{Fe}(\text{DMF})_4\text{Cl}_2^+$. Hence,

$$\tau = \frac{(\text{Fe}(\text{DMF})_4\text{Cl}_2^+)_0}{I} \quad (8)$$

The experimental τ value indicates a value of I of 1.03×10^{-6} mole ℓ^{-1} sec. $^{-1}$ and an f value of 0.59.

Analysis of the Φ_t - time data by the method of Bamford et al.¹ gave k_7 equal to $6.55 \times 10^4 \ell \cdot \text{mole}^{-1} \text{sec}^{-1}$ at 60°C .

Evaluation of k_8

Spectroscopically, it was shown⁶ that all iron(III) species from complex A with LiCl/A molar ratios in excess of about 6:1 exist

as FeCl_4^- ions in DMF/styrene mixtures at 60°C . Calculations indicated that the value of the equilibrium constant for (h) was at least 10^8 . In pure N,N-dimethyl acetamide, a similar type of equilibrium is established¹³ with an estimated equilibrium constant of at least 10^{10} .

Analysis of the ϕ_t - time t data was therefore performed for an experiment at 60°C with a LiCl/A molar ratio of 10:1, and the value of k_8 obtained was $3.14 \times 10^4 \text{ l.mole}^{-1}\text{sec.}^{-1}$. The plot of ϕ_t against $k_8(\text{R}\cdot)_s t + A^*$ is shown in Fig.5.

However, the measured values of τ for LiCl/A molar ratios greater than 6:1, although virtually constant with increase of (LiCl), seemed somewhat lower than suggested by the usual treatment¹, and gave values of f about 0.8. The rate of production of iron(II) species was therefore measured spectrophotometrically in a polymerization experiment with a LiCl/A molar ratio of 10:1. Iron(II) was determined as the tris-phenanthroline complex. The results of an experiment are shown in Fig.6, and indicate a linear rate of production of iron(II) species of $1.11 \times 10^{-7} \text{ mole l.}^{-1} \text{ sec.}^{-1}$.

Assuming that each polystyryl radical is captured by one FeCl_4^- ion during the induction period, simple theory suggests that:

$$\frac{d(\text{FeII})}{dt} = I = 2 k_d f(\bar{\text{In}}) \quad (9)$$

For an average value of (In) equal to $7.52 \times 10^{-3} \text{ mole l.}^{-1}$ during the induction period, the corresponding value of f is 0.62, in good agreement with previous results.

A mechanism of radical scavenging by FeCl_4^- ions preserving a 1:1 radical-ion stoichiometry would be:



The reason for the discrepancy between values of f calculated from τ measurements and those obtained by direct measurement of the rates of production of iron(II) species remains uncertain. However, the difference may be associated, in part, with the formation of other iron(III) chloro-complexes such as FeCl_5^{2-} and FeCl_6^{3-} at very high chloride concentrations¹⁸.

Comparison of Velocity Constants

The velocity constant, k_x , for polystyryl radical attack on $\text{Fe}(\text{DMF})_6^{3+}$, of $847 \text{ l.mole}^{-1}\text{sec.}^{-1}$, is much less than the corresponding values for the iron(III) chloro-complexes, $\text{Fe}(\text{DMF})_5\text{Cl}^{2+}$, $\text{Fe}(\text{DMF})_4\text{Cl}_2^+$ and FeCl_4^- of 4.15×10^4 , 6.55×10^4 and $3.14 \times 10^4 \text{ l.mole}^{-1}\text{sec.}^{-1}$, respectively. The presence of chloride ions in the complexes of iron(III), facilitates the electron transfer process in a way that is relatively unaffected by either the number of chloride ions present, even if a statistical correction is applied, by the net charge carried by the ion, or by the geometry of the complex, octahedral $\{\text{Fe}(\text{DMF})_5\text{Cl}^{2+}$ and $\text{Fe}(\text{DMF})_4\text{Cl}_2^+\}$ or tetrahedral $\{\text{FeCl}_4^-\}$.

The accelerative effect of chloride ions¹⁹, and other ions²⁰, is well established for exchange reactions between iron(III) and iron(II) in aqueous solutions. The Cl^- ion might facilitate electron transfer by acting as a bridge between the two metal ions, or act as

a "conductor" for the transfer of the electron. Precise mechanisms remain uncertain, however²⁰.

For a few other polymer radical-iron(III) reactions, accelerative effects of ions within the complex have also been observed. Thus, velocity constants for termination of polyacrylamide radicals in aqueous solutions at 25°C with $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ and $\text{Fe}(\text{H}_2\text{O})_5\text{Cl}^{2+}$ have values of $2.8 \times 10^3 \text{ l.mole}^{-1}\text{sec.}^{-1}$,²¹ and $18.9 \times 10^4 \text{ l.mole}^{-1}\text{sec.}^{-1}$,²² respectively. The high reactivity of the inner sphere complex $\text{Fe}(\text{H}_2\text{O})_4\text{SO}_4^+$ towards polyacrylamide radicals has also been noted.²¹

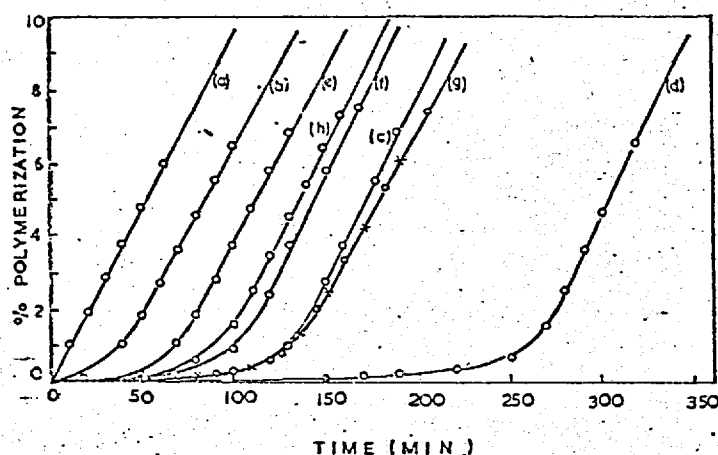


Fig. 1. Polymerization of styrene in DMF solution at 60°C initiated by AIBN in the presence of various iron(III) species: (a) no added iron(III) compound. (b) $[\text{FeCl}_3]_0 = 2.62 \times 10^{-2}$ mole/l.; (c) $[\text{FeCl}_3]_0 = 7.87 \times 10^{-2}$ mole/l.; (d) $[\text{FeCl}_3]_0 = 1.58 \times 10^{-2}$ mole/l.; (e) molar ratio LiCl: A = 0.25:1, $[\text{A}] = 7.87 \times 10^{-2}$ mole/l.; (f) molar ratio LiCl: A = 1:1, $[\text{A}] = 7.87 \times 10^{-2}$ mole/l.; (g) (O) results for a molar ratio LiCl: A = 2:1; (X) results for a molar ratio of LiCl: A = 3:1, $[\text{A}] = 7.87 \times 10^{-2}$ mole/l.; (h) molar ratio LiCl: A = 10:1, $[\text{A}] = 7.87 \times 10^{-2}$ mole/l. At 60°C., $[\text{styrene}] = 2.490$ mole/l.; $[\text{DMF}] = 8.792$ mole/l.; $[\text{AIBN}] = 7.62 \times 10^{-2}$ mole/l.

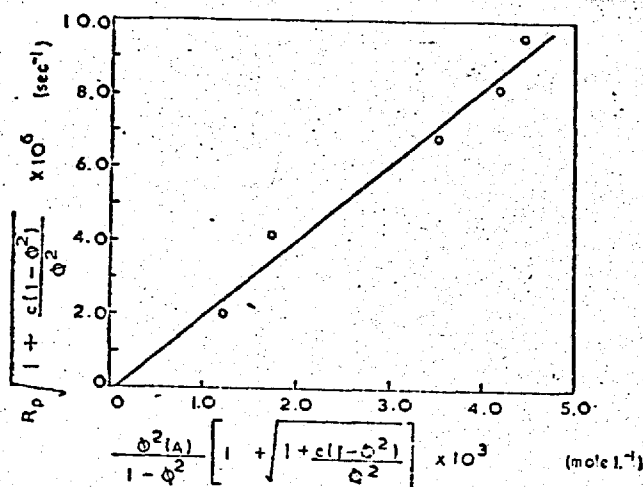


Fig. 2. Kice plot of retardation results with complex A alone. At 60°C., $[\text{styrene}] = 2.490$ mole/l.; $[\text{DMF}] = 8.792$ mole/l.; value of c chosen = 1.0×10^{-6} .

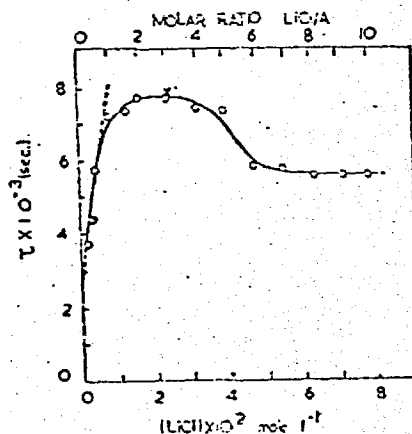


Fig. 3. Induction period τ as a function of added lithium chloride concentration. At 60°C ., $[\text{styrene}] = 2.490$ mole/l.; $[\text{DMF}] = 8.792$ mole/l.; $[\text{A}] = 7.87 \times 10^{-2}$ mole/l.; $[\text{AIBN}] = 7.62 \times 10^{-2}$ mole/l.

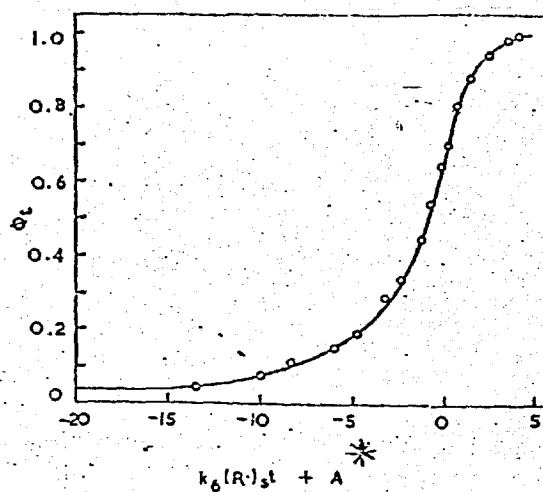


Fig. 4. Reduced rate ϕ_t as a function of reaction time t : (O) experimental points; (—) calculated curve. Molar ratio of LiCl: A = 1:1; at 60°C .; $[\text{styrene}] = 2.490$ mole/l.; $[\text{DMF}] = 8.792$ mole/l.; $[\text{AIBN}] = 7.62 \times 10^{-2}$ mole/l.; $[\text{A}] = 7.87 \times 10^{-2}$ mole/l.; $[\text{LiCl}] = 7.87 \times 10^{-2}$ mole/l.

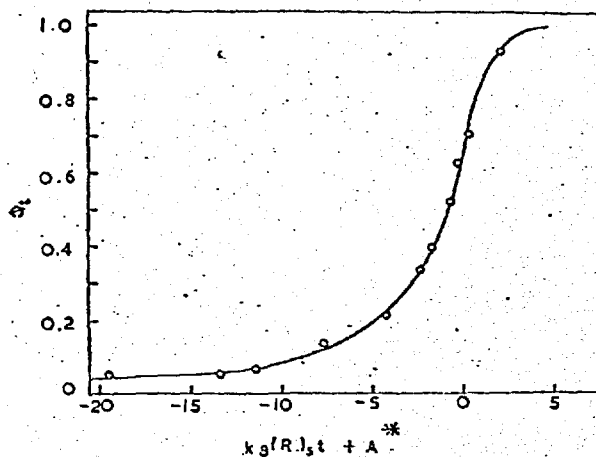


Fig. 5. Reduced rate ϕ_t as a function of reaction time t : (O) experimental points; (—) calculated curve. Molar ratio of LiCl:A = 10:1; at 60°C.; [styrene] = 2.490 mole/l.; [DMF] = 8.792 mole/l.; [AIBN] = 7.62×10^{-2} mole/l.; [A] = 7.87×10^{-3} mole/l.; [LiCl] = 7.87×10^{-2} mole/l.

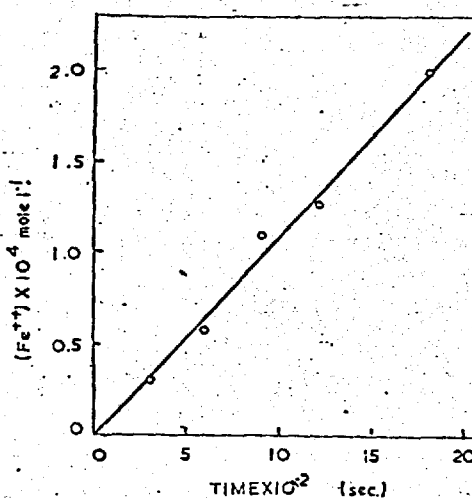


Fig. 6. Concentration of ferrous ions produced during an inhibition period as a function of time. At 60°C.; [styrene] = 2.490 mole/l.; [DMF] = 8.792 mole/l.; [AIBN] = 7.62×10^{-2} mole/l.; [A] = 4.40×10^{-4} mole/l.; [LiCl] = 4.40×10^{-2} mole/l.

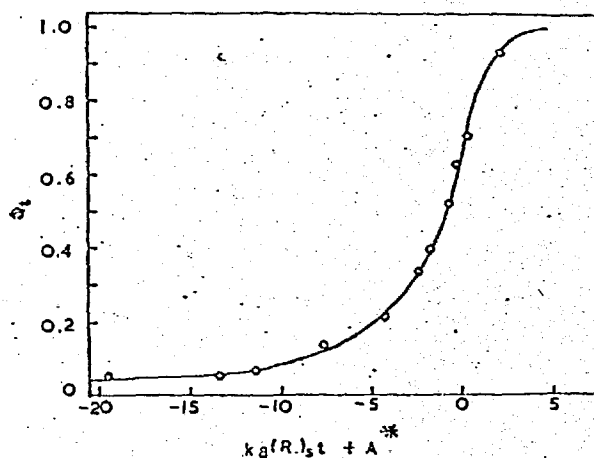


Fig. 5. Reduced rate ϕ_t as a function of reaction time t : (O) experimental points; (—) calculated curve. Molar ratio of LiCl:A = 10:1; at 60°C.; [styrene] = 2.490 mole/l.; [DMF] = 8.792 mole/l.; [AIBN] = 7.62×10^{-3} mole/l.; [A] = 7.87×10^{-3} mole/l.; [LiCl] = 7.87×10^{-3} mole/l.

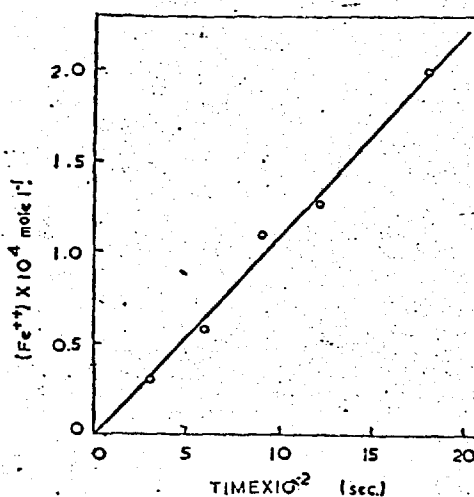


Fig. 6. Concentration of ferrous ions produced during an inhibition period as a function of time. At 60°C.; [styrene] = 2.490 mole/l.; [DMF] = 8.792 mole/l.; [AIBN] = 7.62×10^{-3} mole/l.; [A] = 4.40×10^{-4} mole/l.; [LiCl] = 4.40×10^{-3} mole/l.

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