SOME ASPECTS OF EMULSION POLYMERISATION OF VINYL ACETATE.

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DECLARATION

I hereby declare that this thesis has been written by me and that it is a record of my own research work. It has not been presented in any previous application for a higher degree. All quotations are indicated and the sources of information are specifically acknowledged by means of references.

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THESIS RECOMMENDATION

We hereby recommend that the thesis prepared by Miss L.A. Okolo entitled, "Some aspects of the emulsion polymerisation of vinyl acetate", be accepted in partial fulfilment of the requirements for the degree of M.Sc. Polymer Science and Technology.

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DEDICATION

To my family
for their love.

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ABSTRACT

The emulsion polymerisation of vinyl acetate was investigated using a wide range of sodium lauryl sulphate, (SLS), as emulsifying agent, potassium peroxydisulphate initiation and at two temperatures, 58°C and 6S°C.

Vinyl acetate was found to polymerise appreciably even below the cmc of (SLS). The form of dependence of rate of polymerisation on the exponent of the emulsifier was studied. The rate of polymerisation R_p , was found to show a diminishing dependence on the exponent of the emulsifier concentration contrary to the Sinith-Ewart scheme of ideal emulsion polymerisation of water insoluble monomers. A greater dependence of R on the exponent of the emulsifier concentration was found below the cmc than above the cmc of (SLS). The form of dependence was also affected by temperature. The exponent of the emulsifier concentration increased with temperature below the cmc of (SLS) and decreased with temperature above the cmc of (SLS). This shows that R is less dependent on the $[S_o]$ at increased temperatures.

Viscosity studios were carried out and the intrinsic viscosity was found to be dependent *on* molecular weight and chain branching. The occurence of branching is favoured especially at high temperature. Higher intrinsic viscosity values were obtained for polyvinyl acetate

samples produced below the cmc than above the cmc of (SLS), suggesting that the molecular weight of the polyvinyl acetate samples formed while polymerising vinyl acetate below the cmc of (SLS) as emulsifier are higher than when polymerising above the cmc.

Temperature was found to enhance the occurence of branching hence polyvinyl acetate samples obtained above the cmc are expected to have higher molecular weights at 58°C. The interaction between the polymer and the solvent molecules in the viscosity study were found to be less for polymers produced below the cmc of (SLS) due to the greater molecular weight.

Tests on tensile mechanical properties were also carrie . out on the polyvinyl acetate samples obtained from emulsion polymerisation. These properties were found to be affected by the presence of branches and modification of the macromolecular structures of the polymer. The solvent used was also found to cause some modifications on the polymer structures. The values of the tensile mechanical properties were relatively high. TENSILE strength and initial modulus of the polymers obtained showed opposite trends of variation to that of (%) elongation for different (%) conversion. The observations from the variation of intrinsic viscosity and the tensile mechanical properties showed that these properties are affected by modifications in the polymer chain.

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CHAPTER 1

1.0 I N T R O D U C T I O N

1.1 Poly(vinyl acetate)

Polyvinyl acetate is the product of the polymerisation of vinyl acetate monomer. Vinyl acetate itself, $CH_2=CH-OOCCH_3$, is the acetic acid ester of vinyl alcohol, a simple aliphatic olefinic alcohol and can be prepared by the addition of acetic acid to acetylene.

$$CH \equiv CH + CH_3COOH \longrightarrow CH_3COOHC = CH_2$$

The above reaction can be carried out either in the liquid or vapour phase. Vinyl alcohol does not exist in its free state as it isomerises to acetaldehyde. The low cost of vinyl acetate has made it the principal vinyl monomer of commerce. Vinyl acetate hydrolyses readily when treated with acid or alkali to give acetic acid (or sodium acetate) and acetaldehyde (1). The rate is slowest at pH 4.44 in an aqueous system.

1.1.1 Structure and physical properties of poly(vinyl acetate).

Polyvinyl acetate is an amorphous thermoplastic polymer. The X-ray diagrams of commercial polyvinyl acetate indicate that the polymer does not crystallize (1). Although a patent was issued for the manufacture of crystallizable polyvinyl acetate (1), the experimental work could not be verified (1). Another patent claimed

polyvinyl acetate with 5% crystallinity and the crystallizing capability of polyvinyl acetate is influenced by the precipitating solvent during purification step (1). Polyvinyl acetate is isomeric with poly(methyl methacrylate). Industrially prepared polyvinyl acetate is branched because of the transfer reaction usually conducted to 100% conversion (1). Unbranched polymer can be prepared by polymerisation at low temperatures ($< 50^{o}C$). Side groups have an influence on the various properties of the polymer. Polyvinyl acetate is neutral and non corrosive and softens between 35 - $50^{o}C$ (1). The glass-transition temperature (Tg) of medium molecular weight polyvinyl acetate is $28^{o}C$ (1). Most commercial grades have broad molecular weight distribution and excellent adhesion to surfaces due to the highly polar acetate groups on the polymer and to the unique combination of viscosity, tensile strength, tack and other properties existing during application, formation and ageing of the bond (1).

1.2 Vinyl Polymerisation.

The generally accepted mechanism of vinyl polymerisation involves a chain growth reaction in three distinct steps viz initiation, propagation and termination. Polymerisation reactions are commonly classified

on the basis of the nature of the propagating chain as:

(i) Free radical polymerisation
(ii) Anionic polymerisation
(iii) Cationic polymerisation
(iv) Coordinated anionic polymerisation.

Bacon (2) observed that an oxidation-reduction reaction could efficiently initiate polymerisation. Such reactions are called redox polymerisation reactions. They are characterised by a short induction period, comparatively high molecular weight and high polymer yield.

Free radical polymerisation is very important in the polymerisation of vinyl monomers. In the course of reaction at any instant, the reaction mixture consists of unreacted monomer and high molecular weight polymer. A very small proportion of polymer is undergoing rapid increase in molecular weight by propagation mechanism. However, the mixture may in its essential physical features, be described as a combination of monomer and high molecular weight polymers. Moreover, the high molecular weight polymer does not undergo further growth in the normal course of events. Free radical polymerisation is initiated by a reactive species ($R_\cdot$) produced from some compound (I) termed initiator or catalyst in a typical reaction such as:

$$I \xrightarrow{k_d} R_\cdot$$

where k_d is the rate constant for the initiator dissociation. The reactive species as in the above example are called free radicals. They add to a monomer (M) molecule by opening the π-bond to form a new radical in a step such as:

$$R. + M \xrightarrow{k_i} M_1^{\cdot}$$

in which k_i is the rate constant for the initiation step.

The monomer free radical adds to another monomer molecule to develop a polymer radical over the propagation steps typically represented as:

$$M_1^{\cdot} + M \xrightarrow{k_p} M_2^{\cdot}$$
$$M_2^{\cdot} + M \xrightarrow{k_p} M_3^{\cdot}$$
$$Mn. + M \xrightarrow{k_p} Mn+1$$

Here, k_p is the rate constant for the propagation step.

Polymer growth is terminated at some point by destruction of the reactive centre or free radicals by an appropriate reaction depending on the type of reactive centres and the particular reaction conditions. Possible reactions leading to termination of free radicals are:

$$\text{(i)} \quad Mn\cdot + Mm\cdot \xrightarrow{k_{tc}} Mn+m \quad \text{(dead polymer)}$$

This involves combination of two radicals and is known as termination by combination and

(ii) $M_n \cdot + M_m \cdot \xrightarrow{k_{td}} M_n + M_m$ (dead polymers)

which is termination by disproportionation and involves the transfer of a hydrogen radical to another radical center. From these reactions, k_{tc} and k_{td} are rate constants for termination by combination and disproportionation respectively. The chain nature of the process resides in the propagation step and monomer disappears by both initiation and propagation reactions. Their rates are given respectively as

$$R_i = 2k_d f [I] \qquad ...(1 - 1)$$

$$R_p = k_p [M\cdot] [M] \qquad ...(1 - 2)$$

The rate of termination, R_t, is given as

$$R_t = 2k_t [M\cdot]^2 \qquad ...(1 - 3)$$

The rate of monomer disappearance is assumed to be equal to the rate of polymerisation provided monomer does not escape by other means e.g. evaporation. To a very close approximation, the rate of polymerisation is given as

$$\frac{-d[M]}{dt} = k_p [M\cdot] [M] \qquad ...(1 - 4)$$

where $[M]$ is monomer concentration and

$[M\cdot]$ is the total concentration of all chain radicals.

From the steady state assumption (3) that the concentration of radicals increases initially, but almost instantaneously

reaches a constant steady-state value, it can be stated that $R_i = R_t$

$$R_i = 2k_t [\dot{M}]^2 \qquad \ldots.(1 - 5)$$

$$[\dot{M}] = \left[R_i/2k_t\right]^{\frac{1}{2}} \qquad \ldots.(1 - 6)$$

Equation (1 - 4) thus becomes

$$R_p = k_p [\bar{M}] \left[R_i/2k_t\right]^{\frac{1}{2}} \qquad \ldots(1 - 7)$$

for the rate of polymerisation.

Free radical polymerisation also exhibits a set of reactions known as chain transfer reactions due to radical displacement. The reaction can generally be depicted as

$$Mn. + XY \xrightarrow{k_{tr}} Mn - X + Y.$$

in which k_{tr} is chain transfer rate constant

X is species transferred and

Y. is the new radical which reinitiates polymerisation as

$Y. + M \xrightarrow{k_a} M.$ in which k_a is the reinitiation rate constant.

The rate of a chain transfer reaction is given by

$$R_{tr} = k_{tr} [\dot{M}] [\bar{XY}]$$

Chain transfer reactions result in a decrease in the degree of polymerisation, $(\bar{X}n)$, and molecular weight of the polymer(4). If the rate of re-initiation is slower than that of the original propagation rate, there is a decrease

in the rate of polymerisation (4). Free radical polymerisation can be carried out in bulk, solution, suspension or emulsion.

1.3 Emulsion Polymerisation.

Emulsion is used to describe a dispersion usually of colloidal size of one liquid phase in another. Emulsion polymerisation refers to a unique multiphase process employed for the polymerisation of monomers in emulsion. Emulsion polymerisation is different in its mechanism and reaction characteristics from other polymerisation processes. It differs from suspension polymerisation in the type and size of the particles in which polymerisation occurs and in the kind of initiator employed. Thermal dissipation and high viscosity and therefore difficulty of controlling the polymerisation reaction, as well as the occurence of branching at high polymer-monomer ratios, which can lead to insolubilisation, have made bulk polymerisation unattractive industrially. The low viscosity in emulsion polymerisation facilitates agitation and heat transfer, and the transfer of materials through pumps and pipelines. The physical state of the emulsion system makes it easy to control the process and in most cases, relatively low polymerisation temperatures (0 - 80^{o}C) are involved. It lends itself to easy continuous operation, and high rates of polymerisation can be obtained simultaneously with high

degree of polymerisation and at low temperatures.

The mechanism of emulsion polymerisation is based primarily on the qualitative treatment of Harkins (5a, 5b) and the quantitative treatment of Smith and Ewart (6) and Haward (7). According to Harkins (5_a), an "id al" system contains a dispersing medium (water), a water-insoluble monomer, emulsifier, and a free-radical initiator. For this system in dilute aqueous solution at concentrations above its critical micelle concentration, cmc, the emulsifier molecules aggregate together to form micelles (5a). The micelles are spherical with the hydrophobic portion of each molecule directed towards the centre of the micelle (8). Addition of a water-insoluble or slightly water-soluble monomer to this mixture with agitation, leads to the monomer being dispersed as monomer droplets. After initiation, polymerisation inside the micelles proceeds rapidly and the latex particles grow rapidly from within. The emulsifier is adsorbed on the surface of the growing latex particles and functions as a stabilizer preventing the flocculation of the latex particles. After about 10 - 20% conversion to polymer, no micelles are left due to reduction of the emulsifier concentration, $[S_o]$, in the aqueous phase to below the cmc (8). Further polymerisation thus occurs inside the growing latex particles which are continuously supplied with monomer by diffusion through the aqueous

phase from monomer droplets. Hence, there is a gradual decrease in the quantity of the monomer until at about 60% conversion where they disappear completely into the latex particles (8). The monomer in the latex particles is gradually used up and the reaction rate will gradually fall off and polymerisation will cease completely when all monomer in the particle is consumed. In most cases, an emulsion polymerisation is taken to 100% conversion or as near as 100% as can be achieved as in styrene and vinyl acetate. Commercial polymerisation of vinyl acetate does not however exceed about 70% due to chain transfer reactions leading to branching (1).

Deviations from this mechanism are caused by such effects as monomer solubility, emulsifier type, particle size control, retarders, and inhibitors.

Smith and Ewart (6) and Haward (7) gave the developed mechanism by Harkins (5a,b) a more quantitative basis. An emulsion polymerisation follows the same kinetic laws as have been established for vinyl polymerisation. Smith and Ewart (6) were able to show that for the ideal case, a particle contains either one or no free radical. Thus the average number N, of radicals per particle is $\frac{1}{2}$. If N is the total number of particles per litre, then

$$R_p = Nk_p [M]/2N_A \quad \text{where}$$

N_A is the Avogadro number

Over a very large part of the polymerisation the $[\bar{M}]$ in the particle is constant and hence, at a given temperature, Rp depends only on the number of growing particles present. Smith and Ewart (6) therefore concluded that Rp and average number degree of polymerisation, $(\bar{X}_n)$, are directly proportional to N. The number of growing particles is in turn proportional to the initiator and emulsifier concentrations and therefore:

$$N \propto [\bar{I}]^{0.4} \quad \text{and}$$
$$N \propto [S_o]^{0.6}$$

Thus $Rp = k_i [I]^{0.4} [S_o]^{0.6} [\bar{M}]$

where $[I]$ is the initiator concentration

$[S_o]$ is the emulsifier concentration

$[\bar{M}]$ is the monomer concentration

1.4 Factors affecting Emulsion Polymerisation.

1.4.1 Temperature:

A polymerisation temperature is often chosen mainly because temperature of experiment determines the ability to control the experiment and also because the initiator system used gives optimum efficiency at a particular temperature. Temperature also has some influence on the macromolecular structure of the product. From the kinetic point of view it is readily appreciated that the temperature will affect the rate of polymerisation which appears in the

equation:

$$R_p = k_i [I]^{0.4} [S_o]^{0.6} [M]$$

An increase in temperature is expected to cause:

(i) an increase in the rate of generation of radicals.

(ii) an increase in the rate of flux of radicals diffusing into the particles

(iii) a favour of the rate of diffusion of monomer to the latex particles and the amount contained by the swollen particles.

(iv) an increase in the number of micelles produced by the emulsifier and thus increase in the number of latex particles.

The overall result of the increase in temperature in an ideal emulsion polymerisation is to increase Rp and reduce the average number degree of polymerisation ($\bar{X}_n$) i.e. molecular weight of the polymer formed. Other side effects encountered are usually peculiar to the initiator system employed and the monomer being polymerised (8). These include instability of emulsion resulting in occurence of preflocculation, coagulation or change in viscosity; production of crosslinked, branched, and gelled polymers; change in structure of polymer and molecular weight distribution; effect on efficiency of chain transfer.

1.4.2 Agitation.

Kinetically a constant agitation pattern is assumed. Usually, only sufficient agitation to keep the monomers and other constituents suitably dispersed is required. An increase in agitation may increase the overall rate of reaction and a lowering of $(\overline{X}_n)$. This is due to the effect of agitation on the rate of diffusion of monomer and on the mass transfer and dispersion of the other ingredients (1). The most important influence of agitation is probably on the apparent chain transfer coefficient of modifying agents (8). However, it has been reported that agitation does not affect the rate of emulsion polymerisation of vinyl acetate above a sufficiently high rate of agitation (1). In the solution polymerisation of vinyl acetate with $K_2S_2O_8$ as initiator, it was found that stirring did not affect the rate (1). However, in an otherwise identical emulsion polymerisation, it was found that the $(\overline{X}_n)$ of the resulting polyvinyl acetate increased substantially when the rate of agitation was increased (9). Violent stirring however causes a decrease in the rate of polymerisation (10).

1.5 Major Recipe Constituents.

1.5.1 Emulsifiers:

The choice of emulsifier is probably one of the most important factors involved in a recipe. An emulsifier must produce a stable emulsion between the monomer and

water phases and later a stable latex. It must not interfere adversely with the initiation system or the propagation reaction. It must impart no adverse properties to the product since the emulsifier residue will remain in the product recovered after polymerisation. The different types of emulsifiers are classified, according to the nature of the hydrophilic groups into (8).

(i) Anionic emulsifiers: examples include the alkali salts of the organic carboxylic acids with chain lengths usually between C_{12} and C_{18} commonly referred to as soaps, and most effective at pH between 9 and 11. Alkyl sulphates and alkyl lauryl sulphonates are also used frequently. Their molecules do not possess any easily hydrolyzable groups, hence their pH range of activity runs from the alkaline to the fairly acid ends of the scale. They are good emulsifiers for most polymerisations and latexes prepared with them are stable towards pH changes. These surfactants are very often employed as secondary emulsifiers and stabilizers.

(ii) Cationic emulsifiers: salts of amines, quartenary ammonium salts fall into the group. Their range of activity lies on the acid side of the pH scale. They are unstable in alkaline media.

The rate of polymerisation obtained with them are normally slow and the latexes have poor stability.

(iii) Non-ionic emulsifiers: e.g. esters of polyalcohols (pluronic polyols) (11). Their non-ionic character makes them substantially insensitive to pH changes. Some appear to function in slightly acid media. Polymerisation proceeds slowly in their presence alone but a great improvement in the rate and latex stability results from using them in combination with anionic emulsifiers (11).

1.5.1.1 Role of the emulsifier.

(i) The emulsifier takes an increased amount of monomer into the water phase due to solubilisation in the micelles.

(ii) Emulsifies non solubilized monomer into fine stable droplets.

(iii) Protects latex particles against coagulation during and after polymerisation.

If a hydrophilic monomer is added to an aqueous solution of emulsifier then the monomer becomes mixed with the water by solubilisation and emulsification. The former is the uptake of the monomer into a thermodynamically stable

solution in the emulsifier solution. The latter is the dispersion of the monomer phase into very fine droplets, with emulsifier molecules at the interface of the organic and the water phases. The hydrophobic part of the emulsifier molecule is directed towards the inside of the organic phase, while the hydrophilic portion is in the water. A very important characteristic of an emulsifier is its critical micelle concentration, cmc. Temperature increase causes the cmc to increase slightly since the kinetic energy of the ions will be increased (8). Addition of electrolyte or alcohol to the aqueous phase can cause the cmc to fall but usually improves the solubilising activity of an emulsifier (8).

1.5.1.2 Effect of Emulsifier concentration on Polymerisation.

In most cases, no polymerisation of significance is expected to occur below the cmc of the emulsifier especially for the ideal system proposed by Smith and Ewart (6). But vinyl acetate polymerises at an appreciable rate even in the absence of an emulsifier. In the ideal system proposed by Smith and Ewart (6) they found Rp to be proportional to $[S_o]^{0.6}$. Bovey et al (12) experimentally found Rp to be proportional to the square root of $[S_o]$. Duck et al (13) found that in the case of versatic acid soaps used in a cold styrene-Butadiene-Rubber recipe, Rp α 0.5 power of what they termed soap concentration. The influence of $[S_o]$ and kind of emulsifier on the emulsion polymerisation of some

vinyl monomers were investigated(1). It was found that Rp of styrene and methyl methacrylate increased with increasing $[S_o]$, but that for acrylonitrile, methyl acrylate and vinyl acetate Rp went through a maximum and decreased at high $[S_o]$. Izumi et al (14) studied the role and effect of emulsifiers in the emulsion polymerisation of acrylonitrile compared with a typical emulsion polymerisation and observed that the emulsifier is usually effective at concentrations below the cmc and that the $(\bar{X}_n)$ does not always increase with increasing concentration of emulsifier although Rp increases.

Carr et al (15) studied the rate of emulsion polymerisation of butadiene-styrene (75:25) as a function of the amount and kind of emulsifier used. Commercial and pure soaps were used. They concluded that certain substances in the commercial soaps acted as retarders which decreased the hourly rate of conversion in direct proportion to the amount of these retarders present. The pure soaps gave a small rate of conversion the highest being of the order of 43 - 45% after 12 hours and even after increasing the soap concentration only 58% conversion was obtained after 12 hours as compared to 72% conversion for the commercial soaps. They therefore concluded that the pure soaps are not as suitable as the commercial soaps. Interesting investigation on the effect of emulsifier addition on the course of the polymerisation of styrene in certain cases have been reported by Medvedev

and coworkers (16). With alkyl sulphonate soaps and azobisisobutyronitrile (AIBN), peroxydisulphate initiation at 40 - 50°C, and at $[S_o]$ which give complete soap coverage of the particles, addition of further emulsifier at conversion below 50% resulted in an increased Rp proportional to the extra amount of emulsifier added. At high initial $[S_o]$ which would result in the surface of the particles being saturated with soap, no increase in Rp occured on addition of further soap during the reaction. In some cases, with high initial soap concentration, a reduction in Rp was observed on further addition of emulsifier. Medvedev (16) thus proposed that the polymerisation occuring in a latex actually takes place in the soap layer on the particle or in a zone close to the surface of the polymer particles. The size of the latter remains constant during the process and is determined by the initial $[S_o]$. Lazor (17) studied the effect of the emulsion polymerisation of vinyl chloride initiated by the redox system $K_2S_2O_8$ - Na_2HSO_3 below the cmc of emulsifier. He found that the number of latex particles, N, in unit volume depends principally on the $[S_o]$ and to a lesser extent on the persulphate and bisulphite concentrations. Peggion et al (18) made an extensive study of the effect of the type and concentration of emulsifier on the number of latex particles, N, produced at fixed temperature and $K_2S_2O_8$ concentrations in the emulsion polymerisation of vinyl chloride. It was found that N increased considerably on an increase in soap

concentration and on the type of emulsifier. They also observed that Rp became practically independent of $[S_o]$ when the latter is higher than the cmc. Some workers(19), made extensive studies on the emulsion polymerisation of vinylidene chloride in which was determined the influence of $[I]$ and $[S_o]$, coalescence of polymer particles, and rate of stirring on the reaction rate below the cmc of emulsifier. Three different stages of reaction were identified from the conversion - time curves. The first stage of polymerisation gave a nearly constant polymerisation rate depending on $[S_o]^{0.6}$ and $[I]^{0.5}$ almost obeying the Smith - Ewart equation. Stage II was characterised by a sharp decreasing of Rp occuring at an extent of reaction that depended on the $[S_o]$. A strong coalesence of the monomer droplets was also observed just before the lowering of Rp. Stage III showed an increase in Rp which reached a value that depended on the first power of $[I]$ and does not depend on $[S_o]$. These results do not agree with what one would expect from the Smith - Ewart theory. Okamura and Motoyama (10) studied the emulsion polymerisation of vinyl caproate which resembles vinyl acetate in the reactivity of radicals and styrene in the solubility of water. In addition, they carried out the emulsion polymerisation of styrene in aqueous methanol thereby increasing its solubility to about 2%. From their results, $Rp \propto [S_o]^{0.6}$ for vinyl caproate obeying Smith - Ewart

equation and for styrene the resulting Smith - Ewart equation had a small exponent i.e. $Rp \alpha [S_o]^{0.2}$. They therefore concluded that the main factor in the emulsion polymerisation behaviour of vinyl acetate is the water solubility of the monomer. Brodynan et al (20) studied the emulsion polymerisation of methyl methacrylate and found the dependence of rate on $[S_o]$ to be 0.4 power. It was recently pointed out that the Rp of vinyl acetate in emulsion is very much affected by the kind of stabilization i.e. electrostatic (anionic emulsifier) compared to steric (polyvinyl alcohol) (21). In the peroxydisulphate initiated aqueous polymerisation of vinylacetate for example, anionic surfactants increase both the number of latex particles, N, formed and Rp. Cationic surfactants, in contrast, normally reduce both N and Rp. In the investigation of the influence of $[S_o]$ and kind of emulsifier on some vinyl monomers, it was reported that for styrene, $Rp \alpha [S_o]^{0.6}$, for vinyl acetate with anionic soap, $Rp \alpha [S_o]^{0.0}$ and with non-ionic soap $Rp \alpha [S_o]^{0.6}$. This last result was due to the retardation with increasing non-ionic $[S_o]$ since the reaction took place in the water phase (1). Fagbehingbe (22) concluded from her studies on the emulsion polymerisation of vinyl acetate at three different temperatures using $K_2S_2O_8$ initiation and sodium lauryl sulphate (SLS) emulsifier that $Rp \alpha [S_o]^{0.4}$ at 55°C, $Rp \alpha [S_o]^{0.28}$ at 60°C and $Rp \alpha [S_o]^{0.05}$ at 65°C. Fache (23) also carried out

emulsion polymerisation of vinyl acetate at three different temperatures using $K_2S_2O_8$ below and above the cmc of (SLS). He studied the form of dependence of the $[S_o]$ on Rp below and above the cmc of (SLS) and concluded that the mechanism deviated clearly from the Smith - Ewart (6) equation. The form of dependence also increased with temperature below the cmc and decreased with temperature above the cmc of (SLS).

1.5.1.3 Effect of $[S_o]$ on particle size of latex.

As the $[S_o]$ is decreased, the number of latex particles formed is decreased (8). Kinetically this should lead to an increase in the particle size. French (11) studied the emulsion polymerisation of vinyl acetate using $K_2S_2O_8$ and pluronic polyols as emulsifier and found that the particle size decreased with increasing $[S_o]$. The number of polymer particles however remained constant although the monomer had completely diffused into the polymer particles before 15% conversion, so that no separate monomer droplets existed. Electron-microscope observation of latexes produced by the polymerisation of vinyl acetate in water showed that in the absence of surfactants the particles produced are large (0.1 - 1.0 u in diameter), and their size distribution is narrow (24). In most emulsion polymerisation reactions a spread of particle sizes results, ranging from very small to some large particles, with the bulk of the particles

having diameters closer to the mean value (8). Distribution of particle sizes can vary from very narrow to very broad and depend on the many factors and conditions which are prevalent during the reaction (8). Not the least of these is the type of emulsifier or mixture of emulsifiers employed, together with $[S_o]$ and the manner of addition i.e. all initially, in increments, or continously during polymerisation (8). Dunn et al (25) using the theory of colloid stability to evaluate the mechanism of particle formation in aqueous vinyl acetate solution observed that dispersion prepared in the absence of sodium dodecyl sulphate emulsifier were mono-disperse, while those prepared with emulsifier at high ionic strength were polydisperse.

1.5.1.4 Latex Stability.

The emulsifier type and amount used constitute the main factors in latex stability. Emulsifier type is governed to a great extent by the nature of the monomers being polymerised, the temperature, and the initiator system involved. The choice of emulsifiers is wide. While some impart good stability alone, others require additional stabilizers in order to achieve satisfactory results. Agglomeration, flocculation, and coagulation are known to occur in a latex for some or all of the following reasons, (i) insufficient emulsifier which leads to agglomeration to re-establish equilibrium (ii) effect of pH (iii) presence of alcohols; and (iv) temperature variation i.e. too high or too low temperatures render the emulsifier ineffective and cause instability (8).

1.6 Initiator Systems.

All systems used commercially are based on the liberation of an active free radical produced either by:

(i) a chemical interaction: e.g. peroxidic compounds which are strongly oxidising In the presence of a reducing agent, decomposition of the peroxide is enhanced. Such systems are "redox" systems and they allow a convenient generation of free radicals at lower temperatures (12).

$$H_2O_2 + Fe^{2+} \longrightarrow HO. + HO^- + Fe^{3+}$$

This involves the transfer of one electron.

(ii) Thermal decomposition of a compound into free radicals. Many different types of organic and inorganic compounds will undergo homolytic decomposition on heating to yield free radicals e.g. peroxides, peroxydisulphate ion widely employed in emulsion polymerisation. The ion may be in the Na, K or NH_4 salt. It decomposes thermally to give sulphate ion-radicals as initiating species

$$S_2O_8^{2-} \longrightarrow 2SO_4^-$$

Systems which are to be useful in initiating an emulsion polymerisation should produce the free radicals throughout the polymerisation

and this is achieved by the heat applied during the decomposition.

1.7 Retardation and Inhibition.

Retardation is a slowing down of Rp throughout the reaction by some substances known as retarders. Inhibition of the polymerisation is manifested by an induction period or interruption period by an inhibitor if present at the beginning or after polymerisation respectively. An inhibitor traps free radicals and either destroys them or prevents them from getting to the locus of polymerisation or produce by transfer another free radical which is not active (8) e.g. hydroquinone, benzoquinone. Too high a production of free radicals in the initial stages of a polymerisation can itself give a retarding or inhibiting effect owing to the mutual destruction of radicals or production of inactive radicals such as $RO\dot{O}$ (8). In peroxydisulfate and peroxide initiation systems, the presence of oxygen has an inhibiting effect on the emulsion polymerisation of many monomers. With other monomers and other initiating systems, oxygen can act as a promoter. It would appear that the effect of oxygen depends very much on conditions and environment, and competing effects which may be present. Generally it is advisable to keep air from an emulsion polymerisation reaction.

1.8. Monomers.

Not all vinyl monomers are polymerisable by the use of free-radical initiators in an emulsion system. Monomers bearing relatively electro-negative substituents attached directly to the ethylene nucleus are polymerised best by free-radical catalysts e.g. vinyl monomers like styrene, methyl methacrylate, vinyl acetate, nitrile. Monomers which possess relatively electro-positive groups normally respond better to ionic catalysts e.g. dialkyl olefins, vinyl ethers (8). The solubility of the monomer in water or its reactivity with water is also an important characteristic. Generally, monomers which are water-soluble do not polymerise well according to the emulsion mechanism since, in such a case, far too much polymerisation occurs in the aqueous solution, instead of in the micelles (8). The behaviour of a monomer in an emulsion polymerisation is determined by its solubility in water, the solubility of the polymer in the monomer, as well as the polymerisation properties of the specific monomer (1). If the monomer is partly soluble in water a certain number of monomer molecules are already available for conversion to polymer in the water phase. Also, the solubilizing effect of the emulsifier on the monomer becomes less important than its stabilizing effect. Vinyl acetate can be polymerised in the presence of protective colloids which have little or no solubilising effect e.g. polyvinyl alcohol and reaction proceeds mainly along the lines of the ideal mechanism (1). There is a

great difference between the kinetics of styrene and vinyl acetate that can be explained by their different water solubility (10). Solubility of vinyl acetate has been reported to be 2.1% at 50°C and 3.5% at 70°C (10). A systematic study of vinyl acetate in emulsion was taken (1) in the manner of Smith (26). A constant Rp over 80% of the conversion range was found. The kinetic data was summarised as

$$\frac{-dm}{dt} = k \times N^{0.15} \times [I]^{1.0}$$

where N is the number of particles

$[I]$ is the initiator concentration

No dependence was found on $[S_o]$ in this system suggesting that the polymerisation must have taken place almost exclusively in the aqueous phase where vinyl acetate is dissolved(1). The concentration of the monomer remains constant as long as a free monomer phase is present. After the polymer fraction is large enough to absorb the monomer, the rate will decrease because the monomer will not be replenished in the particle.

1.9 Polymer Characterisation.

1.9.1 Viscosity

Viscosity is the property of liquids and gases by virtue of which they resist relative motion between adjacent parts within them or between them and adjacent

bodies. Solution viscosity is basically a measure of the size or extension and conformation in space of polymer molecules. For dilute polymer solutions, the viscosity is influenced primarily by the properties of isolated single chains surrounded by solvent, or by several chains interacting with each other. Viscosity is of importance in that:

(i) It determines the forces which are to be overcome when fluids are subjected to shear e.g. in pumps, bearings. A polymer molecule is normally regarded as a connected sequence of segments hence the motion of a chain molecule which is subjected to a shearing distortion requires cooperative displacement of its segments. The larger the number of segments, the larger the resistance to motion.

(ii) It determines, under any one particular set of conditions, whether the viscous or the turbulent regimes of flow will obtain in a system. In this way viscosity determines the particular set of physical laws which will apply in problems of flow, heat transfer, mixing of materials, and similar phenomena.

(iii) Being a property which is greatly affected by the shape, size and co-ordination numbers

of molecules, the viscosity of liquids and gases have proved a useful tool in physical chemistry. For instance it affords a means of estimating an average molecular weight for linear polymers in solution and for obtaining information about the molecular weight distribution in the polymer, and sometimes indicates modifications such as presence of branching in polymers.

In addition, the flow behaviour of concentrated solutions, and in particular, undiluted polymer samples is of considerable practical importance to the polymer fabricator and manufacturer. The industrial technology of polymers is intimately dependent on the rheological properties of polymer samples in flow. Therefore, the measurement of polymer flow characteristics and a study of the molecular features of the polymer which control these properties has become an important part of research and development of new or improved polymer samples.

For calculating the forces and power involved in flow and for physical chemistry studies, the dynamic viscosity, (η), is of prime significance. In the field of high polymer viscometry the following functions of (η) and quantities describe the experimental data:

(η)	dynamic viscosity
(η/ρ)	kinematic viscosity
$\eta_{rel.} \equiv (\eta/\eta_o)$	relative viscosity
$\eta_{sp} \equiv (\eta/\eta_o) - 1$	specific viscosity
$(\eta_{sp/c})$	reduced viscosity
$\ln(\eta_{rel./c})$	inherent viscosity
$\lim_{c \longrightarrow 0}(\eta_{sp/c})$ =	intrinsic viscosity

where ρ is density of solution

(η_o) is viscosity of the solvent and

c is concentration in $g.dl^{-1}$ of solution.

The quantity of primary interest in dilute solution polymer characterisation is the intrinsic viscosity, $[\eta]$. This quantity can be regarded as the fractional increase in the viscosity of unit volume of solvent due to the addition of 1g. of non-interacting polymer molecules (27). In order to eliminate the influence of intermolecular interactions, $[\eta]$ is found by extrapolating either $(\eta_{sp/c})$ or $\ln(\eta_{rel/c})$ to zero concentration (27). If these quantities depend on the rate of shear, it is also necessary to extrapolate to zero rate of shear (27). For chemically homogeneous linear polymers, the most important relationship between the $[\eta]$ and the molecular weight is the empirical

Mark-Houwink-Sakurada equation (27).

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

For a given polymer-solvent system, K' and α are constants at a given temperature. Since the above equation is empirical, values of M must be obtained by some absolute metho in order for K' and α to be determined. The validity of the pair of constants is restricted to the range of values of M used in the calibration. If a polymer sample is not a mono-dispersed fraction, the value of the molecular weight calculated by using the Mark-Houwink-Sakurada equation is called the viscosity average molecular weight represented as $\bar{M}_v$. The exponent α is less than unity with the result that the $\bar{M}_v$ will lie between the number and weight average molecular weight viz $\bar{M}_n < \bar{M}_v < \bar{M}_w$. The Mark-Houwink-Sakurada equation is only valid for linear polymers and therefore has little meaning for non-linear or branched polymers. The use of viscosity measurements to obtain the molecular weight is greatly complicated by:

(a) The influence of the molecular weight distribution of the sample.

(b) The occurence of branching (include the type and the extent).

(c) The existence of a compositional and sequential distribution of segments.

(d) The existence of aggregates and entanglements between chains.

1.9.2 Viscosity Measurements.

The basis for the popularity of viscosity measurements lies in the practical areas of the convenience of the measurements and the relatively inexpensive nature of the apparatus required as compared with other methods such as light scattering and osmotic pressure although viscosity methods rest on a shakier theoretical foundation. In general there are two main classes of viscometric measurements:

(i) The absolute methods are those in which $[\eta]$ is explicitly derived from the geometry of the apparatus, the observed rate of flow, and the measured forms involved in the flow.

(ii) The relative methods are those in which the viscosity of the fluid under test is determined by an apparatus calibrated by another fluid of known viscosity. These methods rely on the basic fact that at low speeds the velocity of a smooth, simply shaped body in a liquid or gas is inversely proportional to the dynamic viscosity depending on the conditions of flow. Thus, apparatus is designed to give straight or simple smooth curves for the lines of flow, and the forces producing flow are made as small as convenience and required accuracy will allow.

The viscosities of pure liquids, dilute polymer solutions, concentrated polymer solutions, and undiluted polymer liquids cover a wide range, extending from 10^{-2} poise to 10^{12} poise or greater (27). Consequently, no single method of measurement is available which covers this range. Methods which have generally been employed include capillary and rotational viscometry methods, tensile creep and stress relaxation methods (27).

1.9.2.1 Capillary Viscometry.

Capillary tube methods involve the flow of fluids through capillary tubes, using either an applied pressure or simple gravity flow to drive the fluid through the tube. The capillary viscometers which are made for dilute solution studies are made of glass. Example is the Ubbelohde viscometer which has the advantage of not requiring a fixed volume in the viscometer. The apparatus is calibrated by timing the passage of a standard quantity of a liquid of known viscosity through it, and a calibrations constant is obtained. The intrinsic viscosity, $[\eta]$, is determined using the Huggins equation (27)

$$(\eta_{sp/c}) = [\eta] + k' [\eta]^2 c$$

k' is Huggins constant and has been reported to have a value of $0.3 < k' < 0.4$ for good solvents (27).
Kraemers equation is also often used (27):

$$\ln(\eta_{rel./c}) = [\eta] + k'' [\eta]^2 c, \text{ for which}$$

$$k' - k'' = \tfrac{1}{2}$$

These equations require that a linear relationship exist between ($\eta_{sp/c}$) and c of the solution. The Huggins equation gives information about polymer - solvent interactions, chain dimensions, and branching. For highest precision, the viscosity measurement is made in a constant-temperature bath regulated to at least $\pm$ 0.02°C. The efflux time of the pure solvent is kept long preferably greater than 100 sec. to minimize the need for applying correction to the observed data (27). For accuracy in extrapolating to C = 0, the solution concentration is restricted to the range that gives relative viscosities between 1.1 and 1.5 as this is the narrow concentration range over which the plots either from Huggins or Kraemers equations are often linear.

1.10 Polymer Testing.

1.10.1 Mechanical Properties.

These are the totality of properties determining the response of bodies to external mechanical influences, manifested in the ability of the bodies to develop reversible and irreversible deformations and to resist failure. The basic characteristics of the mechanical properties of solids are normally determined by tests resulting in various deformation - versus - stress dependencies, such as stress - strain. Examination of such dependencies readily brings out characteristics of elasticity, plasticity and strength. The mechanical properties of liquids are assessed by studying the dependence of the rate of strain on the stress applied e.g. viscosity.

However, all these characteristics are insufficient to describe polymeric bodies owing to the specific mechanical properties peculiar to them. The most important of these properties are:

(i) Highly pronounced mechanical relaxation processes (stress, creep), owing to which the mechanical properties of polymers depend strongly on the temperature.

(ii) Ability to develop enormous reversible deformation caused by axial tension, (for instance, as high as several 100%), this ability being the most pronounced in elastomers.

(iii) Intimate connection between mechanical and chemical processes, which affect each other substantially.

The mechanical properties of polyvinyl acetate depend on the molecular weight and its distribution. Tensile properties of polyvinyl acetate unfilled and filled with T_iO_2 showed a strong dependence on humidity, being relatively unaffected at high humidity (8). As the filler content is increased, the stiffness is decreased at a higher humidity.

1.10'.2 Film Deposition Techniques.

A film is a flat section of a thermoplastic resin or a regenerated cellulose material, which is very thin in

relation to its length and breadth and which has a nominal thickness or gauge length not greater than 0.010 in (28). The most important are cellophane and polyethylene (28). Olayemi and Adeyeye (29) have reported the strong dependence of the tensile properties of polyvinyl acetate cast films on solvents used for casting under different conditions of temperature and humidity. They interpreted their results on the basis of the interactions between the solvent molecules and those of the polymer. They concluded that chloroform-produced polyvinyl acetate films had the most constant mechanical properties over the longest period of exposure which depended on the temperature of exposure, decreasing as the temperature increased. Methanol was found to be practically unsuitable while acetone could be used where chloroform is not available. It can therefore be concluded that solvents modify the structure of polymeric films by altering the packaging arrangement of the polymer chains. The effect of the addition of emulsifier and catalysts on the polymer properties in an emulsion polymerisation system for vinyl acetate was studied by Gharapetian et al (30). They observed that as the ratio of completely hydrolysed to partially hydrolysed poly vinyl acetate in the emulsifier was increased, the viscosity of the polyvinyl acetate emulsion decreased and the tensile strength increased for films prepared from the polyvinyl acetate emulsions. Increase in the concentration of the catalyst however increased the viscosity of the

emulsions and the tensile strength for films prepared from the polyvinyl acetate emulsions.

Films are formed by melt extrusion, calendering, chemical regeneration or by solvent casting (28).

1.10.2.1 Film properties and test methods.

Physical properties of plastic films are greatly dependent on the rate of testing, the temperature of testing and on the history of the sample. Films that are ductile with high elongation when elongated at low rates become brittle and shatter at high rates of elongation. A universal tester such as Instron tensile tester is used to measure tensile properties such as yield strength, ultimate elongation, tensile strength at various elongations, modulus and work to rupture. Elongation is important in packaging films and tapes. High modulus is important for the ability to be processed using automatic packaging machines. A packaging films utility is dependent to a great extent on its impermeability or permeability to gases or vapours. The latter is known as the moisture vapour transmission rate (MVTR). The MVTR or gas permeability can be reduced by increasing its thickness or coating with another material. The ASTM E96 - 8 method can be used for testing. This reports the milliliters of gas at STP, or the g of a vapour diffused through the membrane usually per 24 hour and per in of membrane (28).

The resistance of film to various degradative conditions is also an important criterion in selecting a film for a given application. Physical and mechanical properties are highly dependent on the method of manufacture e.g. casting, extrusion or calendering. Cast films have high clarity, and gloss, low gas permeability and MVTR, and are chemically inert. They are extremely tough and have excellent tensile and tear strengths and high elongation. Hayashi et al (31) reported that polyvinyl acetate films prepared by emulsion polymerisation in the presence of $K_2S_2O_8$ catalyst, has a minimum film formation temperature (MFT). Films formed by drying polyvinyl acetate above the MFT is transparent and continous whereas that formed by drying below the MFT is opaque and brittle, since the polyvinyl acetate particles are not fused.

1.11 The Scope of the investigation:

The present study attempts to further clarify the characteristics of emulsion polymerisation of vinyl acetate taking into consideration:

(i) The kinetics of emulsion polymerisation of vinyl acetate using a wide range of sodium lauryl sulphate as emulsifying agent, a constant concentration of $K_2S_2O_8$ as initiator and a constant concentration of monomer at two different temperatures of 58°C and 68°C.

The experiment is meant to study the extent to which the Smith-Ewart theory can be applied to the emulsion polymerisation of vinyl acetate. The form of dependence of rate of polymerisation on the exponent of the emulsifier concentration at the two temperatures is also to be established.

(ii) Variations in the properties of the macromolecular structures of the polyvinyl acetate obtained both below and above the cmc of (SIS) at the two different temperatures using dilute viscosity study.

(iii) Variations in the tensile mechanical properties of the polyvinyl acetate samples obtained both below and above the cmc of (SLS) and low these properties are affected by the macromolecular structures of the various polymer samples.

CHAPTER II

2.0 Polymerisation of vinyl acetate.

2.1 Experimental.

The purity of monomers, diluents, and initiators is of great importance since conversions and molecular weights can be drastically affected by contaminants. This is especially important in polymerisationfor high production (g. polymer/g. initiator/unit time) where low concentrations of initiators are used. The techniques required for purification depend on the monomer to be polymerised and nature of the contaminants present (1). A combination of chemical or physical treatments and a high efficient distillation is generally used to remove impurities. Purified reagents are stored under conditions designed to maintain the desired level of purity.

2.1.1 Materials.

The monomer, vinyl acetate was supplied by British Drug House (BDH) chemicals Ltd. Poole England. It was of the reagent grade and was further purified by distillation at $46^{o}C$ under reduced pressure. The purity of the distillate was tested by treating samples of it with sodium hydroxide solution in a separating funnel. The absence of a yellow coloration indicated absence of the hydroquinone inhibitor. The distillation was also believed to remove any other impurities present. The purified monomer was then stored in a refrigerator until it was needed.

The initiator, potassium peroxydisulphate ($K_2S_2O_8$), the buffer di-potassium hydrogen orthophosphate (K_2HPO_4), and the emulsifier sodium lauryl sulphate ($C_{12}H_{25}OSO_3Na$) were all also supplied by BDH. They were specially pure grades and were used without further purification.

The nitrogen gas used was purified by passing it through alkaline pyrogallol to absorb any oxygen or air present and then through distilled water to remove soluble substances and then dried over calcium chloride.

2.1.2 Apparatus.

A five-necked 1l reaction kettle, a condenser, a monomer dropper, beakers, stirrer and a constant temperature water bath were all used for the polymerisation experiments.

2.1.3 Procedure.

Polymerisations were carried out at two different temperatures, 58°C and 68°C, in a constant temperature water bath. A range of sodium lauryl sulphate concentrations, three below and three above the cmc, were used. A suitable concentration of each of initiator and vinyl acetate was used throughout for the study. The kinetics of the emulsion polymerisation of vinyl acetate was studied. Recipes for the polymerisations are given in tables 2.1

and 2.2. The reaction mixture with the exception of the monomer was introduced into the five-necked reaction kettle. It was stirred with the aid of a metal stirrer attached to the reaction kettle to allow the initiator to dissolve. A condenser was attached to another inlet of the reaction kettle. The kettle was then allowed to attain the bath temperature while stirring and at the same time flushing and eventually blanketing it with a stream of the purified nitrogen gas. The monomer was then introduced within 30 seconds into the reaction mixture from a monomer dropper. Polymerisation was allowed to take place and the course of the polymerisation reaction was followed by taking aliquots of $25cm^3$ from the mixture at suitable intervals. The reaction was stopped by introducing each aliquot into a cold saturated solution of sodium chloride. The solid which separated out was washed thoroughly in large quantities of distilled water to remove traces of contaminants. The clean product was filtered, air dried at first and then dried in a vacuum oven at $40^{\circ}C$ to a constant weight. The polymerisation experiments were labelled (A_1 - A_6) according to the emulsifier concentration used for the polymerisations carried out at $58^{\circ}C$. They were labelled (B_1 - B_6) for the polymerisations carried out at $68^{\circ}C$. The (%) conversion of the monomer to the polymer was calculated and plotted against time of polymerisation

TABLE 2.1

POLYMERISATION RECIPE (58°C)

Number of Polymerisation	Weight of Initiator (g)	Concentration of emulsifier used $g.dm^{-3}$ (Stock solution $25 g.dm^{-3}$)	Volume of buffer cm^3 (Stock solution $76 g.dm^{-3}$)	Concentration of monomer $g.dm^{-3}$	Volume of distilled water (cm^3)	Total volume of reaction mixture (cm^3)
A_1	0.30	0.75	10	1.280	129	200
A_2	0.30	1.50	10	1.280	123	200
A_3	0.30	2.25	10	1.280	119	200
A_4	0.30	3.75	10	1.280	105	200
A_5	0.30	7.50	10	1.280	75	200
A_6	0.30	15.00	10	1.280	15	200

TABLE 2.2

POLYMERISATION RECIPE (68°C)

Number of polymerisation	Weight of Initiator (g)	Concentration of emulsifier used $g.dm^{-3}$ (Stock solution $25g.dm^{-3}$)	Volume of buffer cm^3 (Stock solution $76g.dm^{-3}$)	Concentration of monomer $g.dm^{-3}$	Volume of distilled water (cm^3)	Total volume of reaction mixture (cm^3)
B_1	0.30	0.75	10	1.280	129	200
B_2	0.30	1.50	10	1.280	123	200
B_3	0.30	2.25	10	1.280	119	200
B_4	0.30	3.75	10	1.280	105	200
B_5	0.30	7.50	10	1.280	75	200
B_6	0.30	15.00	10	1.280	15	200

2.2 Results and Discussion.

2.2.1 Stability of the emulsions.

From polymerisations carried out below the critical micelle concentration of sodium lauryl sulphate (SLS), some degree of coagulation was observed. The time, during polymerisation, of occurence of the coagulation increased as the emulsifier concentration increased and very close to the cmc of (SLS), and above it, no coagulation was observed throughout the course of the polymerisation. This clearly shows that the emulsifier has a stabilising effect and the tendency towards coalescence of particles is evidently related to the quantity and efficiency of the emulsion stabilizer. Sodium lauryl sulphate is known to be one of the most efficient from the standpoint of limiting interparticle coalescence (24). Coagulation occured because when the emulsifier concentration fell below the cmc of the emulsifier, no micelles were produced and this left the polymer particles swollen with monomer. Inadequate agitation at this stage caused the monomer droplets to coalesce. Thus below the cmc of (SLS), polymerisation of vinyl acetate could lead to coagulation as the solubilising effect of the emulsifier on the monomer becomes less than the stabilizing effect. The number of particles present at the completion of the polymerisation is the total number of primary particles less the reduction caused by coalescence during the course of the reaction (24). Above the cmc, there was sufficient emulsifier molecules and micelles to both solubilise and stabilise the monomer molecules. The largest portion

of monomer was thus dispersed in the medium as monomer droplets thereby preventing coagulation. It can be concluded therefore that coalescence can be controlled and prevented, where desirable, by the use of emulsifiers in adequate concentration.

2.2.2 Nature of Polyvinyl acetate samples obtained.

The polymer particles obtained from the emulsion polymerisation of vinyl acetate were water-white in colour. The sizes of the polyvinyl acetate particles appeared to depend on the concentration of the emulsifier during polymerisation. At lower emulsifier concentrations and below the cmc of (SLS), the particles tended to separate into large aggregates. Above the cmc, the particles became finer during precipitation with increasing emulsifier concentration. Priest (24) reported from the electron-microscope observations of latexes produced by the polymerisation of vinyl acetate in water that in the absence of surfactants the particles produced are large (0.1 - 1.0 μ in diameter) and their size distribution is narrow. The results of the present study clearly support this finding of Priest, though particle sizes were not determined here.

2.2.3 The induction period observed during polymerisation of vinyl acetate.

An induction period i.e. an initial period of no apparent polymerisation was observed for each polymerisation

experiment carried out particularly below the cmc of (SLS). This fact can be seen from fig. 2.1. The induction period was found to depend on temperature of polymerisation, decreasing as the temperature was changed from 58°C to 68°C. The induction period was also found to decrease with increase in the concentration of the emulsifier while polymerising above the cmc but appears to increase with $[S_o]$ while polymerising below the cmc. The induction time might not affect the rate of polymerisation of vinyl acetate as determined from the slope of the linear portion of the graph. Induction period is believed to reflect a delay in the polymerisation reaction which may be as a result of a delay in the interaction of the reacting species. The work of Fache (23) has suggested that the induction period in this polymerisation should increase with decrease in the solubility of vinyl acetate in water, and is often fairly long in the absence of micelles in the emulsion system. This is because radical-monomer interaction would be inhibited.

2.2.4 The rate of the polymerisation of vinyl acetate.

Plots of (%) conversion versus time of polymerisation of vinyl acetate are given in figures 2.1 and 2.2. The general trends of variation of (%) conversion with time of polymerisation are similar for the two temperatures, 58°C and 68°C, used for the study of the emulsion

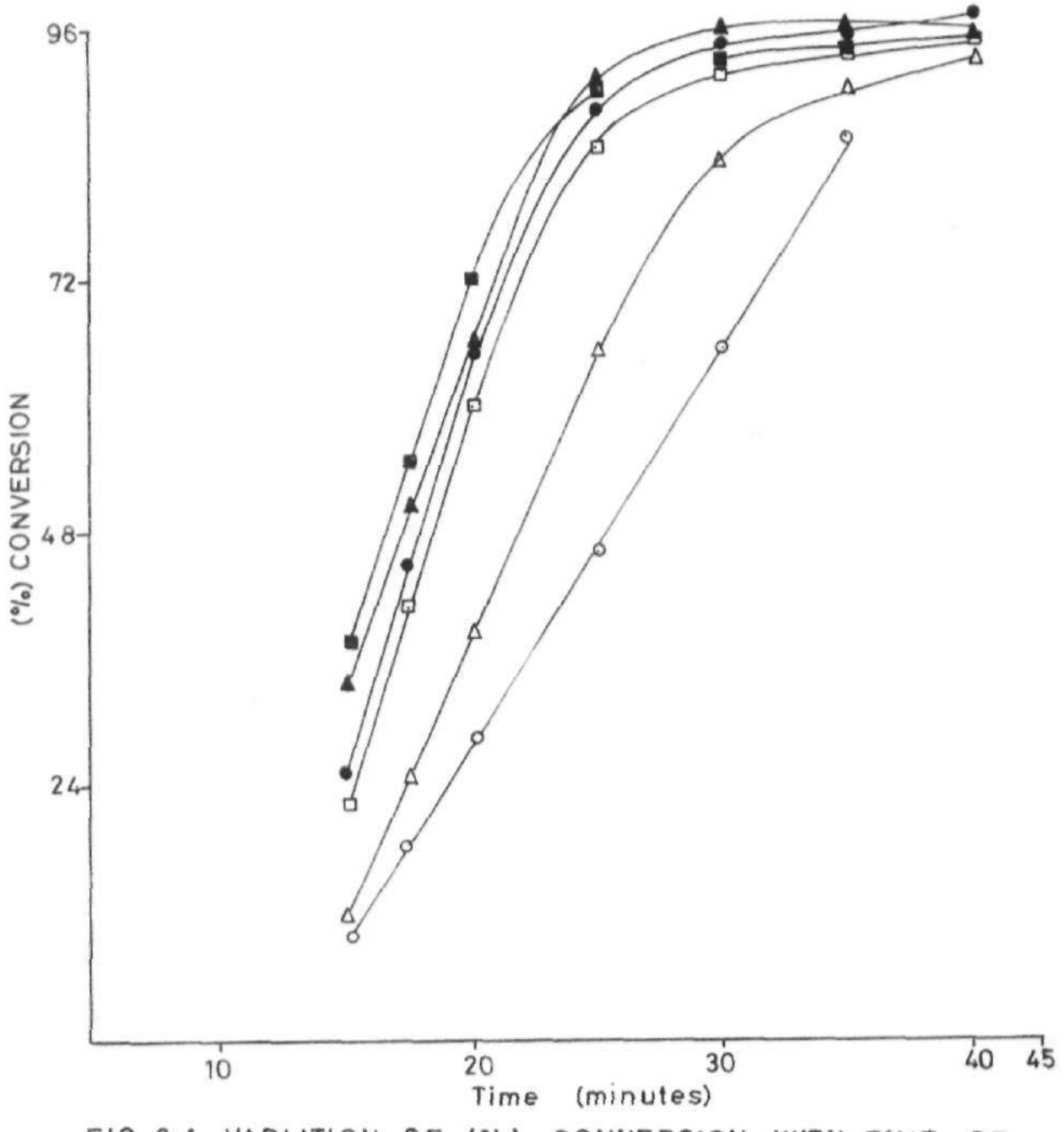


FIG. 2·1 VARIATION OF (%) CONVERSION WITH TIME OF POLYMERISATION OF VINYL ACETATE AT 58°C FOR EMULSIFIER CONCENTRATIONS OF (○) 0·75; (△) 1·50; (□) 2·25; (●) 3·75; (▲) 7·50 AND (■) 15·0g. dm-3

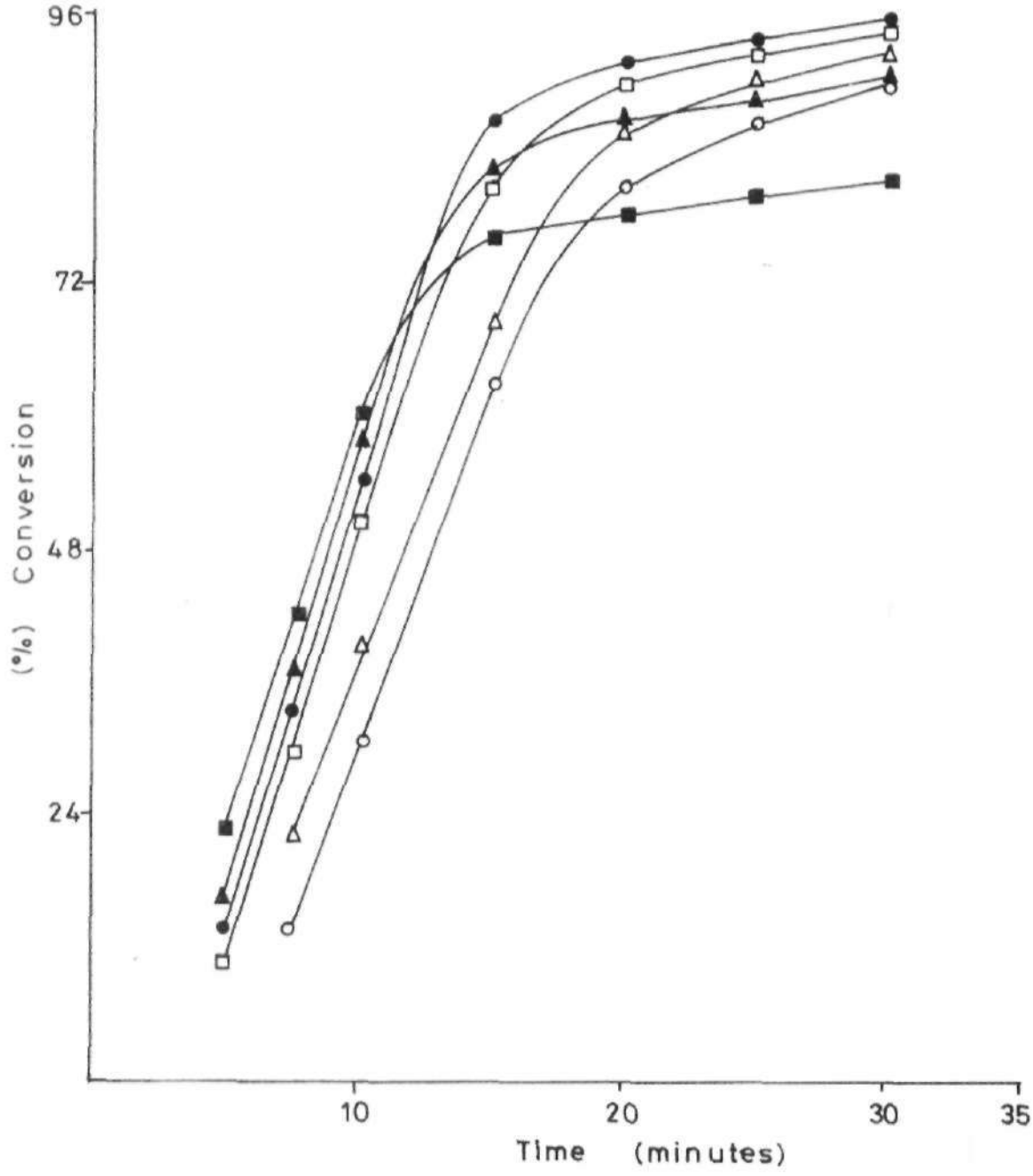


FIG. 2·2 VARIATION OF (%) CONVERSION WITH TIME OF POLYMERISATION OF VINYL ACETATE AT 68°C FOR EMULSIFIER CONCENTRATIONS OF (○) 0·75; (△) 1·50; (□) 2·25; (●) 3·75; (▲) 7·50 AND (■) 15·0 g.dm-3

polymerisation of vinyl acetate. There was polymerisation of vinyl acetate both below and above the cmc of (SLS). This is different from what was obtained when styrene, for example, was polymerised (10). Polymerisation of styrene in pure water proceeds so slowly that it becomes recognisable only when the $[S_o]$ exceeds the cmc of the emulsifier. Thus vinyl acetate emulsion polymerisation shows a deviation from what is expected from the Smith-Ewart theory (6). The inapplicability of the Smith-Ewart theory to the emulsion polymerisation of vinyl acetate, especially below the cmc of (SLS), can be accounted for by the fact that the monomer is sufficiently soluble in water for polymerisation to occur in the aqueous phase. From figs. 2.1 and 2.2 it can be seen that the amount of polymer formed increases with time of polymerisation for the two temperatures studied. The amount of polymer obtained from polymerising vinyl acetate in the presence of micelles is more than in the absence of micelles because polymerisation then occured both in the aqueous phase and in swollen polymer particles. More polymer was formed with time of polymerisation at the higher temperature of 68°C as would be expected kinetically. Thus increasing the reaction temperature usually increases the polymerisation rate. This is because the propagation rate constant, k_p, and the initiator decomposition rate constant, k_d, are temperature

dependent. Increase in temperature increases the rates of radical generation and dissolution. Also the rate of diffusion of radicals and monomers is increased thereby increasing the amount of polymer formed in solution. Below the cmc of (SLS), increase in $[S_o]$ caused a large increase in (%) conversion values. Above the cmc, the (%) conversion values are not so widely separated as there was not much change in the quantity of polymer formed as the $[S_o]$ was increased. This effect is more pronounced at increased temperature and is a deviation from the Smith - Ewart (6) theory applicable to insoluble monomers like styrene and methyl methacrylate. For styrene emulsion polymerisation, little increase in concentration of emulsifier causes much increase in the (%) conversion from below to above the cmc of the emulsifier.

The plots of (%) conversion versus time for each polymerisation carried out given in figs. 2.1 and 2.2 are essentially linear between about 9 - 85% conversion for many of the studies, and approaches a constant value close to 100%, especially for high emulsifier concentrations. This is in agreement with the observed fact that for vinyl acetate emulsion polymerisation, R_p rises constantly until about 85% conversion, although the separate monomer phase has vanished already at or before 30% conversion (32).

Stannett et al (33) have explained this constant rate behaviour by assuming the monomer - polymer particles to act like reservoirs, keeping the monomer concentration in the water phase constant after the disappearance of monomer droplets. In the presence of micelles, there was a marked increase in R_p as soon as the initially formed polymer precipitated. Napper et al (34) have explained this to be as a result of the fact that the locus of polymerisation is the monomer - swollen polymer particles and not the water phase during polymerisation with $[S_o]$ above the cmc of the emulsifier. For some of the curves there was an initial slow R_p which is dependent on $[S_o]$ and temperature. This R_p becomes slower at decreased $[S_o]$ and temperature below and above the cmc of (SLS). The number of particles at various stages of a vinyl acetate polymerisation is variable (24). At the outset of reaction particles are formed at a uniform rate. As the concentration of centres increases the rate of particle combination becomes greater and reaches a maximum at which the rate of production of centres from polymerisation in the aqueous phase is balanced by their rate of removal by combination. Factors favouring production of a large number of particles are high $[S_o]$, high $[I]$ and high temperature (24).

2.2.4.1 Effect of emulsifier concentration, $[S_o]$ on the rate of polymerisation, R_p.

Emulsion polymerisation of vinyl acetate proceeds either with or without micelles at an appreciable rate (8). Higher concentration of emulsifier showed higher rates of polymerisation as can be seen from figs. 2.1 and 2.2, hence $[S_o]$ has a profound effect on the R_p. Generally, an increase in $[S_o]$ increases R_p and the number of growing particles, N and the effect of $[S_o]$ is independent of the initiation rate (32). Sodium lauryl sulphate, an anionic soap, was used for this study, and it was found to increase R_p. This means that R_p of vinyl acetate in emulsion is very much affected by the kind of stabilization. This is in agreement with the report of Napper et al (35) on the effects of added soaps of different types at concentrations below their cmc in the emulsion polymerisation of vinyl acetate in aqueous solution using $K_2S_2O_8$ initiation. They found that neutral soaps produced no appreciable effect on R_p whereas anionic soap increased R_p, the magnitude of the increase being affected by the length of the paraffin chain in the anion. It is also in agreement with the works of Netschey et al (21) on the effects which surfactants at concentration below cmc exert on the kinetics of polymerisation and its correlation with their influence of the colloid stability of the latex. They observed that in the peroxydisulphate initiated aqueous

polymerisation of vinyl acetate anionic surfactants increased both the number of latex particles formed and R_p. Cationic surfactants, in contrast, usually reduce both the number of particles and the rate of reaction.

TABLE 2.3

$[S_o]$ ($g.dm^{-3}$)	R_p (% conversion min^{-1})	
	58°C	68°C
0.75	3.87	4.77
1.50	6.12	8.58
2.25	7.39	8.81
3.75	8.00	12.22
7.50	9.51	10.10
15.00	10.89	8.13

Table 2.3 gives the effect of $[S_o]$ on R_p of vinyl acetate for the two sets of temperatures used. From the results, R_p went through a maximum and decreased at high $[S_o]$ especially at 68°C. This agrees well with the observation on investigating the influence and kind of $[S_o]$ on the emulsion polymerisation of some vinyl monomers (1). It was found that while R_p of styrene and methyl methacrylate increased with increasing $[S_o]$, that of acrylonitrile, and vinyl acetate went through a

maximum and decreased at high $[S_o]$. This observation might be due to the fact that as the $[S_o]$ was increased, the medium became more viscous. This and the speed of agitation could lead to a decreased rate of entry of the free radicals into the monomer molecules. Moreover, as the free radicals diffuse through the polyvinyl acetate moieties, chain transfer to these moieties and branching set in especially at high $[S_o]$. This could also reduce the R_p further. Also R_p did not show much increase as the $[S_o]$ was increased from below to above the cmc of (SLS). This agrees well with the result of Okamura et al, (36) on the emulsion polymerisation of vinyl acetate using sodium dodecyl sulphate emulsifier. For styrene emulsion polymerisation, R_p is very small below the cmc and increases abruptly only when the cmc is exceeded and this increases with increasing $[S_o]$ (10). Thus the $[S_o]$ does not affect R_p to the same extent in vinyl acetate as in styrene. This can be accounted for by the solubility of the vinyl monomers in water, vinyl acetate being more hydrophilic than styrene as concluded from the studies of interfacial tension of the monomers (10). It can also be explained by the reactivity of the radicals towards surfactants i.e. vinyl acetate is easily subject to the influence of retarders or chain transfer agents (10).

For vinyl acetate polymerisation, the form of dependence of the exponent of the $[S_o]$ on temperature and the range of $[S_o]$ was studied from the plots of log R_p versus log $[S_o]$ as presented in fig. 2.3. The two sets of straight lines obtained intersect at a value of $[S_o]$ which corresponds to the cmc of (SLS). The exponent of $[S_o]$ was determined by taking the slopes of these straight lines below and above the cmc of (SLS). The results are tabulated in table 2.4. The form of dependence of the $[S_o]$ exponent was found to vary at different temperatures. Below the cmc the value of the exponent increased as the temperature increased. Above the cmc the value of the exponent decreased as the temperature increased.

TABLE 2.4

The dependence of the exponent of $[S_o]$ on R_p using a wide range of $[S_o]$ and at two temperatures.

Relationship between R_p and $[S_o]$	Range of $[S_o]$ for (SLS)	Polymerisation temperature (^oC)
$R_p \; [S_o]^{0.42}$	below cmc	58
$R_p \; [S_o]^{0.11}$	above cmc	58
$R_p \; [S_o]^{0.58}$	below cmc	68
$R_p \; [S_o]^{-0.14}$	above cmc	68

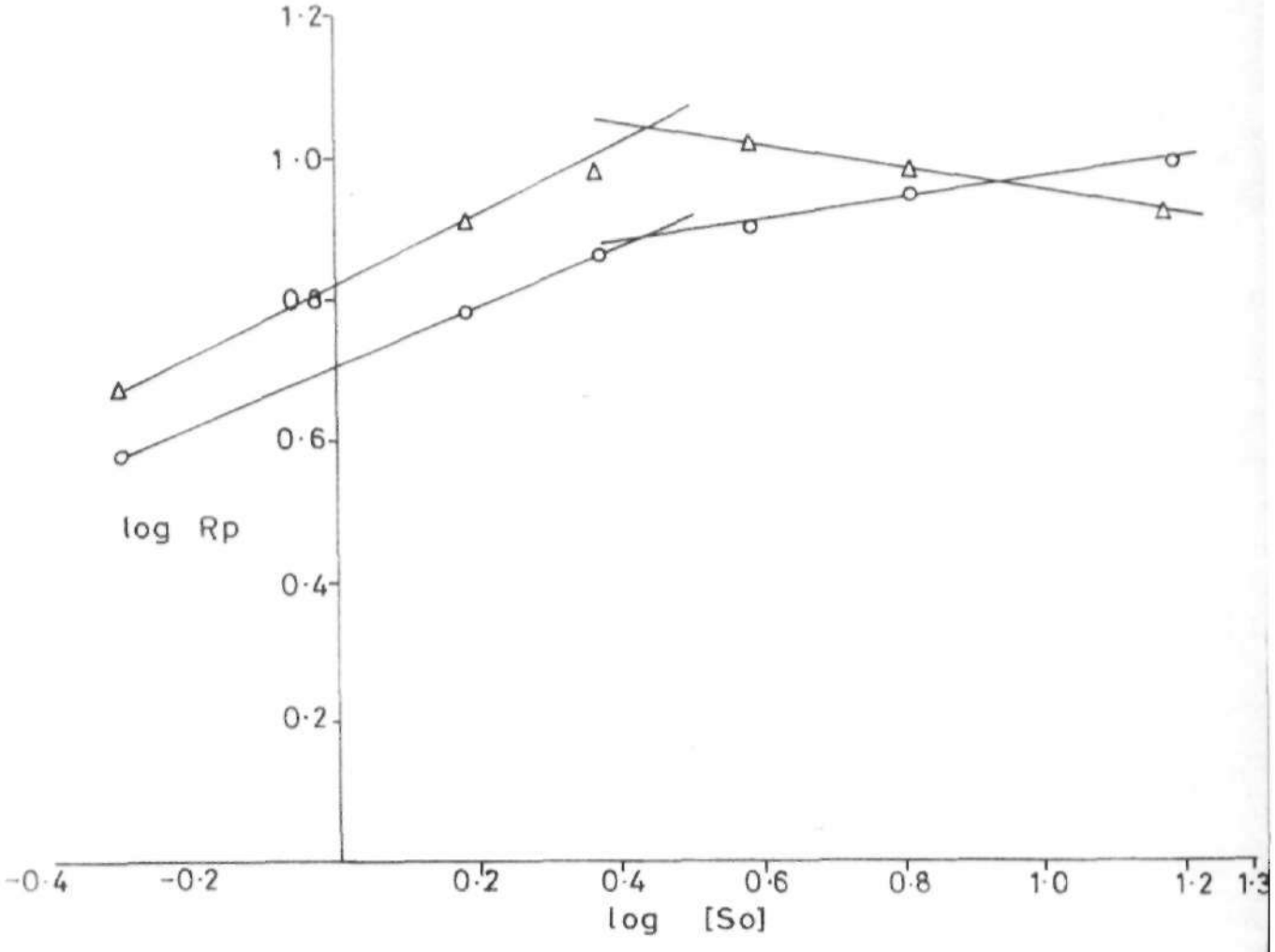


FIG. 2·3 THE RELATIONSHIP BETWEEN THE RATE Rp OF EMULSION POLYMERISATION OF VINYL ACETATE AND THE CONCENTRATION OF SODIUM LAURYL SULPHATE [So], FOR POLYMERISATION AT (o), 58 AND (Δ) 68°C

At 68°C the value of the exponent was negative indicating that at that temperature and possibly above it, R_p is approximately independent of the $[S_o]$. Decrease in the exponent of $[S_o]$ above the cmc suggests that increase in R_p with emulsifier is slower when temperature increases. Higher values of the exponent of $[S_o]$ are obtained below the cmc than above the cmc showing the greater dependence of R_p on $[S_o]$ below the cmc. French (11) found R_p to be proportional to one-third the power of $[S_o]$ and that the monomer droplets disappeared at 8% conversion. O'Donnell and co-workers (37) polymerised vinyl acetate at 70°C with $K_2S_2O_8$ using a partially hydrolyzed polyvinyl acetate as emulsifier. They found the R_p to be dependent on approximately 0.6 power of $[S_o]$ and 0.7 power for $[I]$. Working above the cmc, Friis et al (32) found R_p to be dependent on 0.12 power of the $[S_o]$. Fache (23) working under similar conditions reported in this chapter also came out with some form of dependence of R_p on $[S_o]$ which compares well with the results in table 2.4. It can therefore be concluded that the exponent of $[S_o]$ depends on temperature and the range of $[S_o]$ for the set of experimental conditions employed.

The overall results obtained in this study of emulsion polymerisation of vinyl acetate and those of other workers under different conditions are somewhat

conflicting and show a deviation from the Smith-Ewart equations (6). They have shown from their studies of emulsion polymerisation of styrene that R_p and number average degree of polymerisation are directly proportional to the number of growing particles, N. The number of growing particles is in turn proportional to $[I]$ and $[S_o]$, they therefore concluded that $R_p \alpha N$ and $N \alpha [I]^{0.4} [S_o]^{0.6}$.

Again, it can be suggested that the deviation might be caused by the water solubility of vinyl acetate which does not limit the site of polymerisation to the micelles alone. There is simultaneous polymerisation of the monomer which is in solution to give polymer particles which absorb emulsifier from the rest of the system. As a result N will be less dependent on $[S_o]$ and the exponent of $[S_o]$ will be less than 0.6 as predicted by the Smith-Ewart equation.

Some of the anomalous results are best described by the newer theory of Medvedev et al (16). They have concluded from their studies that for many emulsion polymerisations especially at higher particle numbers (approximately $2 - 3 \times 10^{14}$) the polymerisation rate obeys the relationship

$$R_p \alpha N^{0.2} [So]^{0.5} [I]^{0.5}$$

The mechanism of emulsion polymerisation appears to be different and they have suggested that the site of the reaction apparently becomes the particle surface instead of the interior of the particle. This is due to the fact that radicals cannot penetrate the interior of the particles due to the high viscosity and that polymerisation therefore occurs at the particle surface. In comparing R_p per particle with R_p per surface it was found that the rate per surface was nearly constant whereas the rate per particle increased considerably. This lends support to the Medvedev mechanism (16).

CHAPTER III

3.0 Dilute Solution Viscosity Study.

3.1 Experimental.

3.1.1 Materials:

An Ubbelohde viscometer which was scrupulously cleaned with chromic acid and distilled water and then dried, methanol which was purified by distillation and the polyvinyl acetate samples were used for the viscosity study.

3.1.2 Procedure.

About 0.17g of each polymer sample was accurately weighed and transferred quantitatively into a 50cm^3 volumetric flask. It was dissolved with the purified methanol and made up to the mark. The clean Ubbelohde viscometer was placed in a constant temperature water bath 30^{o}C $\pm$ 0.10^{o}C. 10cm^3 of the purified solvent was first of all introduced into the Ubbelohde viscometer and the efflux time was determined. The viscometer was then cleaned after use. 10cm^3 was measured from the stock solution prepared for each polyvinyl acetate sample into the clean and dry viscometer and the efflux time determined. Dilutions with 4cm^3 of purified methanol were made in five steps and subsequent efflux times were determined.

3.2 Results and Discussion.

3.2.1 Variation of intrinsic viscosity, $[\eta]$, with (%) conversion and $[S_o]$

Plots of $[\eta]$, the intrinsic viscosity or limiting viscosity number, versus (%) conversion are given in figures 3.1 and 3.2. The intrinsic viscosity as contained in Huggins equation

$$(\eta_{sp/c}) = [\eta] + k'[\eta]^2 c$$

was obtained from the intercept along the $(\eta_{sp/c})$ axis. In Huggins equation, k', is Huggins constant and is a measure of the interactions between polymer and solvent. The intrinsic viscosity is a function of the number average degree of polymerisation $(\bar{X}_n)$, and molecular weight. It also gives information about the macromolecular structures including branching. The intrinsic viscosity is related to the molecular weight by the Mark-Houwink-Sakurada (27) equation.

$$[\eta] = kM_v^{-\alpha}$$

where k and α are constant for a given polymer-solvent system at constant temperature.

From figure 3.1, it can be seen that there is a general increase in $[\eta]$ with (%) conversion and this is followed by a decrease. With 0.75g.dm^{-3} of emulsifier,

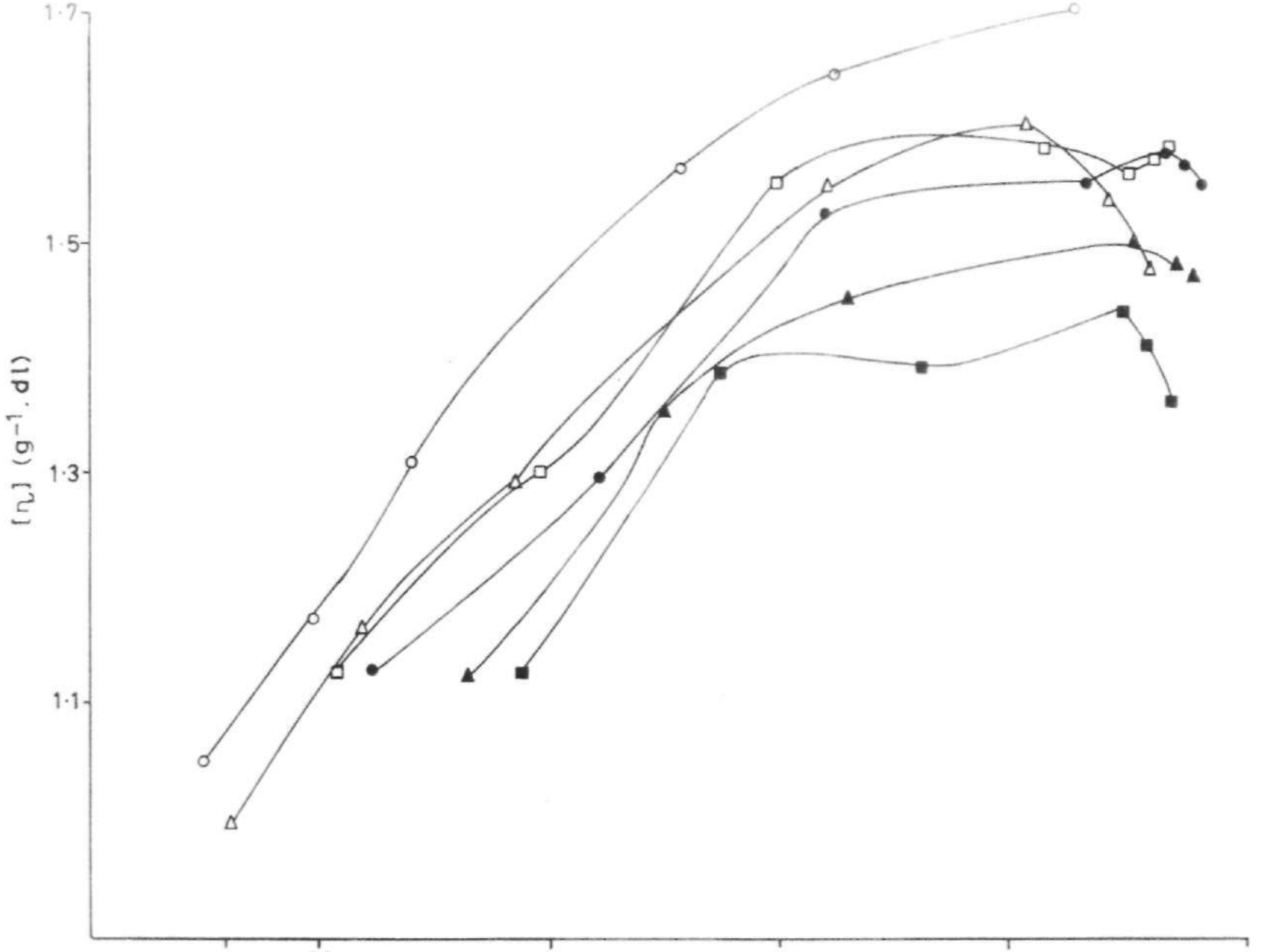


FIG. 3·1 VARIATION OF (%) CONVERSION WITH [η] OF POLY VINYL ACETATE AT 58°C FOR EMULSIFIER CONCENTRATIONS OF (o) 0·75, (Δ) 1·50, (□) 2·25,

So, $[\eta]$ increased steadily till about 86% conversion. Since $[\eta]$ is a function of molecular weight, an increase in molecular weight is expected to cause $[\eta]$ to increase too. Molecular weight is affected by the macromolecular structures. For instance occurence of branching in the polymer backbone decreases molecular weight. Thus it can be assumed that using $[S_o]$ of $0.75g.dm^{-3}$ for the polymerisation, the increase in $[\eta]$ with (%) conversion suggests that molecular weight increased and that branching did not occur. With $[S_o]$ of $1.50g.dm^{-3}$, $[\eta]$ increased steadily till about 87% conversion where it gradually decreased till about 92% conversion. This decrease in $[\eta]$ could have been caused by a decrease in molecular weight of the polyvinyl acetate samples obtained at those conversions. For $[S_o]$ $2.25g.dm^{-3}$, $[\eta]$ increased initially till about 84% conversion and then suddenly decreased to 91% conversion and then rose up to 94% conversion. All these were observed below the critical micelle concentration, cmc, of (SLS) at 58°C. Above the cmc, for $[S_o]$ $3.75g.dm^{-3}$, $7.50g.dm^{-3}$ and $15.0g.dm^{-3}$, a steady increase in $[\eta]$ was observed till about 93% conversion for $3.75g.dm^{-3}$ (SLS), 91% conversion for $7.5g.dm^{-3}$ (SLS) and 89% conversion for $15.0g.dm^{-3}$ (SLS). These observations were followed by a gradual decrease in $[\eta]$ for the respective emulsifier concentrations. Again the decrease in $[\eta]$ values with (%) conversion may be attributed to decrease in

molecular weight or changes in macromolecular structure for those polyvinyl acetate samples. The decrease in molecular weight may be caused by branches of irregular or regular sizes introduced as a result of chain transfer reactions during the polymerisation reactions.

Polymerisations carried out at 68°C are illustrated in figure 3.2 in which (%) conversion was varied with $[\eta]$ For all the polymerisation reactions, a steady increase in $[\eta]$ was followed by a steady or sudden decrease in $[\eta]$ as the case may be with (%) conversion. For polymerisations below the cmc of (SLS) i.e. 0.75g.dm^{-3}, 1.50g.dm^{-3} and 2.25g.dm^{-3} of emulsifier, a steady increase in $[\eta]$ up to 80% conversion, 85% conversion and 90% conversion respectively was followed by a sudden decrease in $[\eta]$ to 86% conversion, about 92% conversion and 92.1% conversion respectively. Above the cmc, 3.75, 7.50 and 15.0g.dm^{-3} of sodium lauryl sulphate, a steady increase in $[\eta]$ up to about 86% conversion 81% conversion and 73% conversion respectively was observed. This was followed by a gradual decrease in $[\eta]$ with (%) conversion for all the emulsifier concentrations. The steady rise in $[\eta]$ is synonymous with a rise in molecular weight or modification of the macromolecular structure. A decrease in molecular weight or the occurence of branches could have led to the decreasing value of $[\eta]$. At the higher temperature, the

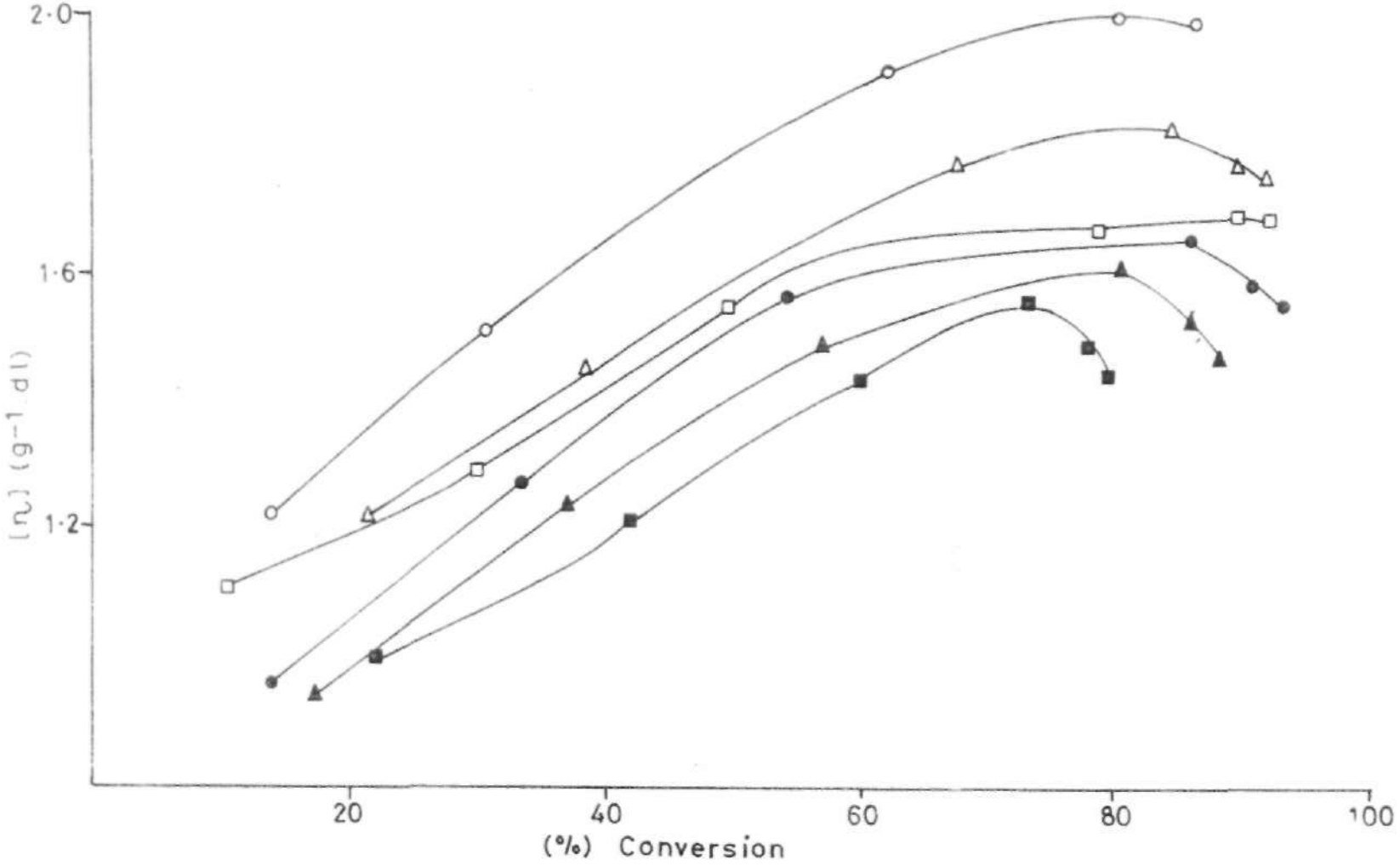


FIG. 3·2 VARIATION OF INTRINSIC VISCOSITY [η] WITH % CONVERSION OF POLY VINYL ACETATE AT 68°C WITH EMULSIFIER CONCENTRATION OF (○) 0·75 (△) 1·50 (□) 2·25 (●) 3·75 (▲) 7·50 AND (■) 15·0 g.dm-3

chain transfer reactions seem to be more pronounced and the intrinsic viscosity values seem to be higher at this temperature below the cmc of (SLS). Thus it can be suggested that $[\eta]$ increases with temperature.

Figures 3.3 and 3.4 show a variation of $[\eta]$ with $[S_o]$ at 58°C and 68°C both below and above the cmc of sodium lauryl sulphate at 35%, 60% and 80% conversion. From fig. 3.3 at 58°C and below the cmc of (SLS), $[\eta]$ seemed to be highest for 0.75g.dm^{-3} (SLS) for all the conversions considered. It decreased at 1.50g.dm^{-3} (SLS) and increased slightly at 2.25g.dm^{-3} near the cmc of (SLS). Above the cmc, $[\eta]$ decreased slightly almost to a constant value as $[S_o]$ increased for all the conversions. In going from below to above the cmc, $[\eta]$ decreased and the values appear to be higher below the cmc than above. In the absence of micelles i.e. below the cmc, basically linear polymers are formed. In the presence of micelles movement of the polymer chains is restricted and chain transfer reactions with emulsifier leading to branching becomes pronounced. The $[\eta]$ being a function of the number average degree of polymerisation, $(\bar{X}_n)$, is proportional to it. Chain branching leads to a decrease in chain length and therefore decrease in $(\bar{X}_n)$ and molecular weight. Thus below the cmc, the effect of chain branching could be considered to be minimal and the polymers are expected

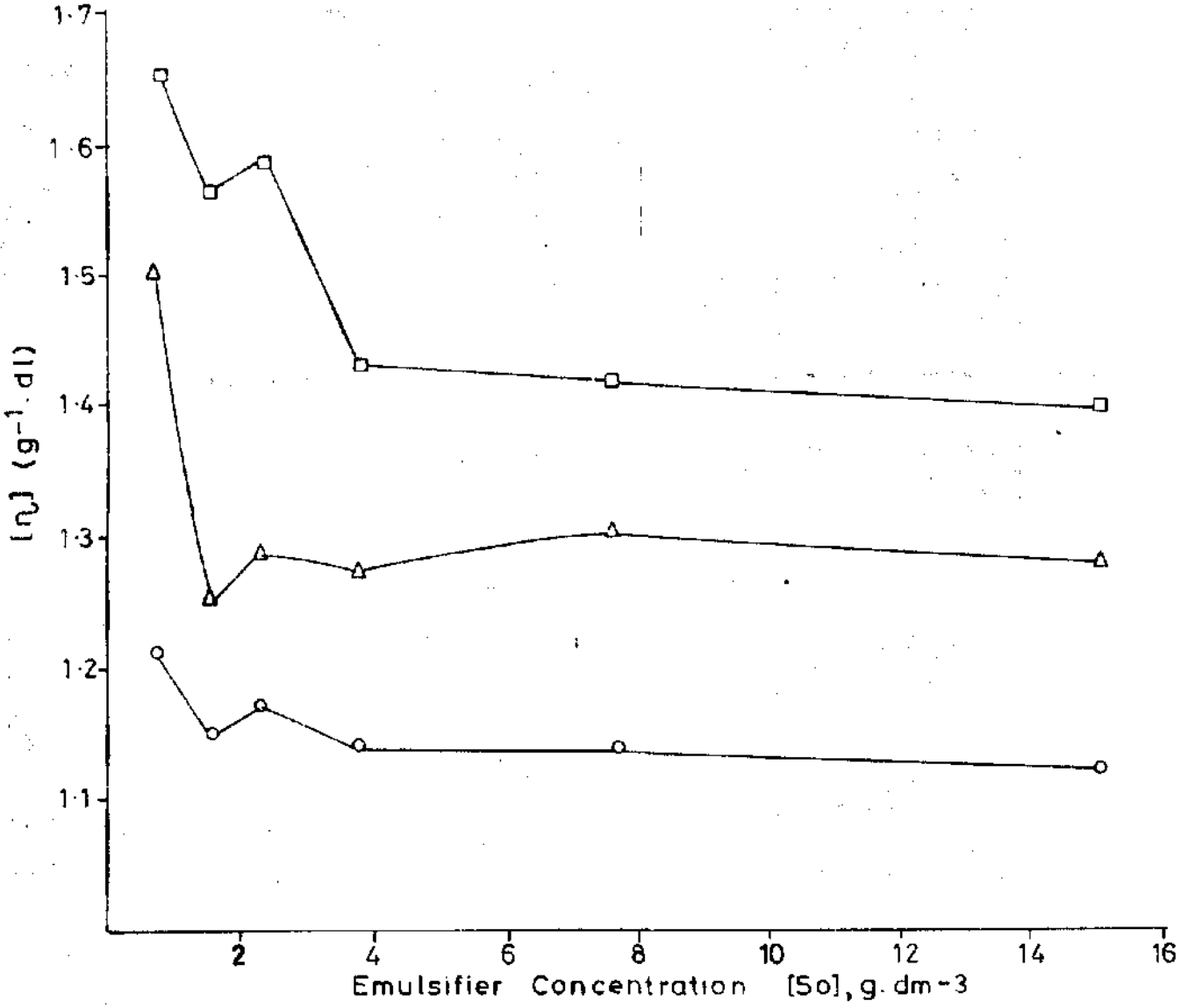


FIG. 3·3 VARIATION OF $[\eta]$ OF POLY VINYL ACETATE SAMPLES PREPARED AT 58°C WITH EMULSIFIER CONCENTRATION USED DURING THE PREPARATION

(○) 35% CONVERSION (△) 60% CONVERSION (□) 80% CONVERSION

to have higher molecular weights. Above the cmc, the $[\eta]$ values are almost constant i.e. not much difference and this is an indication that the macromolecular properties and structure are almost similar. Also branching becomes more pronounced above the cmc due to transfer reactions and this shortens the chain length thereby reducing $(\bar{X}_n)$ and molecular weight. Therefore above the cmc the polymers are expected to have lower molecular weights than below the cmc due to branching. Generally $[\eta]$ increased for all the emulsifier concentrations with (%) conversion, therefore polymers at 80% conversion had the highest values of $[\eta]$ while those at 35% conversion had the lowest values.

At 68°C and below the cmc, there was a general decrease in $[\eta]$ for all the conversion as $[S_o]$ increased. Thus using 2.25g.dm^{-3} (SLS) gave the lowest $[\eta]$ values. In going from below to above the cmc, $[\eta]$ increased from using 2.25g.dm^{-3} to 3.75g.dm^{-3} (SLS) at 60% and 80% conversions. At 35% conversion, a slight decrease was observed. Generally above the cmc, $[\eta]$ decreased as $[S_o]$ was increased though the variation was not much. This phenomenon was also reported in the emulsion polymerisation studies by Friis et al (32) and by Pacho (23). The decrease in $[\eta]$ at this temperature even below the cmc means that chain transfer reaction to the polyvinyl acetate moieties and modification of the polymer structure must have taken place. The decrease above the cmc

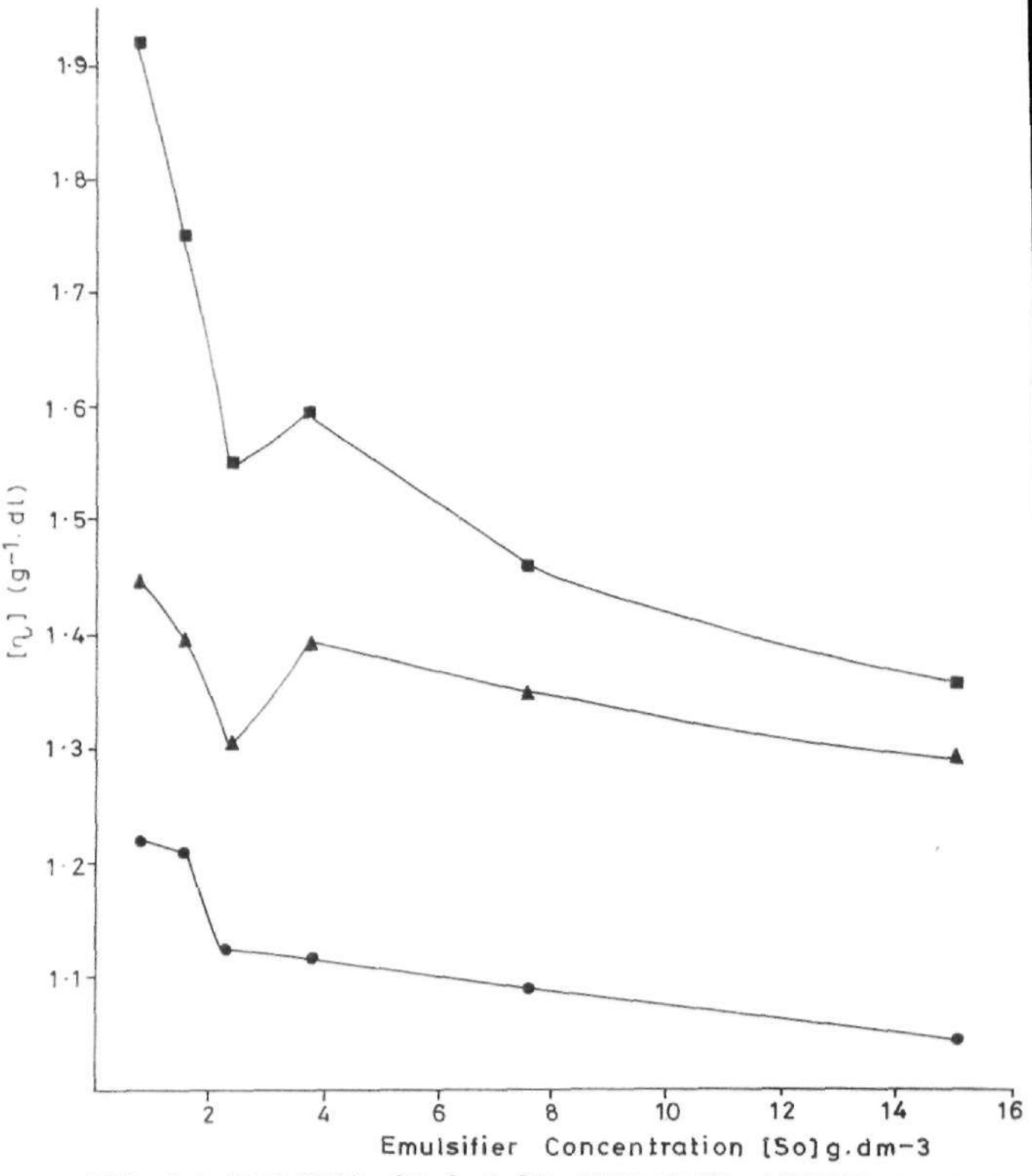


FIG. 3·4 VARIATION OF [η] OF POLY VINYL ACETATE SAMPLES PREPARED AT 68°C WITH EMULSIFIER CONCENTRATION USED DURING THEIR PREPARATION
(●) 35% CONVERSION (▲) 60% CONVERSION (■) 80% CONVERSION

is expected as it is known that chain transfer with the emulsifier occurs. These observations below and above the cmc agree well with those reported by Fagbehingbe (22).

The $[\eta]$ values are higher below the cmc for the polymers at 68°C. This can be explained by the fact that high temperature increases the rate of formation of emulsifier micelles and therefore number of particles, N. Since $[\eta]$ is proportional to $(\bar{X}_n)$, and $(\bar{X}_n)$ is proportional to N, it suggests that $[\eta]$ is proportional to N. Thus increase in N should increase $[\eta]$ and $(\bar{X}_n)$ and the molecular weights of the polymers produced at $[S_o]$ below the cmc of (SLS) are expected to be higher at 68°C. The $[\eta]$ values are higher above the cmc for the polymers at 58°C. This can be attributed to the fact that at higher temperatures chain transfer reaction leading to branching is more pronounced. This shortens the chain length of the polymers at 68°C more than at 58°C. Also at higher temperatures, probability of termination of two radicals is enhanced. Thus $[\eta]$, $(\bar{X}_n)$, and therefore molecular weight are expected to be lower at 68°C when polymerising above the cmc of (SLS), Also as observed with polymerisation carried out at 58°C, $[\eta]$ increased with (%) conversion for all the emulsifier concentrations and polymers at 80% conversion had the highest $[\eta]$ values.

3.2.2 VARIATION OF HUGGINS CONSTANT, k' WITH (%) CONVERSION AND [S_o]

The specific viscosity (η_{sp}), the intrinsic viscosity [η], and concentration are related by the Huggins equation referred to in the preceding section. Huggins constant, k', whose values range between 0.3 and 0.4 for good solvents (27) is a measure of the interactions between a polymer and its solvent. It also gives infrmation about chain dimensions and branching. Smaller k' denotes better solvation (8).

The variation of k' with (%) conversion is given in figures 3.5 and 3.6. From the plots at 58°C and for polymers obtained while polymerising both below and above the cmc of (SLS), 0.75g.dm^{-3} of emulsifier showed a steady decrease in k' value up to about 0.19 at 46% conversion below the cmc and up to 0.21 at 64% conversion above the cmc. The Huggins constant suddenly increased and then decreased again for both below and above the cmc. For 1.5g.dm^{-3} emulsifier below the cmc, an initial decrease followed by a steady increase, and then a decrease up to 82% conversion was observed. This alternatively increased again till 92% conversion. Above the cmc a steady increase followed by a decrease to a minimum value of 0.125 in k' at 91% conversion and then a gradual increase up till about 96% conversion was observed. Using 2.25g.dm^{-3} of

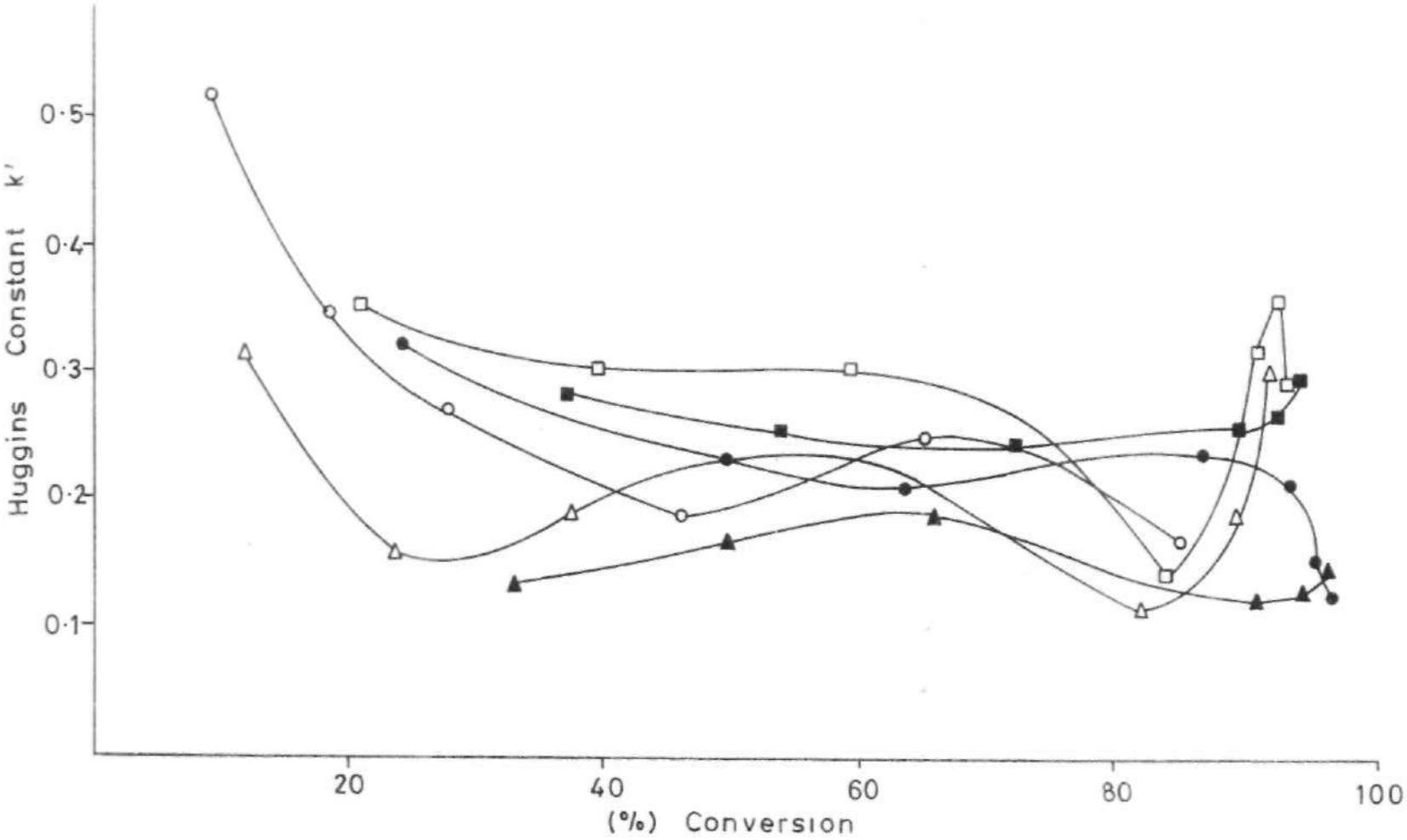


FIG. 3·5 VARIATION OF THE HUGGINS CONSTANT OF POLY VINYL ACETATE SAMPLES PREPARED AT 58°C WITH (%) CONVERSION WITH EMULSIFIER CONCENTRATION OF (o) 0·75 (Δ) 1·50 (□) 2·25 (●) 3·75 (▲) 7·50 AND (■) 15·0g.dm-3

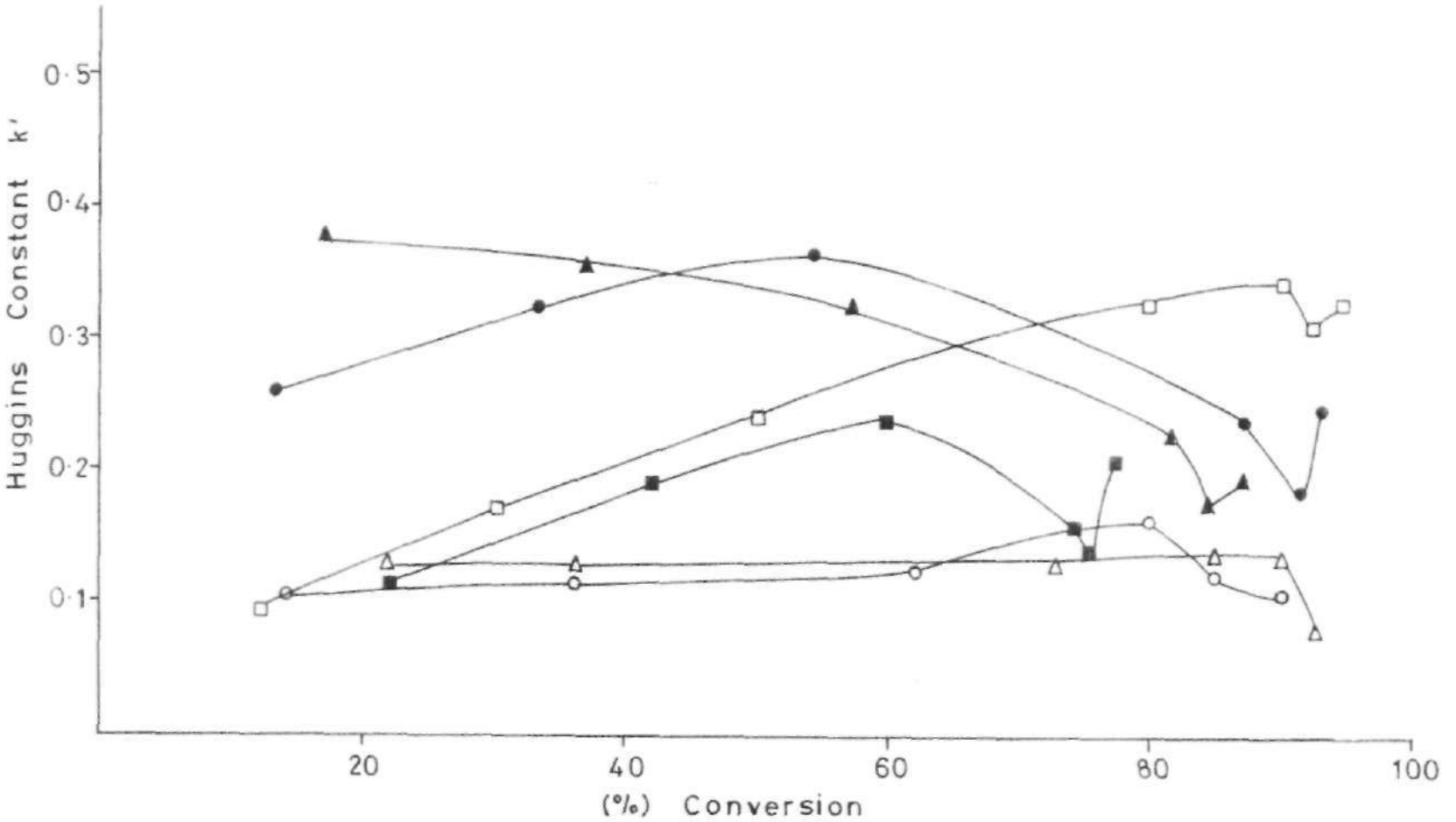


FIG. 3·6 VARIATION OF HUGGINS CONSTANT OF POLY VINYL ACETATE SAMPLES PREPARED AT 68°C WITH (%) CONVERSION WITH EMULSIFIER CONCENTRATION OF (○) 0·75 (△) 1·50 (□) 2·25 (●) 3·75 (▲) 7·50 AND (■) 15·0g·dm-3

emulsifier both below and above the cmc showed a gradual decrease to a minimum value of 0.143 at 82% conversion for below the cmc and about 0.243 at about 72% conversion for above the cmc. These k' values increased gradually to 0.360 then decreased to 0.290 for below the cmc and 0.300 for above the cmc at about 94% conversion for both. At 68°C and for polymers produced with $[S_o]$ below the cmc of (SLS), a general increase in k' was observed followed by a sudden decrease in value for all the $[S_o]$ employed except for 2.25g.dm^{-3} which showed a sudden increase in k'. For samples produced above the cmc, a reverse trend was shown for 7.50g.dm^{-3} of emulsifier in which a gradual decrease was followed by an increase in k'. For $[S_o]$ of 3.75 and 15.0g.dm^{-3}, k' first increased to a maximum value of 0.362 at 54% conversion and 0.239 at 60% conversion respectively, decreased to about 0.180 at 91% conversion and 0.135 at 75% conversion respectively and then increased again.

From the Huggins equation, higher values of k' gave lower $[\eta]$ values and therefore lower molecular weight values and or highly branched structures. Thus for plots where an increase in k' was observed it means a decrease in $[\eta]$ and hence in molecular weight due to branching. Smaller k' denotes better solvation and as such in cases where k' value increases it means that the degree of solvation is reduced. This may be attributed to the effect of chain

transfer reactions giving rise to branching during the polymerisation study and hence bulky side groups. This hinders solvation and hence increases k'. Figures 3.7 and 3.8 show the variation of k' with $[S_o]$ for polymers produced with $[S_o]$ both below and above the cmc at 58°C and 68°C. From figure 3.7, the highest peak is obtained at 35% conversion for $[S_o]$ of 2.25g.dm^{-3} near the cmc. It also has the lowest peak at a value of 0.113 for $[S_o]$ of 7.5g.dm^{-3} above the cmc. Below the cmc for all the conversions considered, k' values decreased in going from 0.75g.dm^{-3} to 1.50g.dm^{-3} (SLS) and increased in going from 1.50 to 2.25g.dm^{-3} (SLS). Above the cmc k' values decreased in going from 3.75 to 7.50g.dm^{-3} (SLS) and increased in going from 7.50 to 15.0g.dm^{-3} (SLS) just as observed below the cmc. Moreover, the k' values do not vary much with $[S_o]$ suggesting that the molecular properties will be almost constant for those set of polyvinyl acetate samples. The increase in k' values indicates that the respective polymers have smaller interactions with solvent as a result of their being more compact, either by virtue of increase in coiling or in the extent of branching on the backbone.

At 68°C, from figure 3.8, a different trend was observed. The highest value for k' was also obtained at 35% conversion but for 7.50g.dm^{-3} $[S_o]$ above the cmc and

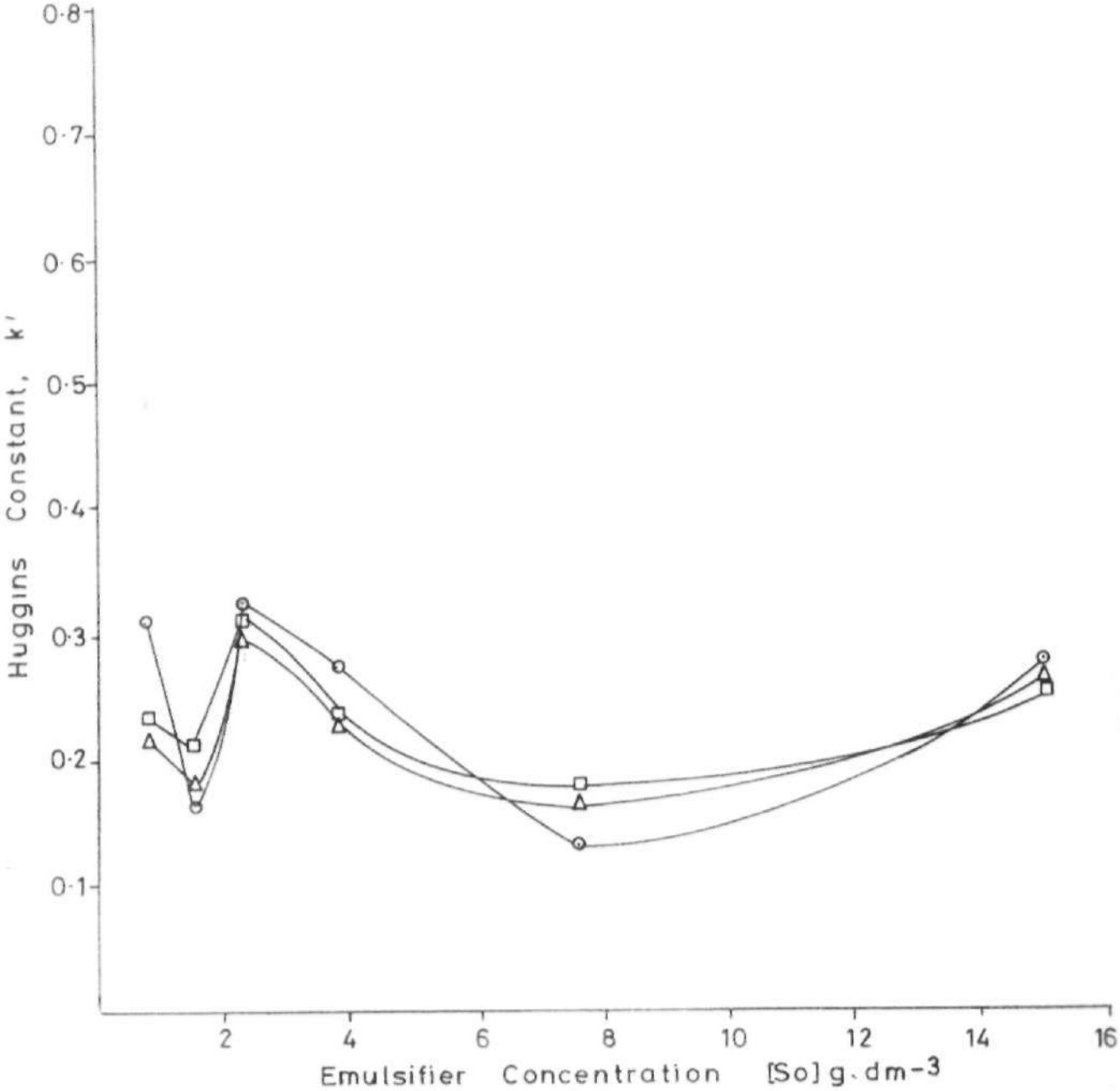


FIG. 3·7 VARIATION OF HUGGINS CONSTANT OF POLY VINYL ACETATE IN METHANOL SOLUTIONS FROM VISCOSITY MEASUREMENTS AT 58°C WITH [So] USED FOR PRODUCING THE POLYMER (o) 35% (Δ) 60% AND (□) 80% CONVERSION

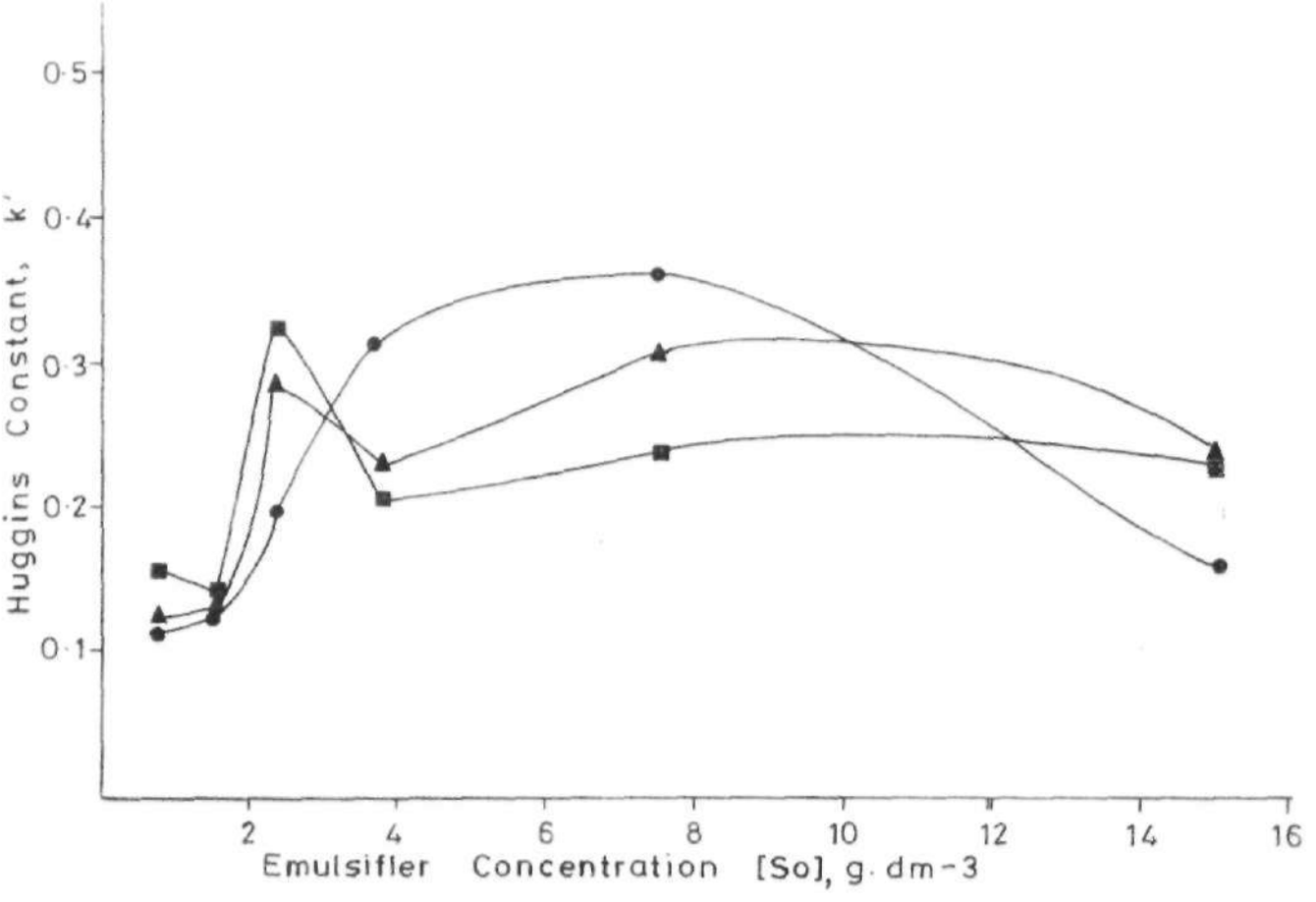


FIG. 3-8 VARIATION OF HUGGINS CONSTANT OF POLY VINYL ACETATE IN METHANOL SOLUTIONS FROM VISCOSITY MEASUREMEMENTS AT 68°C WITH [So] USED FOR PRODUCING THE POLYMER (●) 35%, (▲) 60% (■) 80% CONVERSION

the lowest peak was observed also at 35% conversion but for 0.75g.dm^{-3} $[S_o]$ below the cmc. Below the cmc there was not much variation in k' value in going from 0.75g.dm^{-3} $[S_o]$ to 1.50g.dm^{-3} $[S_o]$ but a significant increase was observed in going from 1.50g.dm^{-3} $[S_o]$ to 2.25g.dm^{-3} $[S_o]$ for all the conversions. While a decrease in k' was observed for 60% and 80% conversion in going from 2.25g.dm^{-3} $[S_o]$ near the cmc to 3.75g.dm^{-3} $[S_o]$ above the cmc, an increase was observed for 35% conversion. For samples produced with $[S_o]$ above the cmc of (SLS), contrary to the trend observed at 58°C, an increase was first observed in going from 3.75g.dm^{-3} $[S_o]$ to 7.50g.dm^{-3} $[S_o]$ followed by a decrease to 15.0g.dm^{-3} $[S_o]$ for all the conversions considered.

The interaction between polymer and solvent gave higher k' values at lower polymerisation temperature below the cmc and do not vary much above the cmc at 58°C. Above the cmc increase in temperature leads to the production of emulsifier micelles at a faster rate which are more freely dispersed. The polymer chains became more compact due to the greater interaction of micelles with the polymer in the medium.

CHAPTER IV

4.0 Mechanical properties of the Polyvinyl acetate samples.

4.1 Experimental.

4.1.1 Casting of polyvinyl acetate films.

4.1.1.1 Materials.

Mercury: the mercury used was obtained from the laboratory. It was purified by first flushing with concentrated nitric acid for twenty four hours and then rinsed with distilled water. It was further filtered to remove traces of dust particles.

Chloroform: the chloroform used was supplied by BDH Chemicals Ltd. Poole England. It was of reagent grade and was further purified by distillation under reduced pressure. It was stored until needed.

Sample bottles and petri-dishes: they were cleaned thoroughly with soap, rinsed with distilled water and then dried in the oven.

Polyvinyl acetate samples: were obtained from the polymerisation experiment reported in chapter two of this book.

4.1.1.2 Procedure.

About 0.5g of each polymer sample was dissolved in $10cm^3$ of the purified chloroform in a sample bottle. The fresh clean mercury was poured gently into a clean

petri-dish (7 - 8cm in diameter) and placed in a fume cupboard. The dissolved polymer was poured gently on the mercury surface and the solvent was allowed to evaporate and the film cast. The cast film was given time to dry. It was then removed by means of a razor blade and kept between two filter papers.

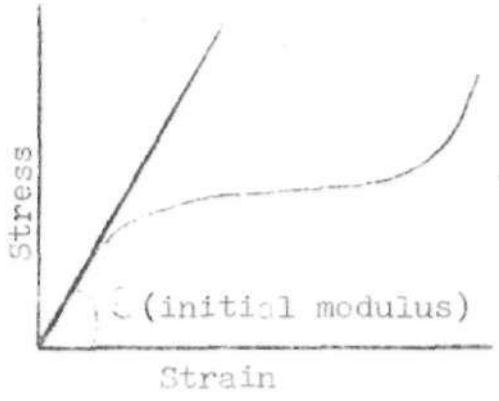
4.1.2 Polymer Testing.

Each cast film was cut into three thin strips of equal dimensions of 4.5 cm by 0.75cm. The average thickness of each thin strip was measured using a micrometer screw gauge. Tensile measurements were carried out using the Instron Tensile Tester (model 1026). Gauge length of each strip was 2cm. A maximum shear load of 1kg was used with chart speed of 10mm per minute and a cross head speed of 50mm.min^{-1}. This made chart to cross head speed equal 1:5. From the stress-strain curves obtained were calculated the following tensile mechanical properties:

Tensile strength: this was calculated using the formula.

$$\frac{\text{Breaking load}}{\text{Cross sectional area}} \ NM^{-2}$$

Initial modulus: this was calculated as the tangent of the stress-strain curve at zero stress and strain.



Elongation at break: this was calculated using the formula:

$$\frac{\text{Chart extension}}{\text{gauge length}} \times \frac{\text{Cross head speed}}{\text{chart speed}} \times 100$$

4.2 Results and Discussion.

4.2.1 Tensile Strength.

Figures 4.1 and 4.2 illustrate the variation of tensile strength with (%) conversion of vinyl acetate to polyvinyl acetate. For polymers produced at 58°C and with $[S_o]$ below the cmc of (SLS) using $0.75 g.dm^{-3}$ emulsifier, there was an initial increase in tensile strength up to about 28% conversion. This was followed by a gradual decrease up till 85% conversion. For polymers produced using $1.50 g.dm^{-3}$ of emulsifier a steady decrease in tensile strength up to $1.05 NM^{-2} \times 10^{7}$

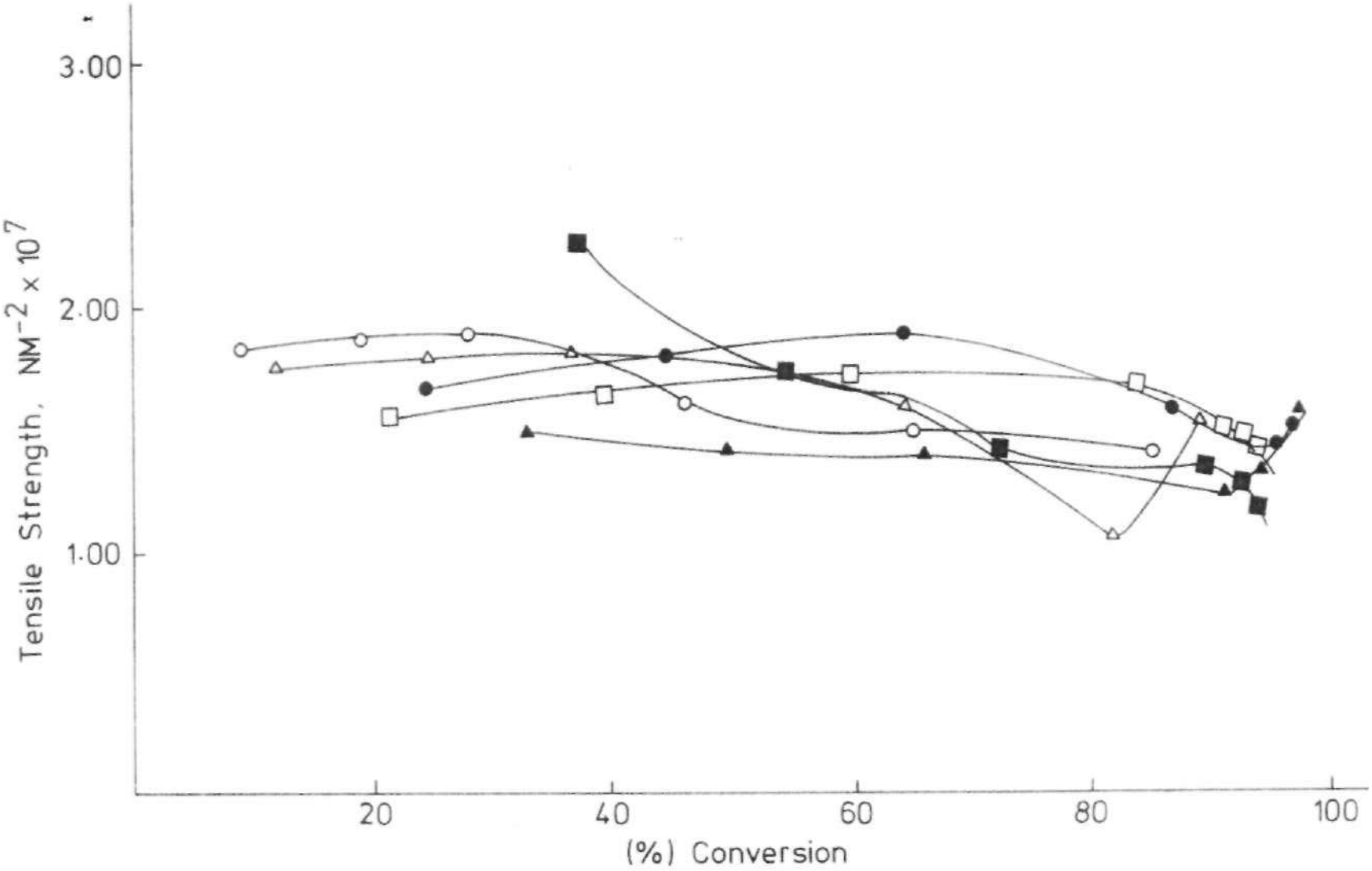


Fig. 4.1 Variation of tensile strength with (%) conversion of Polyvinyl acetate at 58°C with emulsifier concentration of (○), 0.75; (△), 1.50; (□), 2.25; (●), 3.75; (▲), 7.50, and (■), 15.0g. dm^{-3}.

at about 82% conversion was observed. This increased abruptly to about 1.50 $NM^{-2} \times 10^7$ at about 89% conversion. Using 2.25g.dm^{-3} $[S_o]$ gave polymers whose tensile strength also increased steadily from a value of about 1.54$NM^{-2} \times 10^7$ at 21% conversion to a value of about 1.70 $NM^{-2} \times 10^7$ at 59% conversion. This was followed by a gradual decrease reaching a minimum of 1.43 $NM^{-2} \times 10^7$ at 94% conversion. In fact tensile strength appeared not to vary very much with (%) conversion below the cmc especially for $[S_o]$ of 0.75 and 2.25g.dm^{-3}. Above the cmc of sodium lauryl sulphate, using 3.75g.dm^{-3} emulsifier increased tensile strength values of the polymers formed with (%) conversion. This suddenly decreased from 64% conversion to about 95% conversion and then increased again at 97% conversion. For polymers formed by polymerising with 7.50g.dm^{-3} and 15.0g.dm^{-3} of emulsifier, a slight decrease in tensile strength was observed for the former between 33% and 91% conversion followed by an abrupt increase between 91% and 97% conversion. For the latter, tensile strength decreased gradually with (%) conversion from about 2.50 $NM^{-2} \times 10^7$ at 37% conversion to 1.18 $NM^{-2} \times 10^7$ at 94% conversion.

At 63°C and below the cmc polymerisations carried out using 0.75, 1.50 and 2.25g.dm^{-3} of emulsifier gave polymers whose tensile strength decreased gradually from 3.2 $NM^{-2} \times 10^7$ at 14% conversion to 1.38 $NM^{-2} \times 10^7$ at 80% conversion, 2.38 $NM^{-2} \times 10^7$ at 21% conversion to

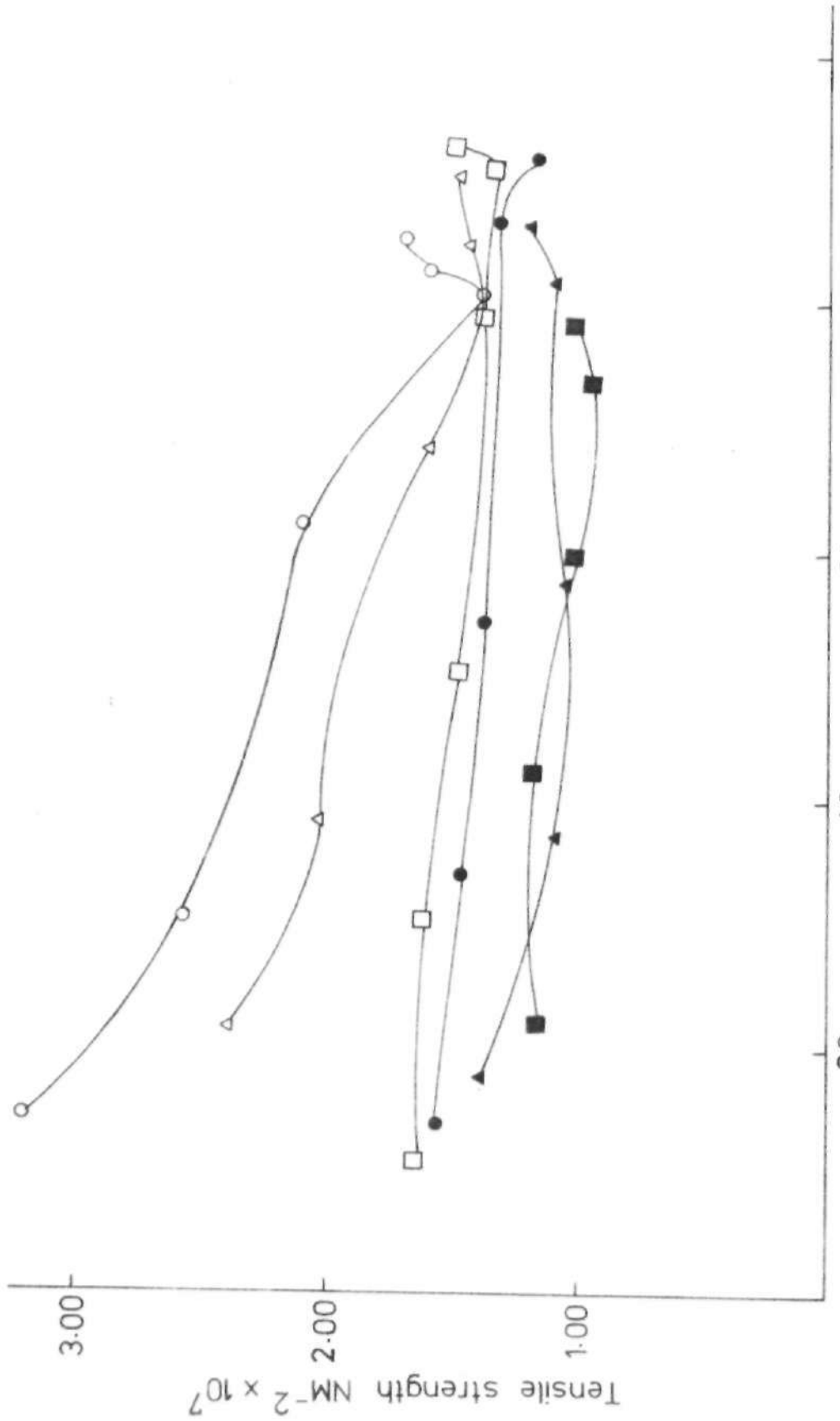


Fig. 4.2 Variation of tensile strength with (%) conversion of Polyvinyl acetate at 68°C with emulsifier concentration of (○), 0.75; (△), 1.50; (□), 2.25; (●), 3.75; (▲), 7.50 and (■), 15.0 g.dm^{-3}

1.45 NM^{-2} x 10^7 at 84% conversion, 1.64 NM^{-2} x 10^7 at 10.8% conversion to 1.34 NM^{-2} x 10^7 at about 91% conversion respectively. This was followed by an abrupt increase in tensile strength for the three emulsifier concentrations. Above the cmc, the same trend was observed with 7.50 and 15.0g.dm^{-3} of emulsifier where tensile strength decreased gradually before increasing. Using 3.75g.dm^{-3} emulsifier, tensile strength of the polymers formed decreased steadily from 1.57 NM^{-2} x 10^7 at 13.7% conversion till 1.18 NM^{-2} x 10^7 at about 91% conversion.

At 58°C, tensile strength values showed no particular trend with increasing $[S_o]$ both below and above the cmc of (SLS). At 68°C, tensile strength values seem to decrease with $[S_o]$ for polymers produced with $[S_o]$ both below and above the critical micelle concentration of sodium lauryl sulphate. Thus polymers formed with 0.75g.dm^{-3} $[S_o]$ seem to have the highest values in tensile strength while those formed using 2.25g.dm^{-3} $[S_o]$ had the lowest values in tensile strength below the cmc. Above the cmc too polymers formed with $[S_o]$ of 3.75g.dm^{-3} had the highest values for tensile strength while those formed with 15.0g.dm^{-3} $[S_o]$ had the lowest values. Moreover tensile strength decreased from below to above the cmc.

Tensile strength of the polymer should be influenced by molecular weight (38), increasing with increasing molecular weight just as $[\eta]$. Thus the decrease in tensile strength may be attributed to decrease in molecular weight caused

by chain transfer reactions leading to branching. This shortens the chain length and hence decreases molecular weight provided the branches are not very long. The decrease in tensile strength with increasing $[S_o]$ suggests that polymers produced with $[S_o]$ below the cmc of (SLS) are expected to have higher molecular weights since basically linear polymers are formed. While polymerising above the cmc of (SLS), chain transfer reactions set in giving rise to a polymer with a more rigid structure. Since tensile strength of the polymer film is strongly dependent on the type of solvent used, penetration of the solvent into the polymer molecules is important. For this study, chloroform was used and it is a very good solvent for polyvinyl acetate. This has been revealed by the report of Olayemi and Adeyeye (29) on some properties of polyvinyl acetate films cast from different solvents. Thus for polymers formed while polymerising vinyl acetate below the cmc of (SLS), the tensile strength values of the films are expected to be higher because they are linear and the interactions between the polymer and the solvent are greater than those of the polymer films above the cmc. Above the cmc the polymers formed are more compact hence penetration of the molecules by the solvent will be reduced. Therefore the films will be expected to have lower tensile strength values. Moreover for the samples produced with $[S_o]$ above the cmc, the tensile strength values of the polymer films do not vary much. This is an indication that the polymers exhibit

almost similar molecular properties. Tensile strength values of the polyvinyl acetate cast films are higher at 68°C than at 58°C. The highest at 68°C is 3.2 NM^{-2} x 10^7 while the highest at 58°C is 2.25 NM^{-2} x 10^7. Also this is an indication that tensile strength increases with temperature.

4.2.2 Initial modulus.

Initial modulus is a measure of the stiffness of polymer chains (38). Variation in initial modulus with (%) conversion and $[S_o]$ is illustrated in figures 4.3 and 4.4.

The initial modulus values for most of the films cast of the polyvinyl acetate samples seem to follow the same trend. The values seem to increase initially and then decrease. For polymers produced below the cmc of (SLS) using 0.75 and 2.25g.dm^{-3} of emulsifier, an initial increase was observed from 2.2 NM^{-2} x 10^2 at about 9% conversion to 3.2 NM^{-2} x 10^2 at about 46% conversion and from 1.07 NM^{-2} x 10^2 at about 21% conversion to 2.18 NM^{-2} x 10^2 at 91% conversion respectively. These values then decreased gradually for both emulsifier concentrations. A different trend was observed for samples produced using 1.50g.dm^{-3} emulsifier. In this an initial increase in initial modulus from about 1.58 NM^{-2} x 10^2 at 12% conversion to about 2.16 NM^{-2} x 10^2 at 38% conversion was observed.

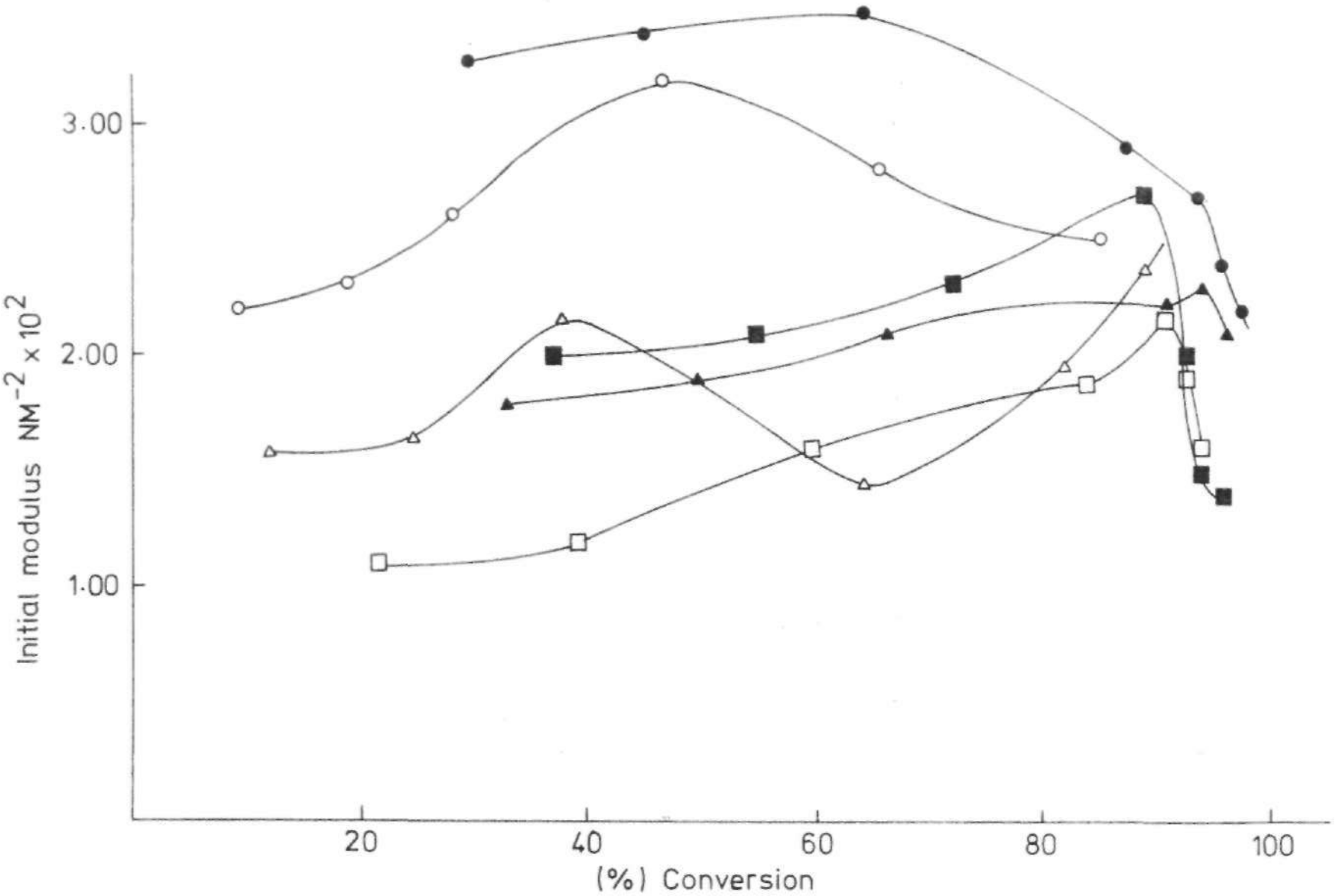


Fig. 4.3 Variation of initial modulus with (%) conversion of Polyvinyl acetate at 58°C using emulsifier concentration of (○), 0·75; (△), 1·50; (□), 2·25, (●), 3·75; (▲), 7·5 and (■), 15·0 g.dm^{-3}.

This was followed then by a sudden decrease down to about 1.45 $NM^{-2} \times 10^2$ at 64% conversion and then an increase again up till about 2.12 $NM^{-2} \times 10^2$ at 89% conversion. Above the cmc of (SLS) a similar trend was observed for all the emulsifier concentrations. An initial increase in initial modulus was observed for polymers produced using 3.75, 7.50 and 15.0g.dm^{-3} of emulsifier from 3.3 $NM^{-2} \times 10^2$ at 29% conversion to 3.5 $NM^{-2} \times 10^2$ at 64% conversion, from 1.78 $NM^{-2} \times 10^2$ at 33% conversion to 2.3 $NM^{-2} \times 10^2$ at 94% conversion and from 2.00$NM^{-2} \times 10^2$ at 37% conversion to 2.7 $NM^{-2} \times 10^2$ at 89% conversion respectively. These values decreased abruptly or gradually as the case may be.

At 68°C and below the cmc of (SLS), polymers formed exhibited the same trend in initial modulus for all the emulsifier concentrations employed. An initial increase followed by a gradual decrease was observed. Above the cmc of (SLS), the same trend was also observed for the polymer samples of vinyl acetate. Initial modulus values decreased steadily with (%) conversion.

With emulsifier concentration, initial modulus increased below the cmc at 58°C, thus emulsifier concentration of 0.75g.dm^{-3} gave polymers with the highest initial modulus values. Emulsifier concentration of 2.25g.dm^{-3} gave polymers with the lowest initial modulus values. Above the cmc of

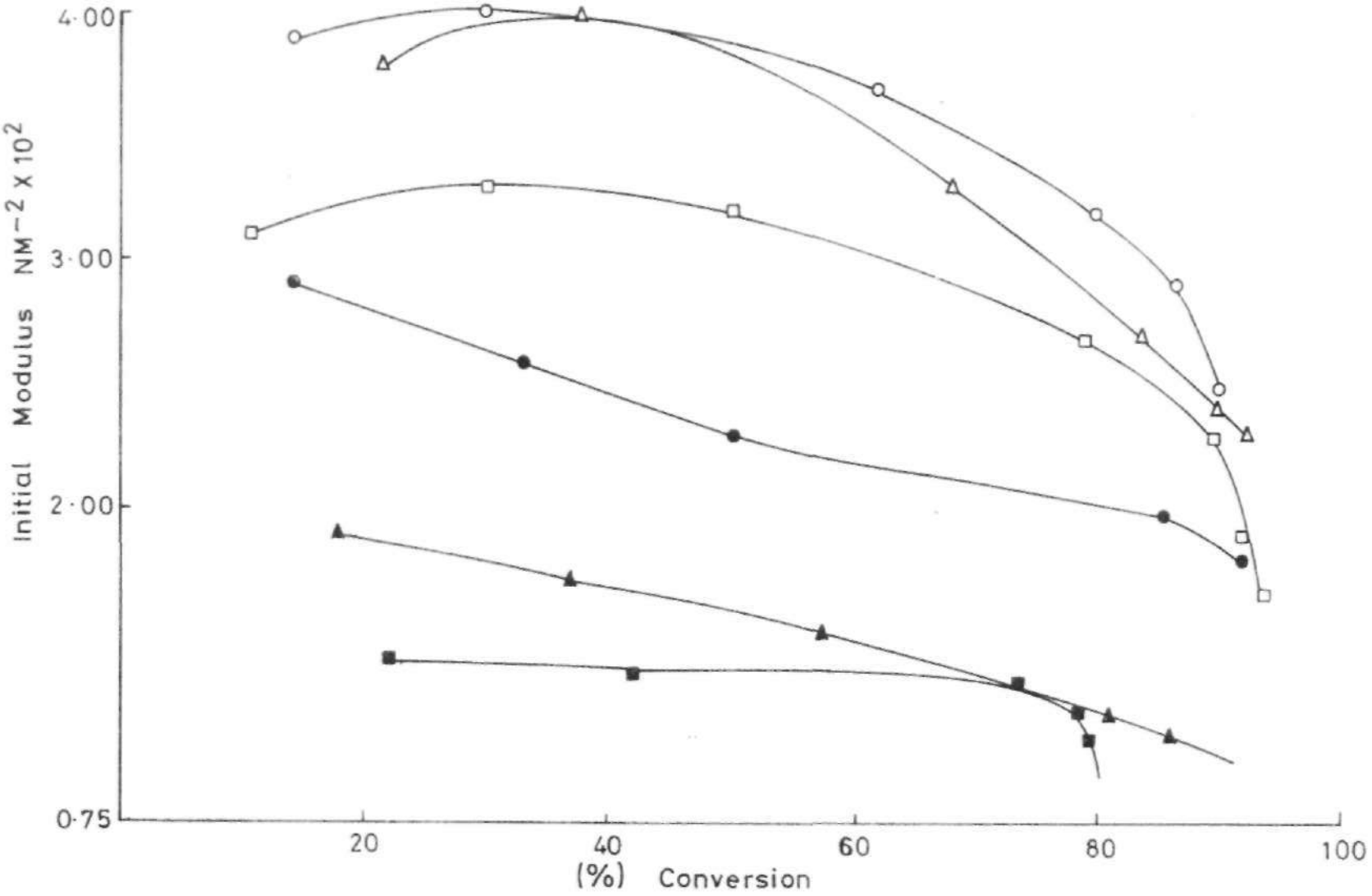


Fig. 4·4 Variation of Initial Modulus with (%) conversion of Polyvinyl Acetate at 68°C using Emulsifier Concentration of (○) 0·75; (△) 1·50; (□) 2·25; (●) 3·75; (▲) 7·50; (■) 15·0g.dm^{-3}

(SLS), initial modulus values decreased from using $3.75g.dm^{-3}$ of emulsifier to $7.50g.dm^{-3}$ of emulsifier and then increased to $15.0g.dm^{-3}$ of emulsifier. However, the values are higher above the cmc than below the cmc of (SLS).

Initial modulus is independent of molecular weight and the degree of crystallinity is effective in determining the stiffness of a polymer (38). It is thus assumed that above the cmc in the presence of micelles the polymer chains became more stiffened due to the presence of branches as a result of chain transfer reactions. Thus initial modulus values are expected to be higher for polymers obtained above the cmc of (SLS). At 68°C, initial modulus values decreased with emulsifier concentration from below to above the cmc of (SLS). Hence polymers obtained from polymerising with $0.75g.dm^{-3}$ below the cmc of (SLS) had the highest values while those obtained from polymerising with $15.0g.dm^{-3}$ above the cmc of (SLS) had the lowest initial modulus values. Initial modulus values are higher below the cmc of (SLS) at 68°C than at 58°C and higher above the cmc of (SLS) at 58°C than 68°C

Solvent also has an influence on initial modulus of the polyvinyl acetate cast films. As earlier mentioned, chloroform is strongly bonded by some secondary forces to the polymer chains and the solvating power is strong. This tends to restrict the movements of the flexible polymer chains hence a stiffened arrangement of the chains takes place.

4.2.3 (%) Elongation.

The plots of (%) elongation of the polymer films versus (%) conversion of vinyl acetate to polyvinyl acetate used for the films are presented in figures 4.5 and 4.6.

Generally, the (%) elongation values are high for the polymers produced at both temperatures. The values range between 400 and 650% elongation. For polymers produced at 58°C and with $[S_o]$ below the cmc of (SLS), a gradual increase in (%) elongation from 487% to 600% elongation at 28% conversion was followed by a gradual decrease to 549% elongation at about 87% conversion when 0.75g.dm^{-3} emulsifier was used. When 1.50g.dm^{-3} (SLS) was used, an initial increase in (%) elongation from 475% to 580% elongation at 37% conversion, followed by an abrupt decrease to 568% elongation at 64% conversion and then a gradual increase again till 612% elongation at 89% conversion was observed. With 2.25g.dm^{-3} of emulsifier, the polymers produced also showed the same trend as has just been described. An initial gradual increase in (%) elongation from 410% at about 21% conversion to 625% elongation at about 91% conversion was followed by an abrupt decrease to 593% elongation at about 93% conversion and again an abrupt increase to 637% elongation at about 96% conversion.

Working above the cmc of (SLS), polymers formed using 3.75 and 7.50g.dm^{-3} of emulsifier showed a reverse

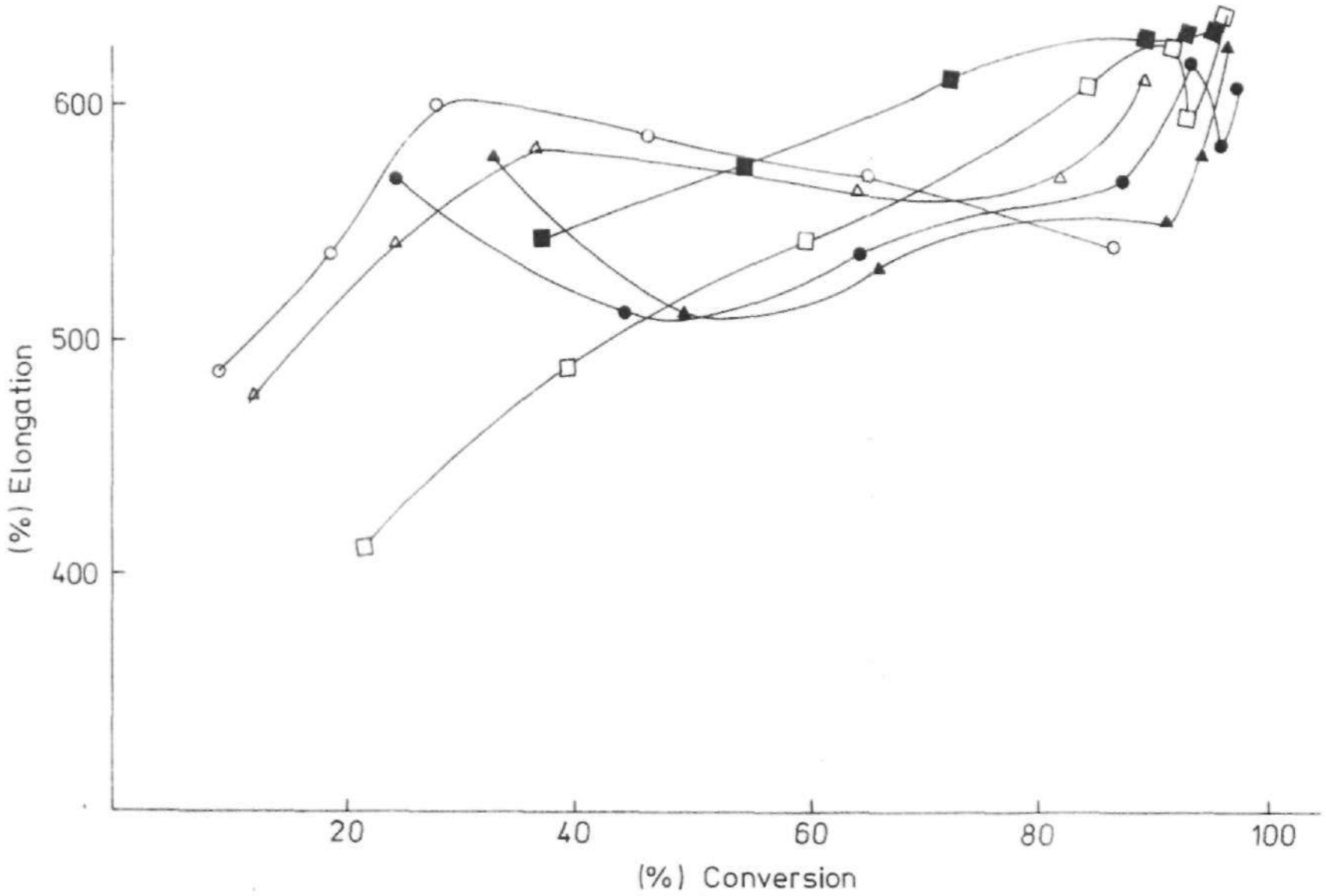


Fig. 4.5 Variation of (%) elongation with (%) conversion of Polyvinyl acetate at 58°C using emulsifier concentration of (○), 0·75; (△), 1·50; (□), 2·25; (●), 3·75; (▲), 7·50 and (■), 15·0 g·dm^{-3}

trend to what was obtained below the cmc of (SLS). The (%) elongation values initially decreased from 565% at about 25% conversion to 512% at 44% conversion and from 576% at 33% conversion to 512% at about 50% conversion respectively. These values then increased gradually with $7.5g.dm^{-3}$ (SLS) but they increased initially with $3.75g.dm^{-3}$ (SLS), decreased abruptly and then increased again. For polymers produced from using $15.0g.dm^{-3}$ emulsifier, the (%) elongation values increased gradually from about 543% at 37% conversion to about 634% at 95% conversion.

At $68^{o}C$ of polymerisation, (%) elongation increased initially, decreased gradually and then increased again for polymers produced from using $0.75g.dm^{-3}$ and $3.75g.dm^{-3}$ both below and above the cmc. For polymers produced from using 1.50 and $7.50g.dm^{-3}$ both below and above the cmc of (SLS), (%) elongation increased initially gradually, decreased abruptly and then remained constant for the former. For the latter concentration, the polymers produced showed an initial increase in (%) elongation, followed by an abrupt decrease, an abrupt increase and then remained constant with (%) conversion. Using 2.25 and $15.0g.dm^{-3}$ both below and above the cmc, (%) elongation values of the polymers showed the same trend. It first of all decreased from about 582% at 22% conversion to 523% at 73% conversion for the polymers produced from using $15.0g.dm^{-3}$ of emulsifier above the cmc. It then increased suddenly to 550% at 78% conversion. For polymers produced from using

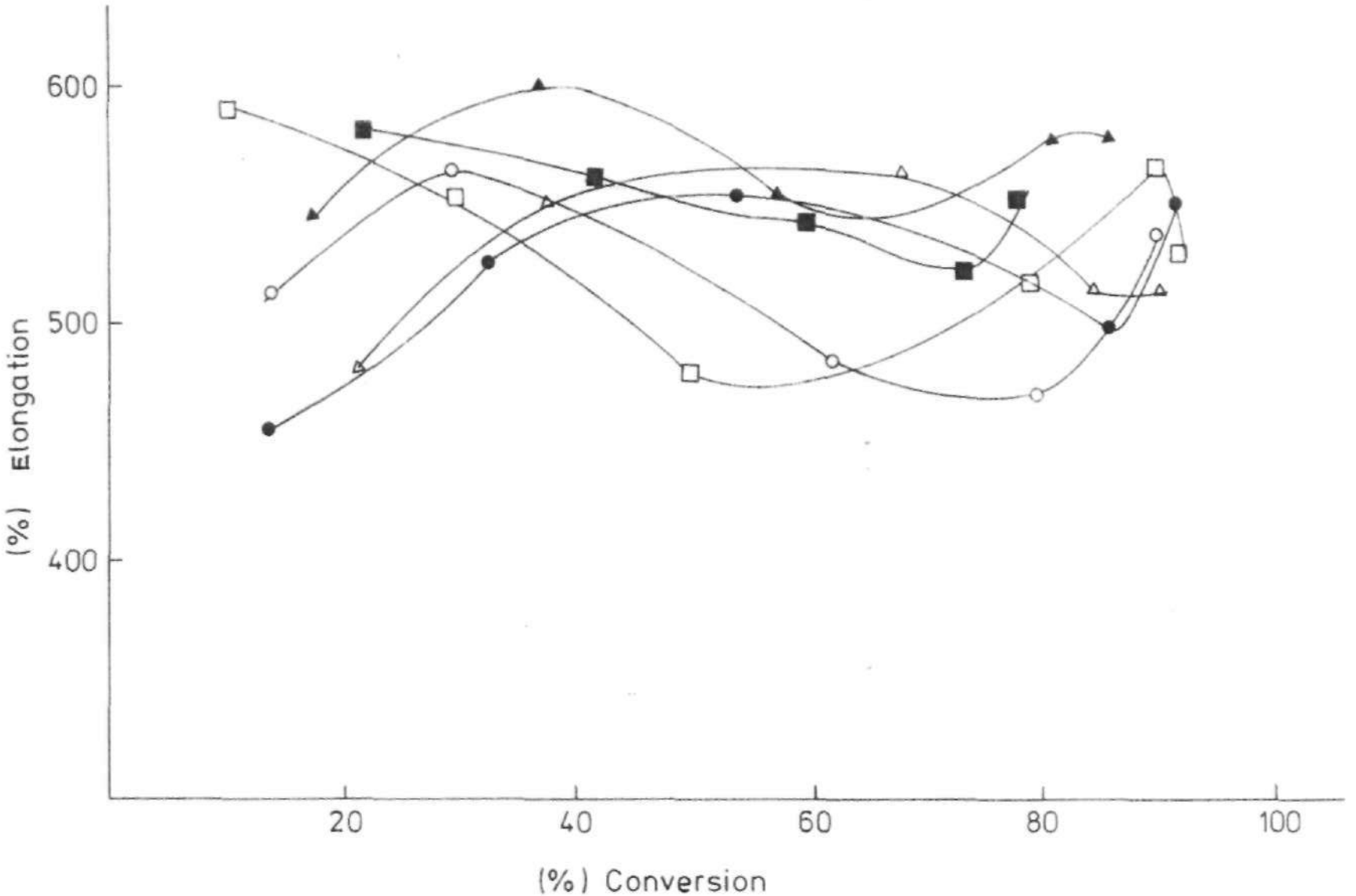


Fig. 4.6 Variation of (%) elongation with (%) conversion of Polyvinyl acetate at 68°C using emulsifier concentration of (○), 0.75; (△), 1.50; (□), 2.25; (●), 3.75; (▲), 7.50 and (■), 15.0 g·dm^{-3}

2.25g.dm^{-3} [S_c], (%) elongation first of all decreased from 590% at 10.8% conversion to 480% at 50% conversion and then it increased gradually to 562% at 95% conversion. In fact, generally (%) elongation did not seem to follow any particular trend as observed for tensile strength and initial modulus.

With increasing [S_c] for the polymerisations, (%) elongation of the polymers produced showed a decrease in its values at 58°C for polymerisations carried out below the cmc of (SLS) i.e. polymers formed from using 0.75g.dm^{-3} of emulsifier had the highest values especially at the initial stages of the (%) conversion. Behaviour of (%) elongation of polymers produced with [S_c] above the cmc is difficult to describe as there is no particular trend. At 68°C of polymerisation the trend too is complicated both below and above the cmc of (SLS) as (%) elongation values show alternate trends for the polymers produced.

Elongation of a polymer is influenced by the morphology of the polymer (38). Polymers with finer - textured spherulites tend to fail at high elongation after drawing, while those with large, coarse spherulites often fail by brittle fracture between spherulites at low elongation (38). Thus (%) elongation of samples produced is expected to increase in going from below to above the critical micelle concentration of (SLS). This was not

observed here for the polymers and it can be assumed that modification of the polymer structures must have taken place. Solvent used plays a part in modifying the macromolecular structures and the high values of (%) elongation obtained may be attributed to the strong forces existing between the polymer chains and the solvent.

4.2.4 Comparison of tensile strength, initial modulus and (%) elongation.

From figures 4.1 to 4.6, tensile strength of the polyvinyl acetate films cast from chloroform appear to show almost the same trend as initial modulus. For polymerisations carried out at 58°C an initial increase in tensile strength with (%) conversion was observed for the polymers produced using $[S_o]$ below and above the cmc except for $[S_o]$ of 7.50 and 15.0g.dm^{-3} where an initial decrease was obtained. For initial modulus for the polymers produced from using $[S_o]$ below and above the cmc, an initial increase was observed. For polymerisations carried out at 68°C both below and above the cmc of (SLS), tensile strength and initial modulus of the polymers were found to decrease with (%) conversion and $[S_o]$.

For (%) elongation at 58°C, the polymers produced showed an initial increase as observed for tensile strength

values for some of the $[S_o]$ used. However while an initial decrease in (%) elongation was observed for polymers produced from using 3.75 and 7.50g.dm^{-3} $[S_o]$ above the cmc, an initial decrease in tensile strength was observed for polymers produced from using $[S_o]$ of 7.50 and 15.0g.dm^{-3}. At 68°C, the polymers produced showed an initial increase in (%) elongation for all the $[S_o]$ used except for 2.25g.dm^{-3} below the cmc of (SLS) and 15.0g.dm^{-3} above the cmc of (SLS). For tensile strength the polymer samples showed a decrease in the values for all the $[S_o]$ employed.

Moreover, tensile strength and initial modulus values for polymers produced at the two temperatures were highest below the cmc of (SLS) at 68°C and highest above the cmc of (SLS) at 58°C. With (%) elongation, no particular trend was observed for the polymers produced both below and above the cmc of (SLS) for the two temperatures employed in the polymerisation.

CHAPTER V

5.1 Relationship between [η] and tensile strength, initial modulus and (%) elongation of polyvinyl acetate films.

Figures 5.1 to 5.6 show plots of the relationship between viscosity and tensile strength, initial modulus and (%) elongation of polyvinyl acetate cast films. As earlier mentioned, [η] is a function of molecular weight and the macromolecular structures of a polymer. It is affected by branching in the polymer backbone including the type and length. As can be seen from fig. 5.1, at 58°C and below the cmc of (SLS) i.e. for emulsifier concentrations of 2.25g.dm^{-3} and below, some form of relationship could be deduced. Starting from the lowest $[S_o]$, 0.75g.dm^{-3}, tensile strength increased slightly initially with [η] up to a value of about 1.57 g^{-1}.dl from where it decreased. Using 1.50 and 2.25g.dm^{-3} of emulsifier also caused tensile strength to increase slightly as [η] increased up to 1.128g^{-1}.dl for 1.50g.dm^{-3} $[S_o]$ before decreasing as [η] increased and up to 1.59g^{-1}.dl for 2.25g.dm^{-3} $[S_o]$. From this point, tensile strength decreased as [η] decreased. Above the cmc of (SLS), only polymers produced from using 3.75g.dm^{-3} of emulsifier showed the same trend as that described for polymers below the cmc. The other two concentrations of emulsifier appeared not to show any form of relationship between [η] and tensile strength hence much could not be said on this.

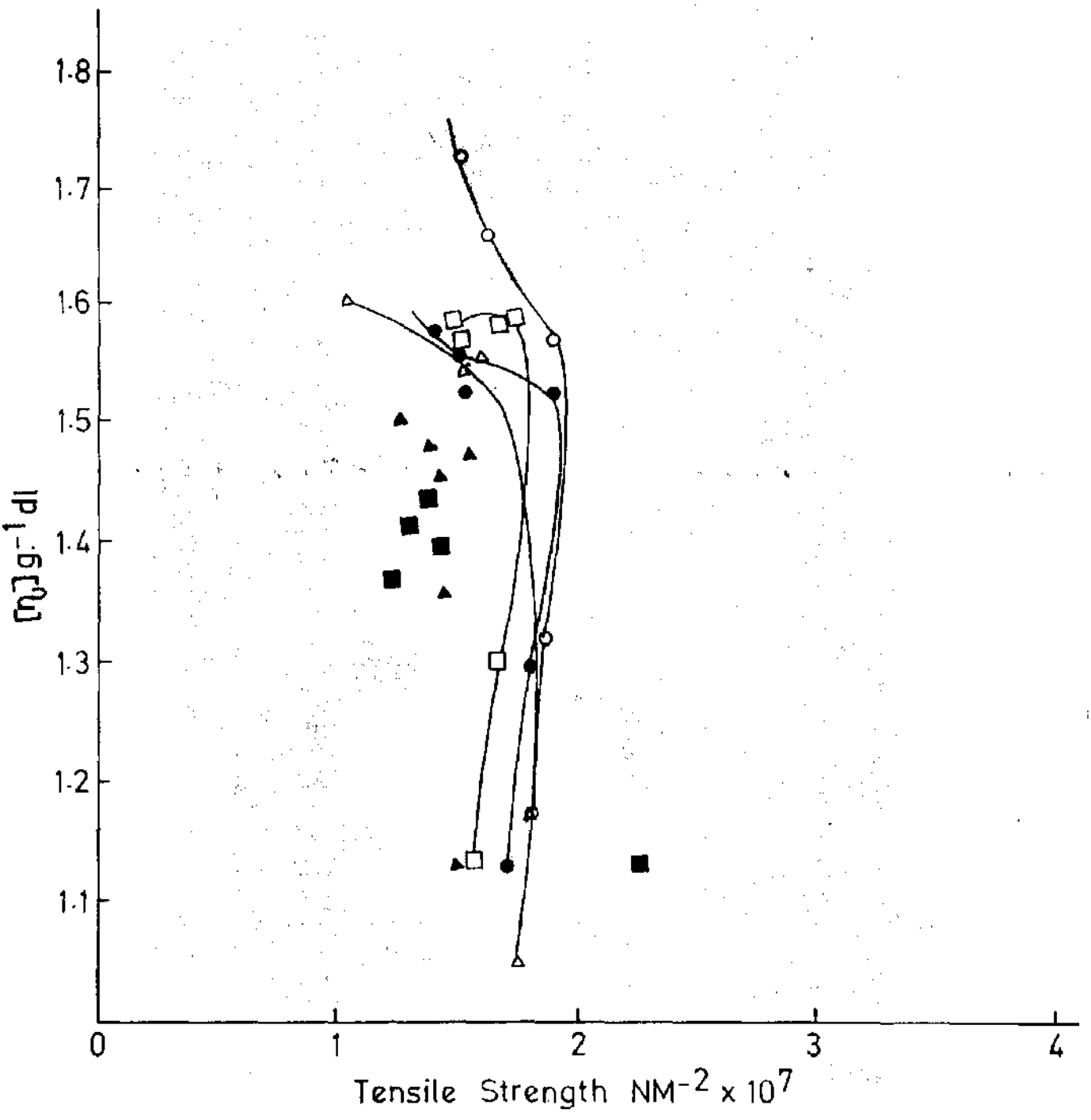


Fig. 5.1 Relationship between $[\eta]$ and tensile strength of Polyvinyl acetate samples prepared at 58°C using emulsifier concentration of (○)–0·75, (△)–1·50, (□)–2·25, (●)–3·75, (▲)–7·50 and (■)–15·0g.dm-3

Tensile strength is also associated with the morphological characteristics of a polymer. Factors that have a significant effect on such characteristic include molecular weight and its distribution and chain modification (39). Molecular weight affects chain mobility through entanglements and hence all those properties which depend on such chain mobilities like crystallinity (39). The higher the molecular weight, the greater the number of points of attraction and entanglement between molecules (39). Usually for linear polymers, molecular weight is expected to increase with conversion as does $[\eta]$. In such a case tensile strength is expected to decrease. The slight increase noticed in tensile strength as described above may be due to some modification of the polymer structure. Branching on the polymer backbone could be one such factor that could modify the characteristics of a polymer thereby increasing the tensile strength and decreasing the molecular weight as a result of shortening of the chain length. Solvents used in casting polymer films could also be responsible for modifying the macromolecular structure. Chloroform used for this study is capable of forming strong secondary bonds with the polymer molecules and this toughens the polymer (29).

Fig. 5.2 gives the relationship between $[\eta]$ and initial modulus for the polymers at 58°C. Below the cmc of (SLS),

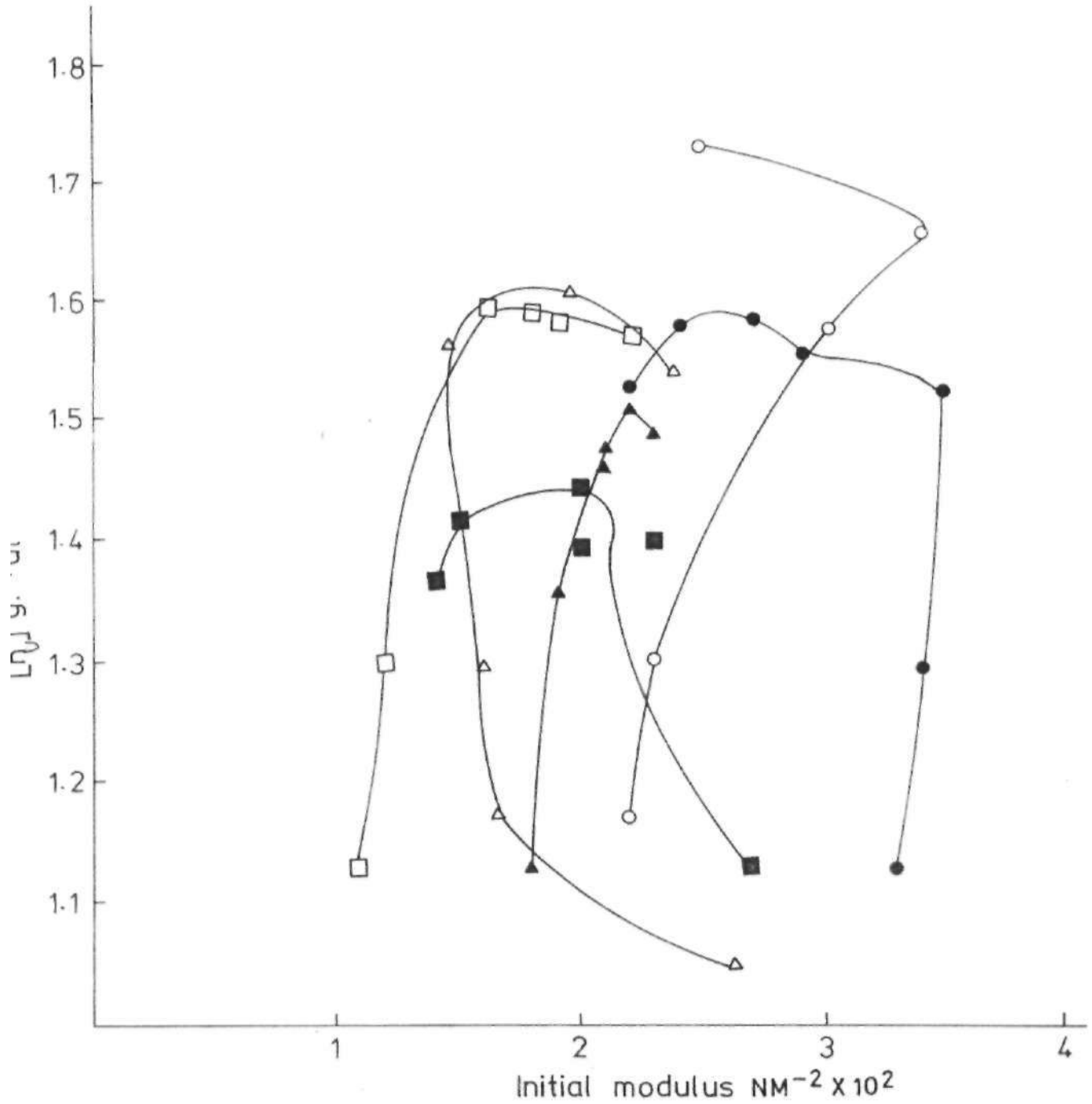


Fig. 5.2 Relationship between $[\eta]$ and Initial modulus of Polyvinyl acetate samples prepared at 58°C using emulsifier concentration of (o)-0.75, (△)-1.50, (□)-2.25, (●)-3.75, (▲)-7.50 and (■)-15.0g.dm^{-3}

for polymers obtained from using 0.75g.dm^{-3} of emulsifier, initial modulus increased steadily up till about 1.66g^{-1}.dl where initial modulus suddenly decreased with increase in $[\eta]$. Using $[S_o]$ of 1.50g.dm^{-3} seemed to cause a decrease in the initial modulus of the polyvinyl acetate cast films as $[\eta]$ increased up to a value of about 1.56g^{-1}.dl where initial modulus started increasing as $[\eta]$ increased to about 1.6g^{-1}.dl. After this point, initial modulus still increased but $[\eta]$ decreased to 1.54g^{-1}.dl. Using 2.25g.dm^{-3} of emulsifier also caused an increase in initial modulus as $[\eta]$ increased. After $[\eta]$ increased to 1.59g^{-1}.dl, initial modulus still increased but $[\eta]$ decreased almost to a constant value. Above the cmc, using 3.75 and 7.50g.dm^{-3} of emulsifier, initial modulus increased as $[\eta]$ increased but it suddenly decreased for 3.75g.dm^{-3} of emulsifier up to a value of about 1.58g^{-1}.dl for which $[\ ]$ still increased. After this point both parameters decreased. Using 15.0g.dm^{-3} of emulsifier, initial modulus generally decreased as $[\eta]$ increased up to a point where both parameters gradually decreased. Initial modulus is also associated with the macromolecular characteristics of a polymer as tensile strength (38). Initial modulus is a measure of the stiffness of a polymer chains. The increase in initial modulus may also be attributed to the fact that modification of the macromolecular structure could have taken place. The occurence of branching and the interaction between the polymer molecules

and the solvent used both tend to give a stiffened arrangement of the polymer chains and these cause initial modulus to increase.

Fig. 5.3 shows the relationship between $[\eta]$ and (%) elongation of the polyvinyl acetate samples prepared at 58°C. From the plot obtained from using 0.75g.dm^{-3} of emulsifier below the cmc, (%) elongation increased as $[\eta]$ increased and then it decreased again. The trend obtained with $[S_o]$ of 1.50g.dm^{-3} below the cmc of (SLS) is not so straightforward. There was an initial increase in (%) elongation as $[\eta]$ increased from 1.05 to 1.3g^{-1}.dl. Then a decrease in (%) elongation was found followed by another increase as $[\eta]$ increased. While (%) elongation increased after this, $[\eta]$ decreased. With $[S_o]$ of 2.25g.dm^{-3} below the cmc of (SLS), (%) elongation increased steadily as $[\eta]$ also increased to about 1.59g^{-1}.dl and while (%) elongation increased, $[\eta]$ decreased to a constant value till about 1.57g^{-1}.dl. Above the cmc, a slightly different trend was obtained. With $[S_o]$ of 3.75 and 7.50g.dm^{-3}, (%) elongation initially decreased and then increased as $[\eta]$ increased. After some time $[\eta]$ decreased though (%) elongation increased for $[S_o]$ of 7.50g.dm^{-3}. Using 15.0g.dm^{-3} of emulsifier gave the same trend described for some $[S_o]$ below the cmc. The (%) elongation values for the polymers increased steadily as $[\eta]$ increased but $[\eta]$ started decreasing after sometime. The (%) elongation of a polymer

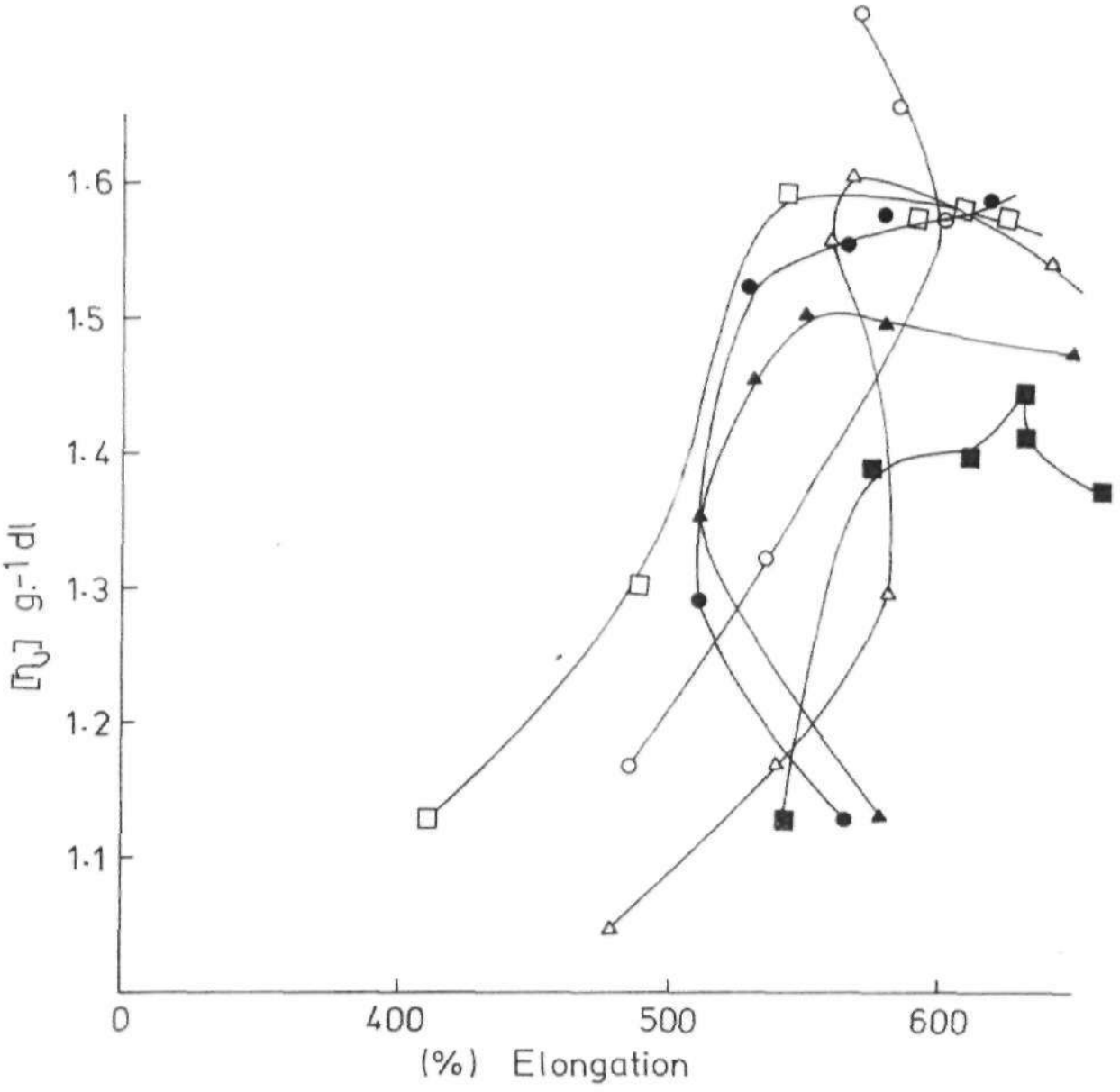


Fig. 5.3 Variation of $[\eta]$ of Polyvinyl acetate prepared at 58°C with (%) elongation of Polyvinyl acetate films using emulsifier concentration of (○) – 0.75, (△) – 1.50, (□) – 2.25, (●) – 3.75, (▲) – 7.50 and (■) – 15.0 g.dm^{-3}

usually has an opposite trend of variation to that obtained for tensile strength and initial modulus. For a linear polymer, increase in tensile strength and initial modulus means a decrease in (%) elongation. The decrease in (%) elongation could be due to the fact that straightening of the flexible chains of the polymer could develop rubbery strains and this causes a decrease in the stress needed for any deformation (38). The suggestion is therefore made that for polymers whose (%) elongation had the same trend in variation as tensile strength and initial modulus, modification of the polymer structure could have led to a more rigid structure thereby increasing the stress needed for any deformation. Moreover, when considering the effect of branching, it could be assumed that branches of irregular sizes i.e. long and short, which could have the same tensile strength could still have different (%) elongation. The increase in (%) elongation could have resulted from long branches on the backbone of the polymer. These long branches could still act as a backbone for other branches which could invariably be short or long.

At 60°C and below the cmc of (SLS), almost the same trend was observed between tensile strength and $[\eta]$ for the three $[S_o]$ employed. Tensile strength decreased as $[\eta]$ increased. Above the cmc, no direct relationship could be obtained between these parameters due to a scattering of

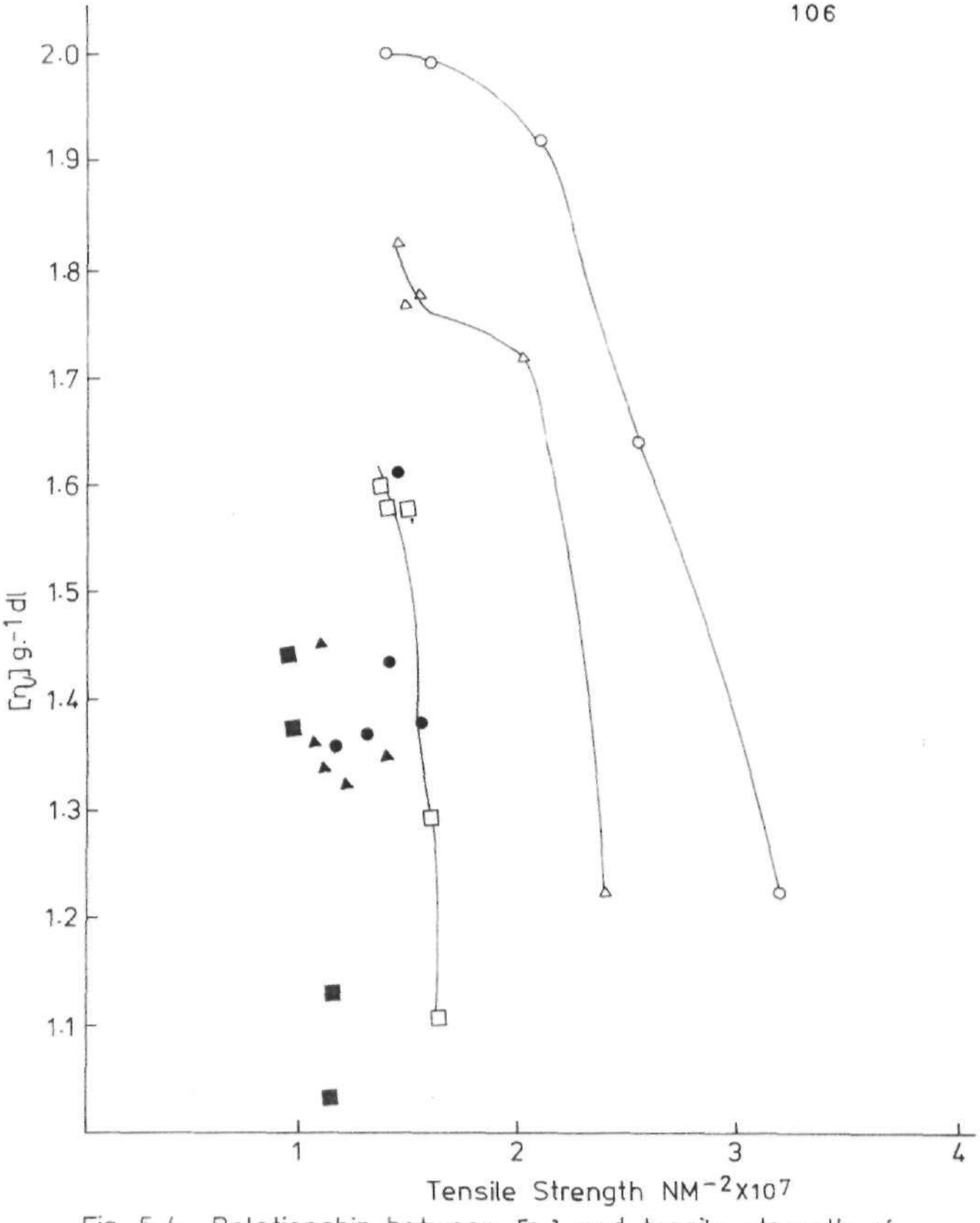


Fig. 5.4 Relationship between $[\eta]$ and tensile strength of Polyvinyl acetate samples prepared at 68°C using emulsifier concentration of (○)–0.75, (△)–1.50, (□)–2.25, (●)–3.75, (▲)–7.50 and (■)–15.0 g.dm^{-3}

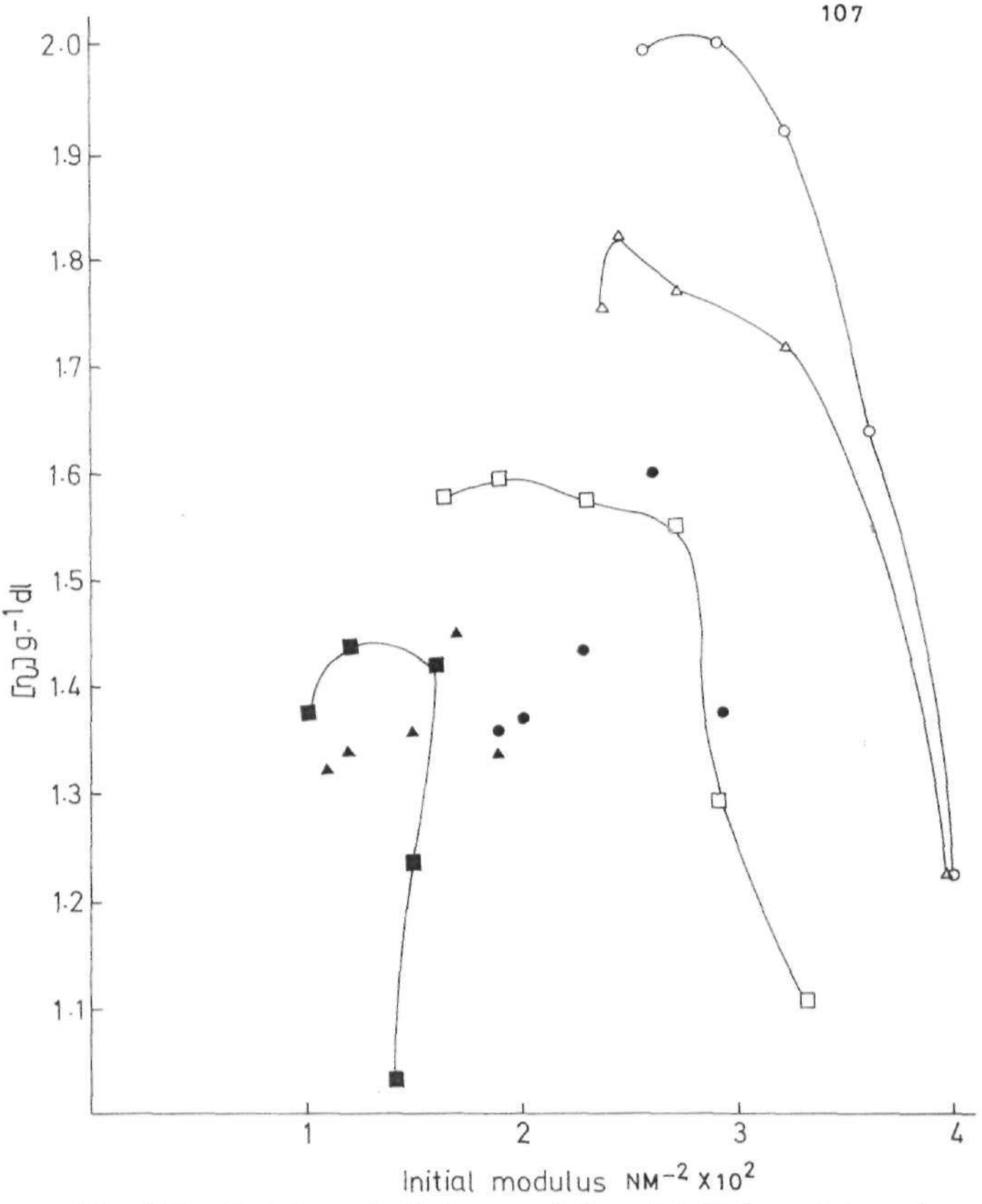


Fig. 5.5 Relationship between $[\eta]$ and Initial modulus of Polyvinyl acetate samples prepared at 68°C using emulsifier concentrations of (o)–0.75, (△)–1.50, (□)–2.25, (●)–3.75, (▲)–7.50 and (■)–15.0g.dm^{-3}

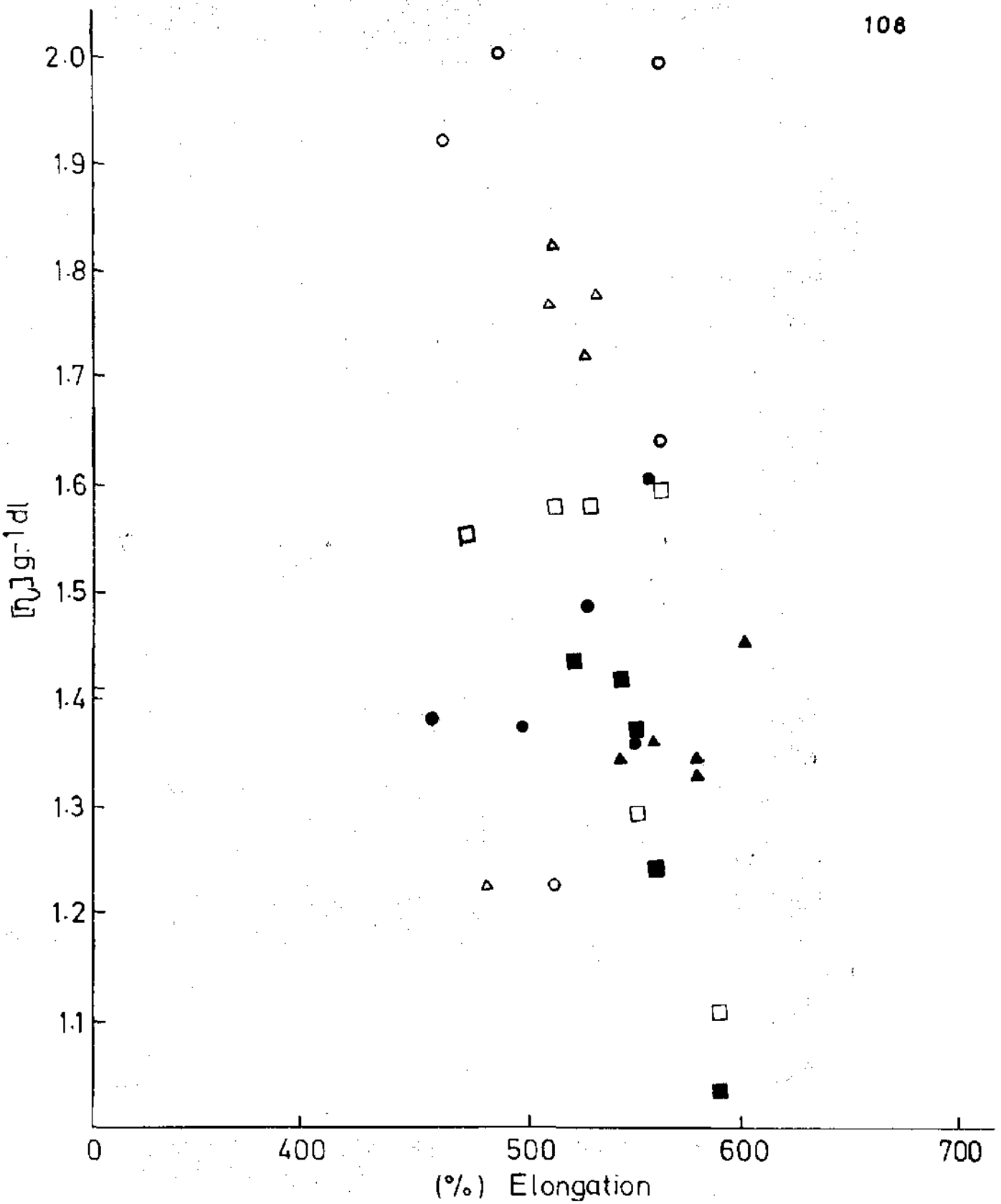


Fig. 5.6 Relationship between [η] and elongation of Polyvinyl acetate samples prepared at 68°C using emulsifier concentration of (○)–0.75, (△)–1.50, (□)–2.25, (●)–3.75, (▲)–7.50 and (■)–15.0g.dm^{-3}

the points. For initial modulus, for all the $[S_o]$ below the cmc, initial modulus decreased steadily as $[\eta]$ increased and then $[\eta]$ suddenly decreased. Above the cmc, no direct relationship could be found using $[S_o]$ of 3.75 and 7.50g.dm^{-3}. Using 15.0g.dm^{-3}, a slight increase in initial modulus was observed as $[\eta]$ increased to about 1.42g^{-1}.dl after which initial modulus decreased. These trends were not obtained for the polymers prepared at 58^{o}C suggesting that temperature plays an important role here. For the (%) elongation, only polymers formed by using $[S_o]$ of 1.50 and 2.25g.dm^{-3} showed a relationship though different from that at 58^{o}C. With 1.50g.dm^{-3} of (SLS), (%) elongation generally increased with $[\eta]$ while using 2.25g.dm^{-3} of (SLS) gave polymers whose (%) elongation showed an initial decrease followed by an increase as $[\eta]$ increased. For the other emulsifier concentrations, no relationship could be established between (%) elongation and $[\eta]$ due to a scattering of the points.

CHAPTER VI

6.1 Conclusions and Recommendations.

1. The emulsion polymerisation of vinyl acetate is characterised by two distinct factors (a) vinyl acetate is sufficiently soluble in water to encourage polymerisation in the aqueous phase, (b) the vinyl acetate radicals are susceptible to chain transfer agents or retarders in the process of the polymerisation. This gives rise to branching.

2. An induction period which was found to depend on temperature of polymerisation decreased as the temperature was changed from 58°C to 68°C. The induction period was also found to decrease with increasing $[S_o]$ from below to above the cmc. It was however concluded that the induction time might not affect the rate of polymerisation of vinyl acetate whenever polymerisation begins as determined from the slope of the linear portion of the graph.

3. The general trends of variation of (%) conversion with time of polymerisation were similar for the two temperatures used for the study. There was polymerisation both below and above the cmc of (SLS). It is concluded that vinyl acetate emulsion polymerisation shows a deviation from the classic theories of Smith and Ewart and Haward. This was explained in terms of the solubility

of vinyl acetate. The rate of polymerisation increased with increase in $[S_o]$ and temperature. At high emulsifier concentrations chain transfer reactions set in slowing down R_p especially at the higher temperature.

The form of dependence of R_p on the exponent of the emulsifier concentrations was established at the two temperatures, 58°C and 68°C and a range of $[S_o]$. It was concluded that R_p showed a greater dependency on $[S_o]$ below the cmc of (SLS) than above it and that at 68°C and possibly at much higher temperatures, R_p would become independent of $[S_o]$. Generally the value of the exponent of $[S_o]$ obtained did not compare well with those of other monomers. This clearly shows a deviation as far as emulsion polymerisation of vinyl acetate is concerned.

2. Intrinsic viscosity values do not vary very much with $[S_o]$ both below and above the cmc of (SLS) at both temperatures. However, $[\eta]$ decreased in going from below to above the cmc of (SLS), indicating the presence of branches especially above the cmc of (SLS). It was concluded that polymers formed below the cmc of (SLS) will be expected to have higher molecular weights than those formed above it. Branching became more pronounced as temperature increased thus molecular weight is expected to be less above the cmc at 68°C than at 58°C. Generally, the interaction between polymer and solvent gave high values of Huggins

constant k' below the cmc at the lower temperature of 58°C although did not seem to be much variation above the cmc for the two temperatures. It is thus reasonable to conclude that this could be due to the greater molecular weight values for polymers below the cmc at 58°C. The difference in k' values obtained from the different $[S_o]$ suggests differences in the interaction between polymer and solvent and probably in the macromolecular structure and size.

3. Branching was believed to be responsible for some strange variations in the mechanical properties as a result of the modification of the polymer macromolecular structures. It was also concluded that the solvent used in casting films played an important role in the modification and therefore the mechanical properties of the polymer are somewhat dependent on the type of solvent used. As tensile strength and initial modulus increased, (%) elongation decreased.

Recommendations.

1. More extensive and comprehensive research on the emulsion polymerisation characteristics of other soluble vinyl monomers below the cmc of emulsifier should be carried out and compared to the polymerisation characteristics of vinyl acetate.

2. The form of dependence of the exponent of $[S_o]$ using a range of $[S_o]$ and varying the temperature should be established for other vinyl monomers both soluble and insoluble.

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