

POLYMERISATION OF VINYL ACETATE IN AQUEOUS
EMULSIFIER WITHOUT MICELLES

by

YETUNDE OLUREMI MOSURO,
B.Sc., (Hons.), Chem. U.I.

A thesis submitted to the Postgraduate School,
Ahmadu Bello University, in partial fulfilment
of the requirements for the degree of; MASTER
OF SCIENCE in POLYMER SCIENCE AND TECHNOLOGY.

Department of Chemistry,
Faculty of Science,
Ahmadu Bello University,
Zaria.

JUNE, 1983.

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.

SUPERVISOR
Dr. J. Y. Olayemi

CANDIDATE
Yetunde O. Mosuro

Date: -----

Date: -----

THESIS RECOMMENDATION

We hereby recommend that the thesis prepared by Miss Y. O. Mosuro entitled, "Polymerisation of vinyl acetate in aqueous emulsifier without micelles", be accepted in partial fulfilment of the requirements for the degree of M.Sc. Polymer Science and Technology.

Internal Examiner

External Examiner

Date: -----

Date: -----

DEDICATION

This work is fondly dedicated to every member of my family for their love support and patience throughout the course of this work.

ACKNOWLEDGEMENTS

I wish to express my sincere gratitude to my supervisor, Dr. J.Y. Olayemi, for his guidance, useful and meaningful discussions, encouragement and cooperation throughout the course of this work.

My thanks also go to the head of Chemistry department, Dr. H.T. Bozimo, for providing me the opportunity to carry out this work.

I would like to express my appreciation to Mr. Smith and other technical staff of the department for their kind assistance in the laboratory and the store.

I am indebted to Mrs. A.A. Nwaokorie who typed this project and to all who contributed in various ways to the success of this work and whose names are too numerous to be listed, I say a big thank you and may Lord continue to shower his blessings on you all (Amen).

YETUNDE MOSURO.

ABSTRACT

The effect of four different monomer and emulsifier concentrations and two different initiator concentrations on the kinetics of polymerisation of vinyl acetate at 55 ± 0.05 °C, below the critical micelle concentration of sodium lauryl sulphate as emulsifier, using potassium persulphate as the initiator, and on some properties of the polymer samples produced have been studied. The form of the dependence of the rate of polymerisation (R_p), on the exponent of the emulsifier and initiator concentrations was also studied. The forms of the variation of limiting viscosity and Huggins• constant with (%) conversion of monomer to polymer were also studied.

The rate of polymerisation of vinyl acetate under the conditions studied was appreciable, increasing with increase in the emulsifier concentration. The form of the dependence of rate on the exponent of emulsifier concentration on the rate of polymerisation was independent of monomer concentration but dependent on the initiator concentration. The rate of polymerisation decreased as the monomer concentration increased. Generally, polymerisation of vinyl acetate in the absence of micelles is explained as due to the combination of factors including partial solubility of vinyl acetate in water, agitation which allows for interaction of monomer molecules with the free radicals, and diffusion of free radicals from the aqueous to the monomer layer. Delay in the

action of these factors have caused an induction period to the polymerisation reaction.

Limiting viscosity values for the polyvinyl acetate - methanol systems at $30 \pm 0,05$ C were obtained and used to qualitatively describe the pattern of the dependence of polymer molecular characteristics mainly (molecular weight with branching) on the conditions of the polymerisation. Conclusions were drawn showing that molecular characteristics of the polymers produced at lower conversions of the monomer are significantly different from those at higher conversions. These properties, are also affected by emulsifier, monomer and initiator concentrations. Huggins constant was used as a measure of polymer-solvent interactions and an estimate of size of polymer backbone, degree of branching and length, as described qualitatively.

Generally, the study shows that many of the results can not be explained in terms of the classical theories of emulsion polymerisation of vinyl monomers.

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CHAPTER 1

1.0 INTRODUCTION

1.1 GENERAL CONCEPT OF THE KINETICS OF EMULSION POLYMERISATION REACTION

In the study of the kinetics of polymerisation of a monomer, it is important to first determine if the polymerisation reaction would proceed in the absence of an initiator. In the present investigation, information exists that initiators are required. The type of initiator chosen for this study is called free radical producing initiator. Polymerisation carried out using this initiator is termed free radical polymerisation. It is a three step reaction and these are given briefly as:

(a) Initiation step:

This step is a two-stage reaction involving

- (i) initiator decomposition to form free radicals and
- (ii) radical attack on a monomer unit to form an active chain carrier. Hence, the initiation step involves the production of the active centre known as a free radical which acts as a chain carrier.

(i) Production of free radicals

A free radical is usually formed by the thermal decomposition of a relatively unstable material called an initiator (1). The radical thus produced is sufficiently stable and can react with a monomer and create an active

centre. A free radical can also be produced by interaction of chemical reagents.

(ii) Mechanism of radical formation

If the radical formed by the decomposition of the initiator is designated $R\cdot$, then the reaction can be written as



where k_d is the initiator dissociation constant. The reaction between the radical and the monomer gives the reaction below;



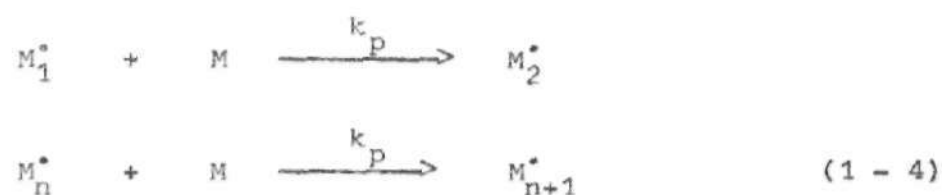
where k_i is the initiation rate constant. The initial decomposition of the initiator is slow compared with both the rate of addition of primary radical to a monomer and the termination reaction. Thus the initial decomposition reaction is regarded as the rate determining step (2). The rate of initiation V_1 , is then the rate of production of chain radicals and is represented by the equation;

$$V_1 = \frac{d[RM\cdot]}{dt} = 2k_d f [I] \quad (1 - 3)$$

where the factor 2 is introduced because two potentially effective radicals are produced in the decomposition, and f , measures the ability of these free radicals to propagate chains in the reactions.

(b) Propagation step:

This is the addition of more monomer to a growing chain usually very rapidly to obtain a high molecular weight for the polymer. It is thus a simple step which involves a simple collision between the monomer and the active growing chain end. The chain radical formed in the initiation step is capable of adding successive monomers to propagate the chain. The successive steps in the propagation reactions are:



where M is the monomer and k_p is the rate constant for propagation.

The propagation steps are assumed to have the same rate constant k_p , since the radical reactivity is presumed to be independent of chain length (1).

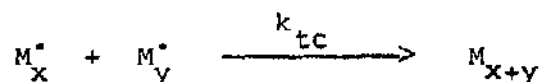
$$\text{Hence, } v_p = k_p [M] [M^*]$$

where $[M^*]$ represents the concentration of growing chain ends and is usually low at any particular time, while v_p is the rate of propagation.

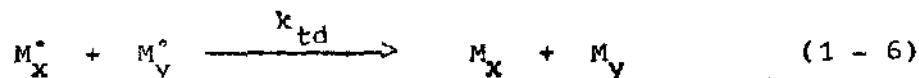
(c) Termination step

This is also a bimolecular process involving the collision of two active centres thereby leading to the disappearance of the active centre. Termination can come in

the form of either combination i.e.



or disproportionation i.e.



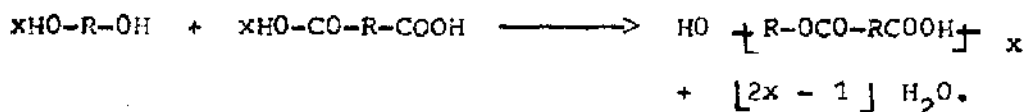
The rate of the reaction is then given as

$$V_t = 2k_t [M^*]^2$$

The rate constant k_t is actually $(k_{tc} + k_{td})$ where the two mechanisms are possible. Except where it is necessary to distinguish between the two mechanisms, the termination rate constant is denoted as k_t . (2).

1.1 TYPES OF POLYMERISATION REACTIONS

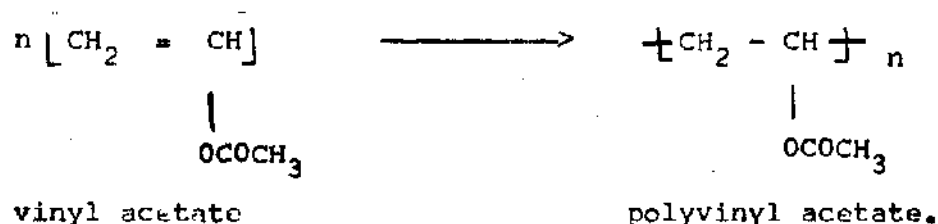
There are two major types of polymerisation reactions, namely addition and condensation reactions. Addition reaction is the reaction between molecules of similar structure. These link themselves together to form the larger macromolecule without change in chemical composition. Condensation reaction on the other hand is the reaction between two or more dissimilar compounds which react with each other to form the macromolecule and the by-product which must be eliminated. A polyester for example, is formed by a typical condensation reaction between bifunctional monomer with the elimination of water:



There are four general methods of polymerisation in use commercially. These are bulk (mass); solution; suspension and emulsion polymerisation reactions.

1.2 POLYVINYL ACETATE

Polyvinyl acetate is the polymer of vinyl acetate monomer, $\text{CH}_2 = \text{CH}-\text{O}-\text{COCH}_3$. Vinyl acetate is the acidic ester of vinyl alcohol and it dissolves in water only to an extent of about 2% (3). The polymerisation reaction can be generally represented by the following chemical equation;



1.2.1 GENERAL PROPERTIES OF POLYVINYL ACETATE

Polyvinyl acetate is an atactic material and is amorphous. Being an amorphous polymer with a solubility parameter of $19.4 \text{ (MJ/m}^3)^{1/2}$, it dissolves in solvents with similar solubility parameter e.g.

benzene	=	18.8 $\text{(MJ/m}^{-3})^{1/2}$
chloroform	=	19.0 $\text{(MJ/m}^{-3})^{1/2}$
methanol	=	29.7 $\text{(MJ/m}^{-3})^{1/2}$

Polyvinyl acetate has a density of 1.19g/cm^3 and a refractive index of 1.47.

1.2.2 USES OF POLYVINYL ACETATE

Polyvinyl acetate is successfully used in emulsion paints as adhesives for textiles, paper and wood, as a sizing material and as a permanent starch because of its good adhesion to a number of substrates and to some extent because of its cold flow (3). In addition to its use as a plastic and chewing gum base, poly(vinyl acetate) is used to produce poly(vinyl alcohol) and poly(vinyl acetal) which cannot be made directly since their monomers are not known.

1.3 EMULSION POLYMERISATION

Emulsion polymerisation is a radical chain reaction and involves the polymerisation of monomers which are in the form of emulsions. An emulsion can be simply defined as a solution containing colloidal particles which are thoroughly dispersed within the medium. The dispersion medium is usually water and it is a liquid in which the various components are dispersed in an emulsion state by means of the emulsifying agent. Thus emulsions usually are comprised of small particles 0.05 - 5.0 microns in diameter (4).

An ideal emulsion polymerisation system comprises of;
(i) monomer which should be water insoluble as in the case of styrene or slightly water soluble as in the case of vinyl acetate,

- (ii) water which is the dispersing medium;
- (iii) emulsifier which is the substance capable of dispersing the colloids freely in the medium and exists either as cationic, anionic, non-ionic or amphoteric according to the nature of the hydrophilic groups, and
- (iv) water soluble free radical initiator.

Initially, in the aqueous solutions, the surfactant is in the form of micelles, spherical or rod-like aggregates of 50 - 100 surfactant molecules with their hydrophobic "tails" oriented inward and their hydrophilic "heads" outward (4).

In an emulsion polymerisation system, there are four phases which play important roles in the overall process (5). These are external water phase, monomer droplets dispersed throughout the water phase, emulsifier micelles containing solubilised monomer and polymer latex particles swollen with monomer. In the aqueous phase, free radicals are generated by decomposition of the initiator and these radicals initiate polymerisation in the monomer swollen soap micelles. If the monomer is added to a micellar dispersion, most of it remains as rather larger droplets, but some of it dissolve in the micelles. Since they are smaller, the micelles present much greater surface area than do the droplets. After a few percentage conversion of the

monomer to the polymer, the micelles disappear and polymer particles, swollen with monomer and stabilised by the soap molecules which made up the original micelles become the loci for further polymerisation (5).

The presence of micelles is of fundamental importance in emulsion polymerisation (6). The micelles are formed when the critical micelle concentration (cmc) which is the lowest concentration of the emulsifier molecules required for the formation of micelles, is exceeded. Polymerisation of vinyl acetate has been shown to take place both below and above the critical micelle concentration of the emulsifier in use for the reaction (6). Emulsion polymerisation affords a means of increasing the polymer molecular weight without decreasing the polymerisation rate and the products of emulsion polymerisation have applications involving coatings, floor polishes and paints (6).

1.3.1 THEORY OF EMULSION POLYMERISATION

The general theory of the mechanism of emulsion polymerisation was formulated by W. D. Harkins (7, 8) and placed on a quantitative basis by W. V. Smith (9), W. V. Smith and R. H. Ewart (10) and R. N. Haward (11). The theory of emulsion polymerisation as it was developed, indicated that in the emulsion polymerisation of a relatively insoluble monomer like styrene, almost every polymer latex particle is initiated in its growth in the monomer solubilized inside the micelles.

According to D. M. French (12), micelles are aggregates of surfactant molecules in a water solution so arranged that the hydrophobic portion of the molecules are close together. In effect, the interior of a surfactant micelle may be regarded as a separate organic phase. Both surfactant micelles and the catalyst are water soluble but not soluble in the monomer. Hence, polymerisation must begin in the water phase. The micelles thus provide a place for the monomer and catalyst to react and produce a growing particle chain.

Harkins (8), has shown that monomer for the polymerisation reaction is supplied by diffusion from the monomer emulsion droplets through the aqueous phase and into the polymer particles thus forming monomer-polymer particles. Smith and Ewart (10) have shown from their study of the kinetics of styrene emulsion polymerisation, that the rate of polymerisation R_p , and the number average degree of polymerisation (\bar{X}_n), are directly proportional to the initiator and emulsifier concentrations, each raised to a power often

less than one.

$$R_p = \frac{N k_p [M]}{2} \quad (1 - 8)$$

$$\bar{X}_n = \frac{N k_p [M]}{R_i} \quad (1 - 9)$$

$$N \propto [I]^{2/5} \quad (1 - 10)$$

$$N \propto [S_o]^{3/5} \quad (1 - 11)$$

where k_p is the propagation rate constant,

R_i is the rate of initiation,

$[M]$ is the monomer concentration,

$[I]$ is the initiator concentration and

$[S_o]$ is the emulsifier concentration.

O'Donnell et al (5) have also shown that the rate of emulsion polymerisation above the critical micelle concentration is found to be independent of the total monomer concentration but dependent on the number of polymer particles which in turn is proportional to the soap concentration to 0.6 power and the initial rate of free radical production to 0.7 power.

These equations are believed to be valid for the emulsion polymerisation of water-insoluble monomer like styrene using water soluble initiator like potassium persulphate ($K_2S_2O_8$). In emulsion polymerisation with relatively water insoluble monomer, nearly all of the polymer particle nuclei are initiated in the monomer solubilised in the interior of soap micelles.

When the monomer is slightly water soluble like vinyl acetate, some deviations from the general theory of emulsion polymerisation are observed. These deviations are caused by the fact that the site of emulsion polymerisation of water soluble monomer is not limited

to the micelles alone. It also involves simultaneous polymerisation of the monomer which is in solution to give polymer particles which absorb emulsifier from the rest of the system (12).

Okamura and Motoyama (13) indicated from their work that emulsion polymerisation of vinyl acetate is characterised by two distinct factors; one, the water solubility of vinyl acetate and the other, the susceptibility of vinyl acetate radical to the effects of other substances. Hence, the general theory of Smith and Ewart equation with regards to emulsion polymerisation is not applicable to vinyl acetate.

1.3.2 EMULSION POLYMERISATION BELOW CMC

Below the critical micelle concentration, the soap solution contains no micelles when the hydrocarbon chain is long and are therefore ineffective in solubilization or penetration and thus in initiating polymer particles. When micelles are absent, the relatively small number of collisions between a free radical and the individual molecules of a monomer in the aqueous phase produce only a very small number of polymer molecules. It is these few polymer molecules that capture monomer molecules diffusing through this phase thus forming polymer particle nuclei. After a polymer particle is formed in the aqueous phase it exhibits no essential difference from a particle initiated in a soap micelle (14).

In the absence of soaps, the number of polymer particles achieves a constant value very early in the reaction and it is envisaged that this reaction occurs in the following way, Each sulphate radical produced by the thermal decomposition of the initiator is captured by a monomer molecule in the aqueous phase and then begins to propagate (14).

It has been reported by Priest (15), that in the case of non-micellar system, rapid rate of polymerisation and well dispersed lattices may be obtained for monomers which have appreciable water solubility.

The kinetics of the polymerisation of vinyl acetate in aqueous peroxy disulphate suggests that polymerisation occurs primarily with the polymer particles which form as a stable suspension (16). In the absence of soaps, the kinetics of the aqueous polymerisation of vinyl acetate can be explained by assuming that all the free radicals generated in the aqueous phase enter the polymer particles. The kinetics of the system cannot yet be readily expressed in a convenient mathematical form (16).

1.4 FACTORS INFLUENCING EMULSION POLYMERISATION

1.4.1 TEMPERATURE

A polymerisation temperature is often chosen because the initiator system used gives optimum efficiency at a particular temperature (6). The effect of increase in

temperature in an ideal emulsion polymerisation is to increase the rate of polymerisation and reduce the average degree of polymerisation i.e. molecular weight of the polymer formed. Other side effects can be generated by increase in temperature. These side effects listed below are usually peculiar to the initiator system employed and the monomer being polymerised.

- (a) instability of emulsion e.g. coagulation or peflocculation.
- (b) production of crosslinked, branched and gelled polymer and
- (c) change in structure of the polymer and molecular weight distribution.

1.4.2 AGITATION

Constant agitation is usually maintained in an emulsion polymerisation reaction to keep monomer and other components suitably dispersed. Agitation should be a continuous process because it prevents the coalescion of the monomer droplets when inactive micelles are produced below the critical micelle concentration. An increase in the degree of agitation may result in an overall increase in the rate of reaction and lowering of degree of polymerisation (6).

1.4.3 EMULSIFIER

The choice of emulsifier is very important in an emulsion polymerisation reaction. The role of the emulsifier is three fold (6):

- (a) an increased amount of the monomer is taken into the water phase owing to solubilisation in the micelles,
- (b) the non-solubilised monomer is emulsified into fine droplets and
- (c) the latex particles created are protected against coagulation during and after the polymerisation. The emulsifier is chosen such that it produces a stable emulsion between the monomer and water phases and remains in the product such that it imparts no adverse properties to the product.

1.4.4 INITIATOR SYSTEM

There are many varieties of initiator for use in emulsion polymerisation. The initiator becomes active in the system on being generated as an active radical by means of;

- (a) thermal decomposition of a compound or
- (b) interaction of chemical reagents to produce free radicals.

In order to function as a useful source of radicals, an initiator system, should be readily available, stable under ambient or refrigerated conditions, and possess a practical rate of radical generation at temperatures which are not excessive (approximately $< 150^{\circ}\text{C}$).

1.5 SCOPE OF STUDY

The present study is aimed at studying the kinetics of the polymerisation reactions of vinyl acetate and the dilute solution viscosities of the polymer samples produced in methanol. The kinetics of the polymerisation reaction, which shows the dependence of the rate of emulsion polymerisation of vinyl acetate, on the various potassium persulphate (initiator), and vinyl acetate (monomer) concentrations, together with sodium lauryl sulphate (emulsifier) concentrations below the critical micelle concentration, carrying out the reactions in a water bath at $55 \pm 0.05^{\circ}\text{C}$, is studied. The effect of these parameters on the degree of (%) conversion of the monomer to the polymer with time of polymerisation is also considered. The effect of the initiator, monomer and emulsifier concentrations on the molecular parameters of the polymer samples, in terms of macromolecular properties of the polymer, type of polymer, indications of various types and extent of branching in the polymer, and the interaction between the branches, polymer and the solvent is studied from the combined results of limiting viscosities and Huggins' constant, k' .

CHAPTER 22.0 POLYMERISATION STUDIES2.1 EXPERIMENTAL

The purity of monomers, diluents and initiators is of great importance since conversions and molecular weights can be drastically affected by contaminants. Thus, it is recommended that all reactants should be purified and their purity should be determined prior to polymerisation studies (17). The impurities most frequently encountered in polymerisation include water and compounds containing functional groups principally carbonyl and olefinic unsaturation.

2.1.1 MATERIALS

(i) The initiator, potassium persulphate ($K_2S_2O_8$), emulsifier i.e. sodium lauryl sulphate ($NaLSO_4$) and the buffer i.e. dipotassium hydrogen orthophosphate (K_2HPO_4) were all from British Drug Houses Limited i.e. B.D.H. analytical grade reagents. They were used without further purification.

(ii) VINYL ACETATE MONOMER

The vinyl acetate monomer was obtained from the Nigerian Hoechst Limited, Lagos.

Normally, quantities of an inhibitor are present as contaminants in most commercially available monomers

that are amenable to free radical initiation (17).

These were removed from the vinyl acetate samples by washing the monomer with 2% sodium hydroxide solution in a separating funnel.

Both monomer and the 2% sodium hydroxide (NaOH) were shaken several times, releasing the pressure in the funnel at intervals. However, the absence of a yellow colouration of the aqueous layer after the separation of the two mixtures indicated the absence of inhibitor such as hydroquinone from the vinyl acetate monomer was dried on calcium sulphate drying agent and finally distilled under reduced pressure. The purified monomer was stored in the refrigerator until needed for use.

(iii) NITROGEN GAS

An inert gas like nitrogen is commonly used during a polymerisation reaction as a combination purge stream and blanketing medium.

For the emulsion polymerisation reactions carried out, nitrogen gas was used and it was rid of inhibitors and impurities by passing it over several tubes of alkaline pyrogallol to remove any traces of oxygen, water to remove soluble matter and impurities and anhydrous calcium chloride to absorb the surrounding moisture.

2.1.2 POLYMERISATION PROCEDURE

A one-litre, four necked, reaction kettle was used for the polymerisation reactions. One of the necks served the purpose for the inlet of purified nitrogen gas; the centrally placed neck accommodated the stirrer while the third neck housed the condenser. At the other end of the condenser was placed a calcium chloride tube to absorb moisture from the surrounding.

Appropriate quantities of water, buffer, emulsifier and initiator were put in the reaction kettle before it was placed in the water bath with a thermostat set at $55 \pm 0.05^{\circ}\text{C}$ being the temperature at which the reactions were carried out. Stirring and passing of purified nitrogen gas were allowed to continue for about twenty minutes to ensure proper mixing of solution and flushing action of the nitrogen gas before the addition of vinyl acetate monomer from a monomer dropper over a period of thirty seconds. The monomer dropper was attached to the fourth neck of the reaction kettle and removed after introduction of the monomer when the neck was plugged. Stirring was done at suitable constant speed throughout the polymerisation experiments.

After a while, the solution turned milky and aliquots of 25cm^3 were taken at appropriate time intervals

until enough samples had been collected from each polymerisation reaction. The reaction of the contents of each aliquot was quenched by adding the aliquot to a large quantity of ice-cold saturated solution of sodium chloride in a large beaker with rigorous stirring during the addition. The polymer separated out by settling at the bottom of the beaker. The solids were quickly washed several times with distilled water until they were rid of emulsifier, monomer and other impurities that were soluble. They were filtered and air dried for about 24 hours before being oven dried to constant weight in a vacuum oven at 40°C. The dry samples were stored in separate bottles and kept in the dessicator until ready for use.

The polymerisation reactions were carried out using four different concentrations of each of sodium lauryl sulphate (SLS) and monomer and two different concentrations of the initiator. The idea of different concentrations of both emulsifier and monomer was to study their effect on the yield and properties of the polyvinyl acetate produced.

2.2.0 RESULTS AND DISCUSSION

2.2.1 INFLUENCE OF EMULSIFIER CONCENTRATION ON

(%) CONVERSION OF VINYL ACETATE TO POLYVINYL ACETATE

Figures 2.1 and 2.2 represent the results obtained from the kinetic study of the emulsion polymerisation of vinyl acetate with 0.25 and 2.25g.dm^{-3} of sodium lauryl sulphate respectively, a constant initiator concentration of 1.50g.dm^{-3} and four different monomer concentrations of 0.931 ; 1.455 ; 2.095 and 2.851g.dm^{-3} . The polymerisation reaction studies were carried out at a constant temperature of $55 \pm 0.05^{\circ}\text{C}$ in a water bath. All the studies were carried out with emulsifier (SLS) concentration below the critical micelle concentration. ($8.9 \times 10^{-3} \text{ mol dl}^{-1}$)

From fig. 2.1, (%) conversion was found to increase linearly with time of polymerisation for each of the monomer concentration investigated. Conversions were generally low with this very low emulsifier concentration

2.2.2 PRESENCE OF AN INDUCTION PERIOD

For each polymerisation there was an induction period before the linear portion of the graph was defined. The occurrence of the induction period can be explained as the result of the time required for proper interaction of monomer molecules and initiator

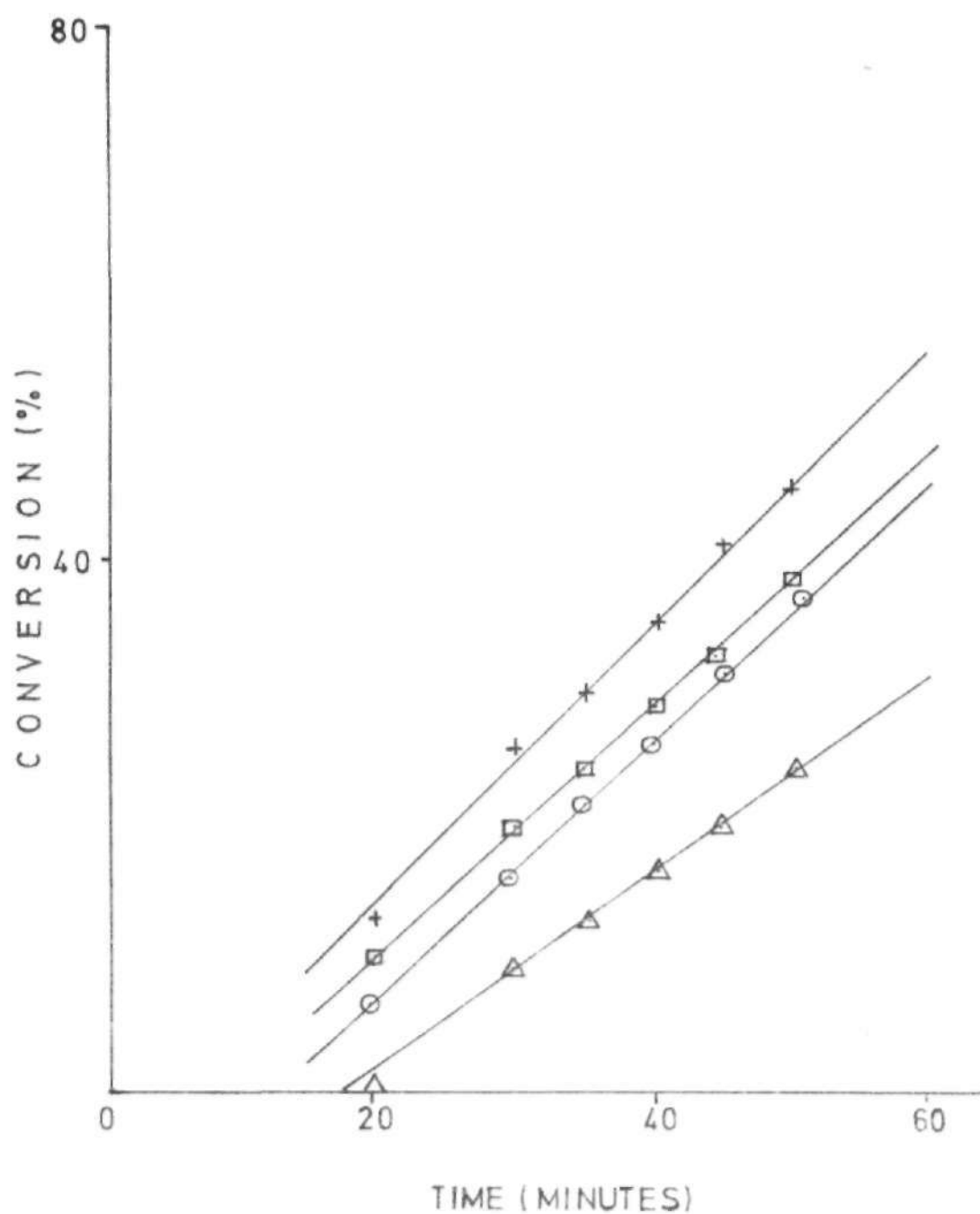


FIG.2.1

- Plots of (%) conversion versus time of polymerisation using $0.25 \text{ g} \cdot \text{dm}^{-3}$ of (SLS) and (+) 0.931 ; (o) 1.455 ; (□) 2.095 and (Δ) $2.851 \text{ g} \cdot \text{dm}^{-3}$ of vinyl acetate with initiator concentration of $1.50 \text{ g} \cdot \text{dm}^{-3}$

free radicals which were in different phases, the latter in the aqueous layer. Until effective interaction was achieved between the monomer and the initiator by the process of agitation, possibly combined with diffusion of free radicals to the monomer - water layer, no appreciable polymerisation reaction, if any, would be expected. In these sets of experiments, the other factors that might have led to presence of induction periods to polymerisation is the presence of inhibitors e.g oxygen. This has confidently been ignored as the polymerisation mixture was thoroughly flushed with purified nitrogen prior to addition of the monomer. The polymerisations were also carried out in atmosphere of pure nitrogen.

The value of the induction period seems to decrease as monomer concentration decreased. This strongly supports a mechanism of 'delayed interaction' between monomer molecules and the initiator radicals in the two separate layers. The larger the volume of water into which the initiator is dispersed, the greater the total exposed surfaces for monomer - initiator interaction and hence the shorter the induction period. Also the quantity of vinyl acetate that dissolves in water should increase with $[H_2O] / [VAc]$ ratio thus encouraging faster monomer-initiator contact in the absence of micelles that should

disperse and solubilise the monomer. Thus, right from the initiation steps, polymerisation of vinyl acetate in concentrations below the cmc of (SLS) should not be expected to conform to the typical Smith and Ewart (10) theory or that of Haward (11).

Comparing results obtained for the four emulsifier concentrations with respect to induction period as shown in table 2.1, it has been found that in each case, though only the results for two emulsifier concentrations are shown in figs. 2.1 and 2.2 graphically, the results for others being presented in table 2.2 and 2.3, an induction period was obtained in each case. The induction period obtained by extrapolating the conversion-time curve to zero conversion appears to increase as emulsifier concentration increases, but still kept below the cmc of (SLS). This might not be completely unexpected if one considers the interaction between the surfactant behaving as simple electrolytes below the cmc and its interaction with the initiator. This might lead to a competition of the type monomer - initiator and surfactant - initiator and might effectively reduce the overall extent of monomer initiator interaction.

TABLE 2.1

Polymerisations with 1.50g.dm^{-3} ($\text{K}_2\text{S}_2\text{O}_8$)

Monomer concentration (g.dm^{-3}) of mixture	Emulsifier concentration (g.dm^{-3}) of mixture			
	0.25	0.50	1.50	2.25
	Induction period (mins)			
0.931	9	14	12	10
1.455	10	20	22	17
2.095	12	21	23	20
2.851	17	22	24	23

TABLE 2.2

Polymerisations with 0.50g.dm^{-3} (SLS) and
 1.50g.dm^{-3} ($\text{K}_2\text{S}_2\text{O}_8$)

Time of polymerisation (mins).	Monomer concentration (g.dm^{-3}) of mixture			
	0.931	1.455	2.095	2.851
	(% Conversion)			
20	17.27	-	-	-
25	30.52	7.46	9.34	8.31
30	53.86	16.29	17.81	12.71
35	59.89	25.57	25.63	19.21
40	70.91	36.98	31.99	25.41
45	71.66	42.73	40.58	33.28
50	72.82	43.27	52.74	37.91

TABLE 2.3

Polymerisation with 1.50g.dm^{-3} (SLS)
and 1.50g.dm^{-3} ($\text{K}_2\text{S}_2\text{O}_8$)

Time of polymerisation (mins).	Monomer concentration (g.dm^{-3}) of mixture			
	0.931	1.455	2.095	2.851
	(% Conversion)			
20	9.15	-	-	-
25	38.80	7.58	3.44	3.31
30	62.77	26.33	18.70	13.04
35	86.02	40.68	34.27	19.99
40	94.16	58.10	46.47	26.63
45	95.90	67.40	59.11	41.12
50	96.78	76.30	66.76	51.84

2.2.3 MONOMER CONVERSION

The (%) conversion w_3s found not to exceed about 50 when 0.25g.dm^{-3} of the emulsifier was used when coagulation was observed. The low conversion could be explained in terms of genuine slow rate of polymerisation under the conditions of the experiment, and coagulation might be explained as due to high solid content which was not dispersed and stabilised at low emulsifier concentration. This seems reasonable in the light of previous report(6) claiming that particles need to be dispersed and stabilised if the emulsion is to be stable.

Coagulation normally occurred in some of the experiments whenever the amount of emulsifier in the recipe was quite low particularly with the two lowest (SLS) concentrations examined. Instability of polymer emulsion is usually avoided by making use of a sufficiently high emulsifier concentration preferably above the cmc in the medium or by simple addition of other stabilizing surfactants (6).

The (%) conversion was also found to increase linearly with time over a considerable period of polymerisation or range of conversion. The actual range over which conversion is linear depends on the emulsifier concentration and monomer concentration. For very low emulsifier concentration, conversion is linear from about 5% till coagulation set in, fig. 2.1. For the same recipe but higher emulsifier concentration, fig. 2.2, the linearity extends to and is sometimes above 80%, as there was no coagulation observed during the polymerisation.

In fig. 2.2, the emulsifier concentration was 2.25g.dm^{-3} and the pattern of variation of (%) conversion with time of polymerisation followed the pattern previously discussed for the results obtained using 0.25g.dm^{-3} of the emulsifier, fig. 2.1. The set of monomer concentration used were the same as in fig. 2.1.

Polymerisation of vinyl acetate with 2.25g.dm^{-3} (SLS) and with the same initiator and monomer concentrations and

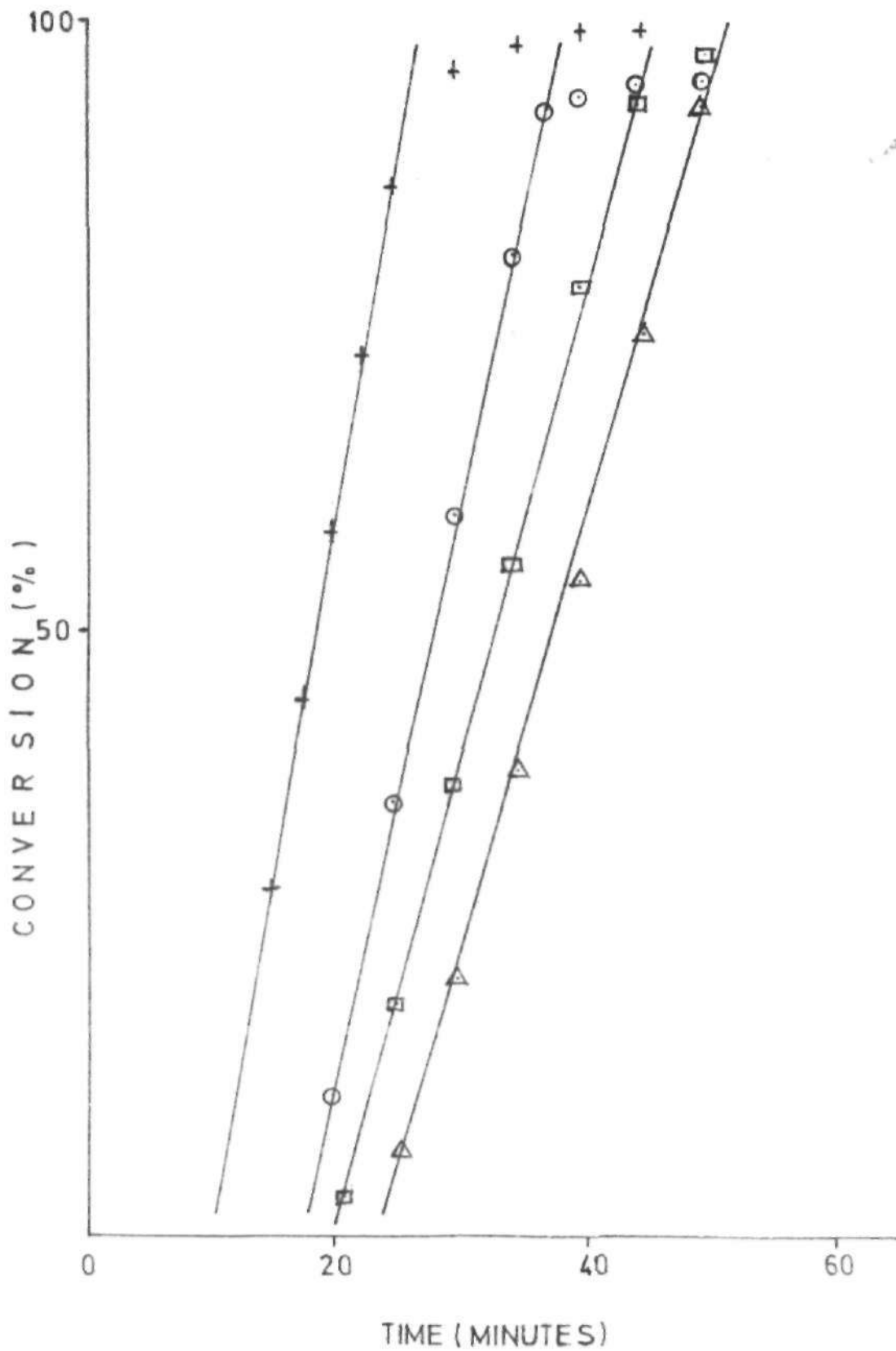


FIG-2-2

Plots of (%) conversion versus time of polymerisation using $2.25 \text{ g} \cdot \text{dm}^{-3}$ of SLS and (+) 0.931 ; (\odot) 1.455 ; (\boxplus) 2.095 and (Δ) $2.851 \text{ g} \cdot \text{dm}^{-3}$ of vinyl acetate with initiator concentration of $1.50 \text{ g} \cdot \text{dm}^{-3}$

temperature with the same speed of agitation give results which show generally a resemblance to the set of results obtained for 0.25g.dm^{-3} (SLS). However, the range of monomer conversion over which the curve is linear with time of polymerisation is wider, below about 10 to about 80%. Also, the rates of polymerisation are much higher, as would be found later. In addition, no coagulation of the latex particles was observed during the polymerisation study, and separating solid polymers from aliquots during sampling, by addition of ice-cold salt distilled water was more difficult. All these suggest that below and close to the cmc of (SLS) as an emulsifier, a mechanism of polymerisation of vinyl acetate which is essentially different from those predicted by the classical theories of Smith and Ewart (10), Haward (11), Harkins (8), and Harriott (18) begins to undergo a transition into the classical form. Consequently, the behaviour of the polymerisation, kinetics, the macromolecular properties of the polymer and the emulsion characteristics i.e stability and dispersion, all change in favour of the requirements from the classical theories. In summary the deviation from the expectations of the classical theories would be largely determined by the extent to which the emulsifier concentration is lower than the cmc of the emulsifier.

The maximum value of conversion obtainable for the polymerisation reaction prior to coagulation, where it occurs, is

dependent on the emulsifier concentration. The higher the emulsifier concentration the higher the limiting (%) conversion.

2.2.4 POLYMERISATION USING LOWER INITIATOR CONCENTRATION

Another set of polymerisation reactions using the four different monomer and emulsifier concentrations and 1.00g.dm^{-3} of the initiator ($\text{K}_2\text{S}_2\text{O}_8$) was carried out. The results of some of this set of experiments are presented in figs. 2.3 and 2.4 while others are in tables 2.4 and 2.5.

From fig 2.3, (%) conversion was also found to increase linearly with time of polymerisation for each of the monomer concentration investigated.

2.2.4.1 Presence of an induction period

For each polymerisation, there was an induction period. The induction period in this case was slightly longer than the result obtained in table 2.1 as shown in table 2.6. This can be explained as the result of a reduction in the amount of inhibitor in the medium thereby giving rise to a fewer number of initiator radicals thus increasing the average time of effective interaction between the monomer molecules and initiator radicals which are in different phases. However, the occurrence of the induction period is as previously explained.

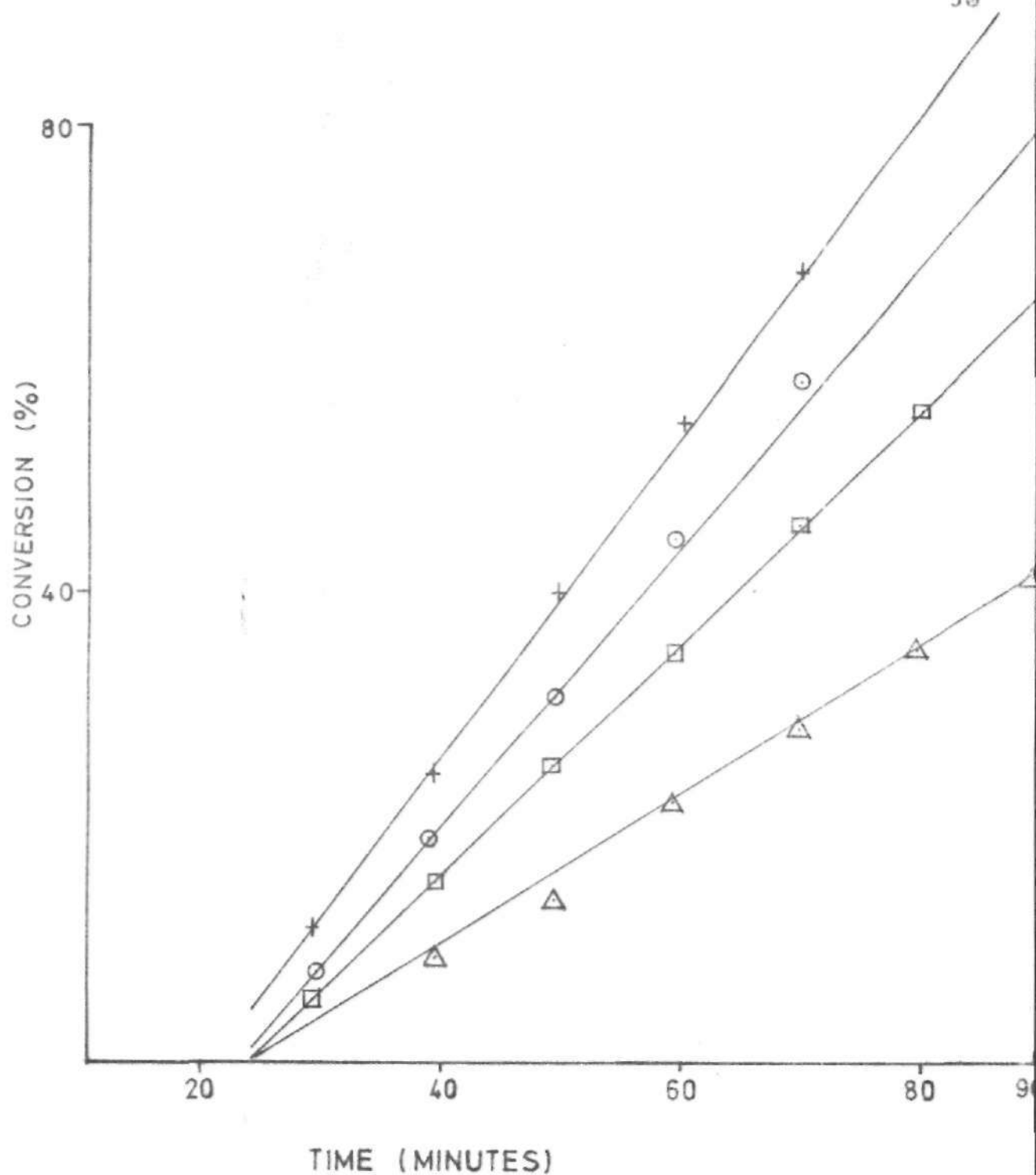


FIG. 2.3

Plots of (%) conversion versus time of polymerisation using $0.25\text{g}\cdot\text{dm}^{-3}$ of (SLS) and (+) 0.931 ; (\odot) 1.455 ; (\square) 2.095 and (\triangle) $2.851\text{g}\cdot\text{dm}^{-3}$ of vinyl acetate with initiator concentration at $1.00\text{g}\cdot\text{dm}^{-3}$

TABLE 2.4

Polymerisations with 0.50g.dm^{-3} (SLS)
and 1.00g.dm^{-3} ($\text{K}_2\text{S}_2\text{O}_8$).

Time of polymerisation (mins.)	Monomer concentration (g.dm^{-3}) of mixture			
	0.931	1.455	2.095	2.851
(%) Conversion				
30	9.11	3.54	11.07	7.38
40	32.05	18.53	22.52	18.18
50	55.05	34.01	36.02	29.34
60	83.59	51.90	53.43	40.69
70	86.85	84.00	76.68	52.12

TABLE 2.5

Polymerisations with 1.50g.dm^{-3} (SLS)
and 1.00g.dm^{-3} ($\text{K}_2\text{S}_2\text{O}_8$).

Time of polymerisation (mins.)	Monomer concentration (g.dm^{-3}) of mixture			
	0.931	1.455	2.095	2.851
(%) Conversion				
20	31.90	-	-	-
30	65.71	2.75	23.54	9.69
40	89.79	11.04	42.92	27.35
50	94.76	49.72	65.82	48.17
60	98.41	76.68	90.03	72.26
70	98.90	86.52	97.70	89.21
80	-	86.77	98.72	89.26

TABLE 2.6

Polymerisations with 1.00g.dm^{-3} ($\text{K}_2\text{S}_2\text{O}_8$)

Monomer concentration (g.dm^{-3}) of mixture	Emulsifier concentration (g.dm^{-3}) of mixture			
	0.25	0.50	1.50	2.25
	Induction period (mins)			
0.931	21	26	20	12
1.455	22	28	25	18
2.095	23	29	30	21
2.851	26	30	36	27

2.2.4.2 Monomer conversion

In fig. 2.4, the emulsifier concentration was 2.25g.dm^{-3} and the pattern of variation of (%) conversion with time of polymerisation followed the pattern previously discussed for the results obtained using 0.25g.dm^{-3} of the emulsifier and 1.50g.dm^{-3} of the initiator. The (%) conversion increased linearly with time over a considerable range of conversion. The induction period also obtained for this set of polymerisation reactions is also as shown in table 2.6. No coagulation was observed with this set of polymerisation experiments.

The results of the studies are essentially the same as described for figs. 2.1 and 2.2. Other results, not shown graphically are represented in tables 2.4 and 2.5

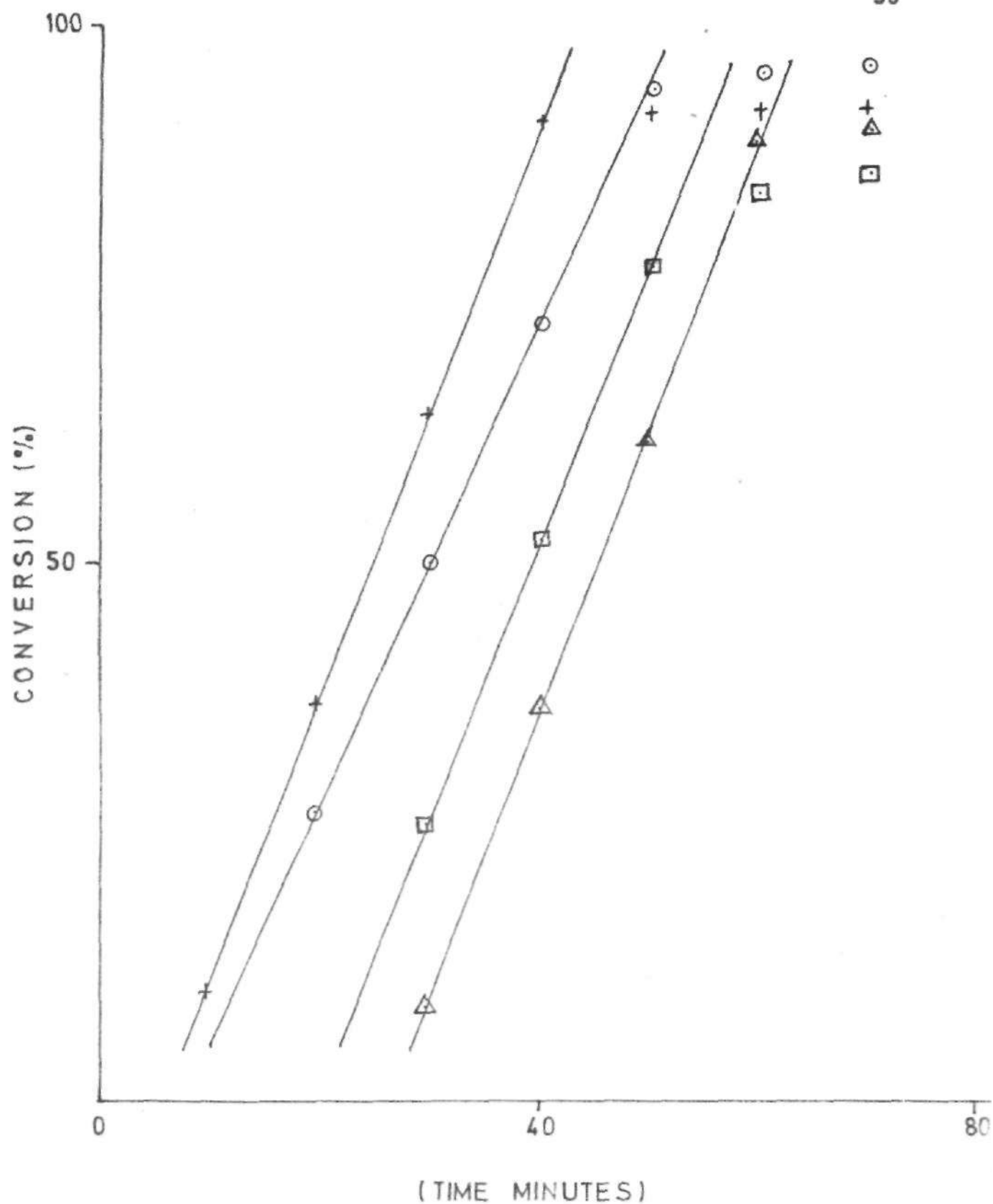


FIG. 2.4

Plots of (%) conversion versus time of polymerisation using $2.25 \text{ g}\cdot\text{dm}^{-3}$ of (SLS) and (+) 0.931 , (\odot) 1.455 ; (\boxplus) 2.095 and (Δ) $2.851 \text{ g}\cdot\text{dm}^{-3}$ of vinyl acetate with initiator concentration of $1.00 \text{ g}\cdot\text{dm}^{-3}$

in the text. The tables show the variation of (%) conversion with time of polymerisation of vinyl acetate using different emulsifier, monomer and initiator concentrations.

2.2.5 INFLUENCE OF MONOMER CONCENTRATION ON RATE OF POLYMERISATION

The rates of the polymerisation reactions were obtained as the slopes of the straight line portions of the (%) conversion versus time curves in figs. 2.1 and 2.4 and those from the results in tables 2.2 to 2.5. The slopes were arrived at by the least square calculations. From the plots of (%) conversion versus time of polymerisation in figs. 2.1 to 2.4, it is evident that with increase in the concentration of the monomer in the recipe, polymerisation rate decreased. Figures 2.5 and 2.6 actually confirm this quantitatively, indicating an inverse relationship between rate of vinyl acetate polymerisation and initial vinyl acetate concentration in the mixture.

These observations could suggest that at very high monomer concentrations, emulsion polymerisation under this sets of conditions adopted here might not be possible. When the $\frac{[VAc]}{[H_2O]}$ ratio becomes very large, both the initiator and emulsifier molecules might not be able to dissolve and interact with the monomer molecules, hence no initiation of polymerisation

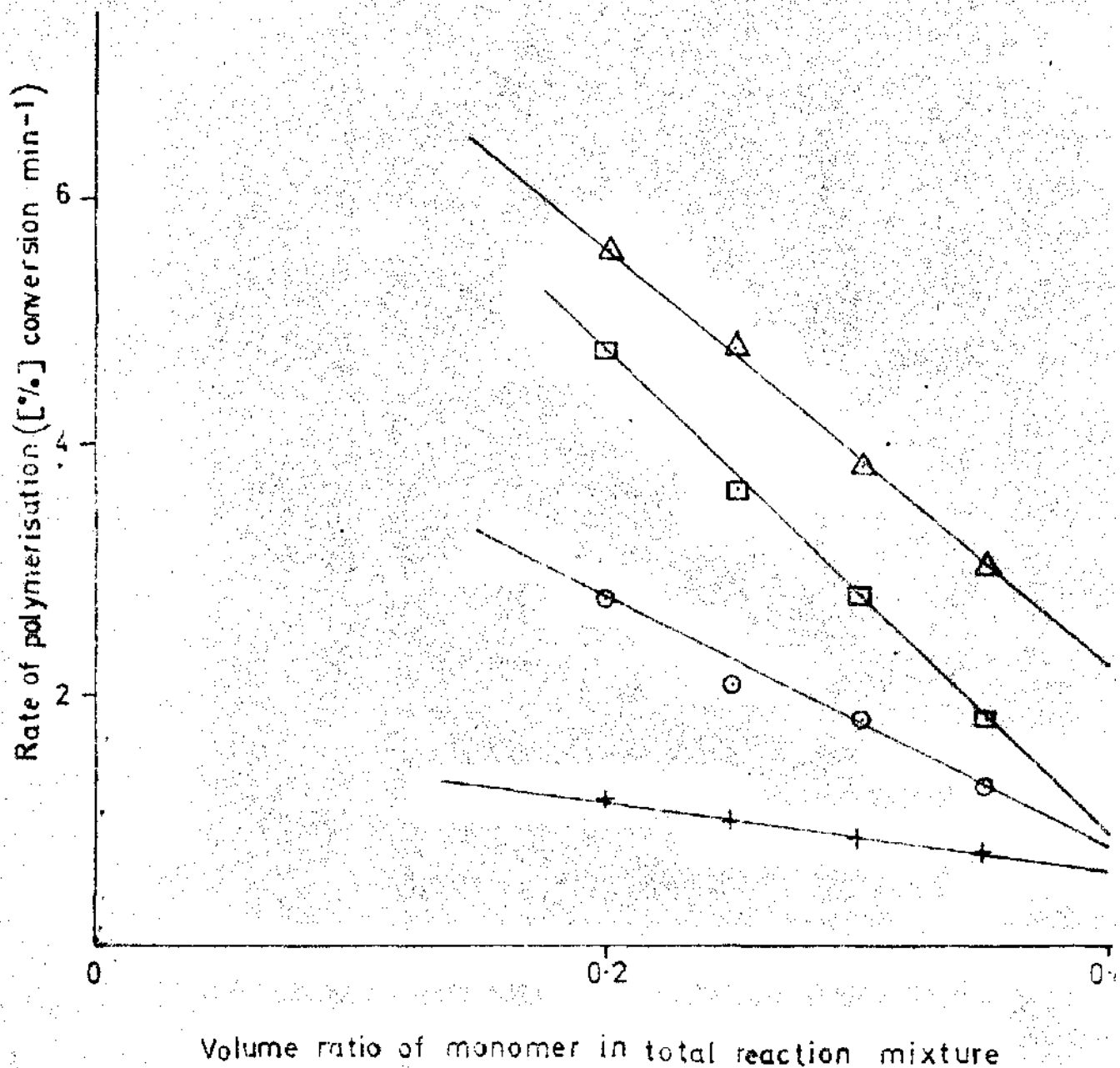


FIG. 2.5

Plots of rate of polymerisation versus volume ratio of monomer in the reaction mixture using (+) 0.25 ; (o) 0.50 ; (□) 1.50 and (Δ) 2.25 g.dm⁻³ of emulsifier and 1.50 g.dm⁻³ of the initiator (K₂S₂O₈)

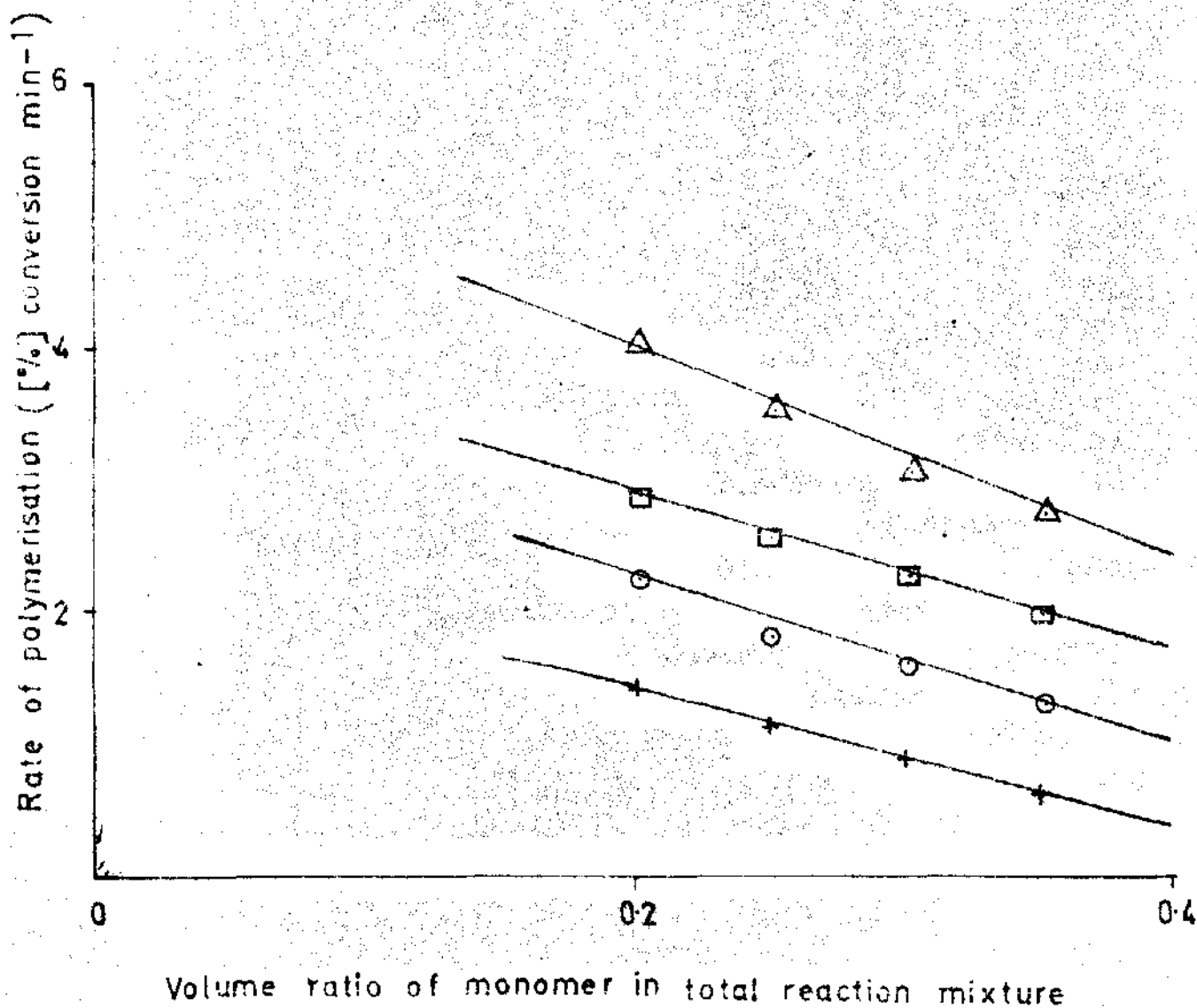


FIG. 2.6

Plots of rate of polymerisation versus volume ratio of monomer in the reaction mixture using (+) 0.25 ; (⊙) 0.50 ; (⊠) 1.50 and (Δ) 2.25 g.dm⁻³ of emulsifier and 1.00 g.dm⁻³ of the initiator.

might be expected. There exists therefore, the possibility of self polymerisation of vinyl acetate at elevated temperatures in the absence of an initiator.

Also with increase in the monomer concentration in the recipe, the amount of water used also decreased since total volume was kept constant. Vinyl Acetate is about 2% soluble in water whilst its polymer is water insoluble but both the monomer and polymer are completely miscible (14). With this possibility then, a situation with large quantity of water would be required for a high yield of the polymer. Therefore, with low monomer concentration, there would be a high (%) conversion since the ratio of the water to monomer would allow for the formation of a fairly high yield of the polymer samples. With high monomer concentration on the other hand, the little amount of water that solubilises the monomer gives rise to low (%) conversion in situations where the emulsifier concentration is much less than the cmc of the (SLS).

2.2.6 SUMMARY OF THE DEPENDENCE OF RATE OF THE POLYMERISATION REACTION ON MONOMER AND EMULSIFIER CONCENTRATIONS

The values obtained as the rates of polymerisation of vinyl acetate were plotted against the volume ratio of the monomer in the polymerisation recipe with a total

volume of 200 cm³ as shown in figs. 2.5 and 2.6. In these graphs straight lines were clearly obtained through the various experimental points over the concentration of vinyl acetate studied. From the values of the variation of the rates of emulsion polymerisation reactions of vinyl acetate on the different monomer, emulsifier and initiator concentrations quoted in tables 2.7 and 2.8, the rate of the emulsion polymerisation of vinyl acetate under the stated conditions was found to decrease with increase in monomer concentration when the emulsifier concentration is constant. The values however increase with increase in emulsifier concentration when the monomer concentration is constant. Figures 2.5 and 2.6 also show the same trend in the reaction rate with the different monomer, initiator and emulsifier concentrations.

The fact that the rate of the vinyl acetate polymerisation reaction is greatly increased in concentration of detergent even when no micelles were present at constant monomer concentration was put forward by Baxendale (19). The results obtained in tables 2.7 and 2.9 show a similar trend with that described by Baxendale.

The rapid increase of rate of polymerisation with soap concentration might be due to the emulsifying effect of the soap on the monomer-polymer particles. The soap prevented the aggregation of the particles and thus kept

TABLE 2.7

Polymerisations with 1.50g.dm^{-3} ($\text{K}_2\text{S}_2\text{O}_8$)

Monomer concentration (g.dm^{-3}) of mixture	Emulsifier concentration (g.dm^{-3}) of mixture			
	0.25	0.50	1.50	2.25
Rate of reaction ((%) conversion min.^{-1})				
0.931	1.20	2.75	4.77	5.60
1.455	1.00	2.10	3.63	4.80
2.095	0.86	1.83	2.83	3.80
2.851	0.75	1.29	1.86	3.20

TABLE 2.8

Polymerisations with 1.00g.dm^{-3} ($\text{K}_2\text{S}_2\text{O}_8$)

Monomer concentration (g.dm^{-3}) of mixture	Emulsifier concentration (g.dm^{-3}) of mixture			
	0.25	0.50	1.50	2.25
Rates of reaction ((%) conversion min^{-1})				
0.931	1.43	2.25	2.89	4.10
1.455	1.20	1.85	2.50	3.55
2.095	0.92	1.62	2.24	3.10
2.851	0.64	1.33	2.00	2.80

their number high as previously suggested (8). Although there were no micelles below the critical micelle concentration, an appreciable number of polymer particles were formed by the precipitation of low molecular weight polymers in solution since minute amount of monomer dissolved in water. The number of particles formed in the absence of micelles is expected to be very small (20).

The decrease in the rate of the emulsion polymerisation of vinyl acetate with increase in monomer concentration and at constant initiator concentration might be due to the increase in the quantity of vinyl acetate which dissolved in water as the latter increased i.e. as $[H_2O]/[VAc]$ increased.

The rate of emulsion polymerisation of vinyl acetate has been found to be independent of the total monomer concentration above the critical micelle concentration but is dependent on the number of polymer particles which in turn is proportional to the soap concentration to the 0.6 power and the initial rate of free radical production to 0.4 power (21). The polymerisation results obtained in these set of study do not agree with the above as also shown in table 2.7 and 2.8. The polymerisation rate was found to be monomer concentration dependent decreasing with increase in monomer concentration. The difference in the results might be due to the fact that the emulsifier concentrations employed here were below the critical micelle concentration of (SLS) for the various polymerisation reactions where the

solubility of vinyl acetate in water becomes very important at least at the initiation if not also at the propagation stage of the polymerisation reactions. It has been reported by Priest (15) that in the case of non-micellar systems for which relatively little information is available, rapid rates of polymerisation and well dispersed lattices may be obtained for monomers which have appreciable water solubility.

From the different ratios of monomer to water studied, the lowest concentration of the monomer at 0.931g.dm^{-3} was found to be the most suitable as observed from the results of the rates of the polymerisation reactions. If the experimental curves are extended along the dotted lines on theoretical grounds, as shown in figs 2.5 and 2.6, the rate of reaction becomes a little higher at still lower monomer concentration. It is logical then to assume that rate of polymerisation increases with monomer volume ratio to a maximum and thereafter decreases linearly with further increase in monomer volume ratio as observed in figs 2.5 and 2.6. This appears reasonable since the rate of reaction should be zero in the absence of the monomer. It is also assumed that the maximum value of R_p would be obtained at lower values of monomer ratio as emulsifier concentration is increased. Also, the maximum value of R_p should increase with increase in emulsifier concentration. It is difficult to predict whether R_p should increase linearly with volume ratio of monomer

prior to its peak value and actual experiments would be required to determine this.

2.2.7 RATE VERSUS EMULSIFIER CONCENTRATION RELATIONS

The phenomenon that polymerisation rate decreases with increase in concentration of the surfactant is often observed when a non-ionic surface active agent is used as a surfactant (21). Sodium lauryl sulphate however decreased the rate of polymerisation of vinyl acetate with increase in the monomer concentration as shown in tables 2.7 and 2.8. In figs 2.7 and 2.8, the values of the slopes of rate versus volume ratio were plotted against emulsifier concentrations using 1.50 and 1.00g.dm⁻³ (K₂S₂O₈) respectively. The shape of the curves, shows a decrease to a minimum in rate with increase in emulsifier concentration. The role of the surfactant is to solubilise the monomer thus increasing the monomer concentration in the water phase and hence effectively increasing monomer - initiator interaction. If the soap concentration is kept constant and the concentrations of the monomer and other reactants are allowed to increase gradually, the little amount of the emulsifier would solubilise just a small amount of the monomer in the total volume of the reaction recipe which is constant thereby reducing the rate at which reaction takes place. With increase in the emulsifier concentration therefore, there is subsequent increase in its solubilisation power and therefore an increase in the rate of polymerisation reaction.

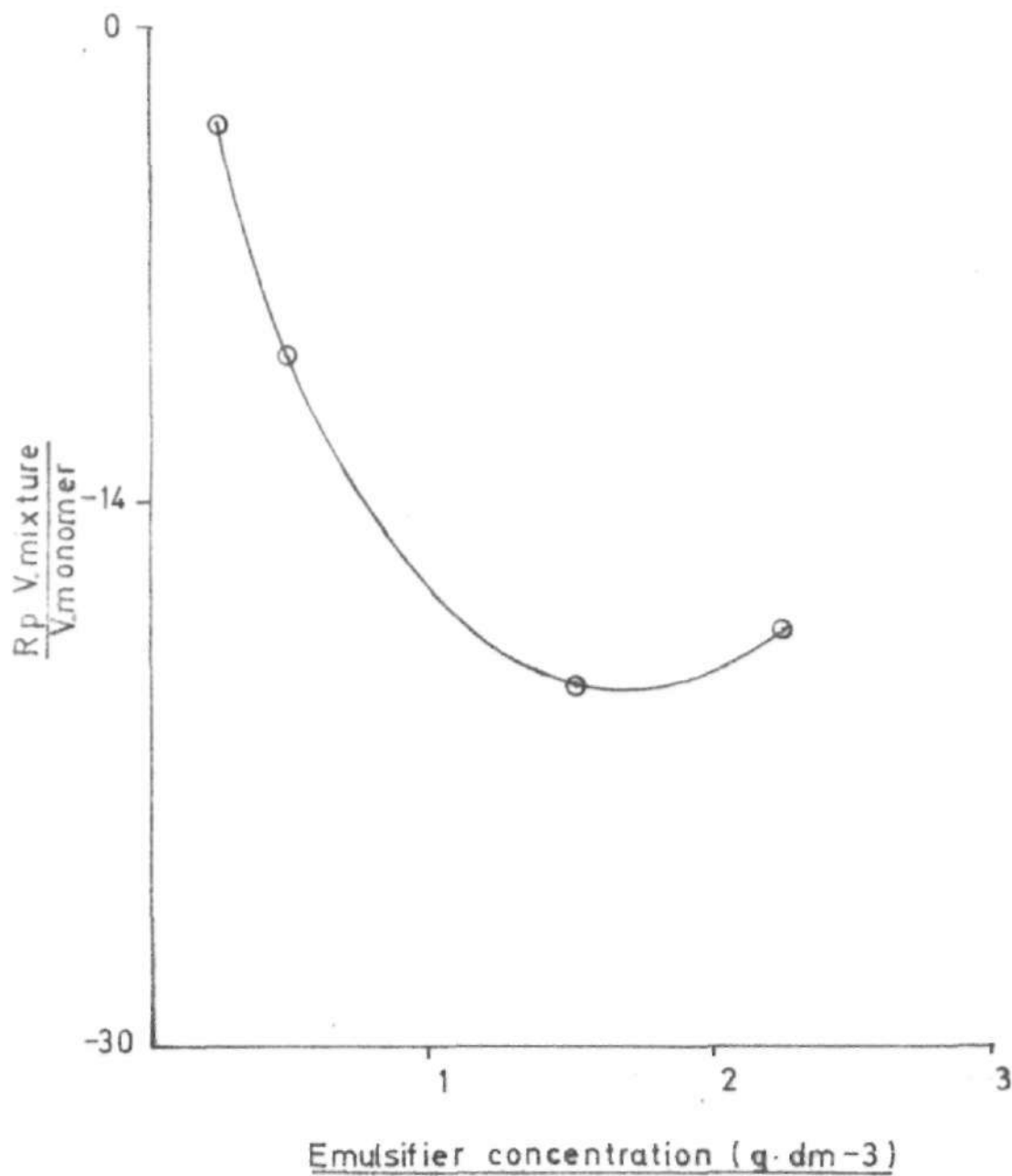


FIG. 2.7

Plots of the values of slopes of rate versus emulsifier concentrations using $1.50 \text{ S}\cdot\text{dm}^{-3}$ ($\text{K}_2 \text{S}_2 \text{O}_8$)

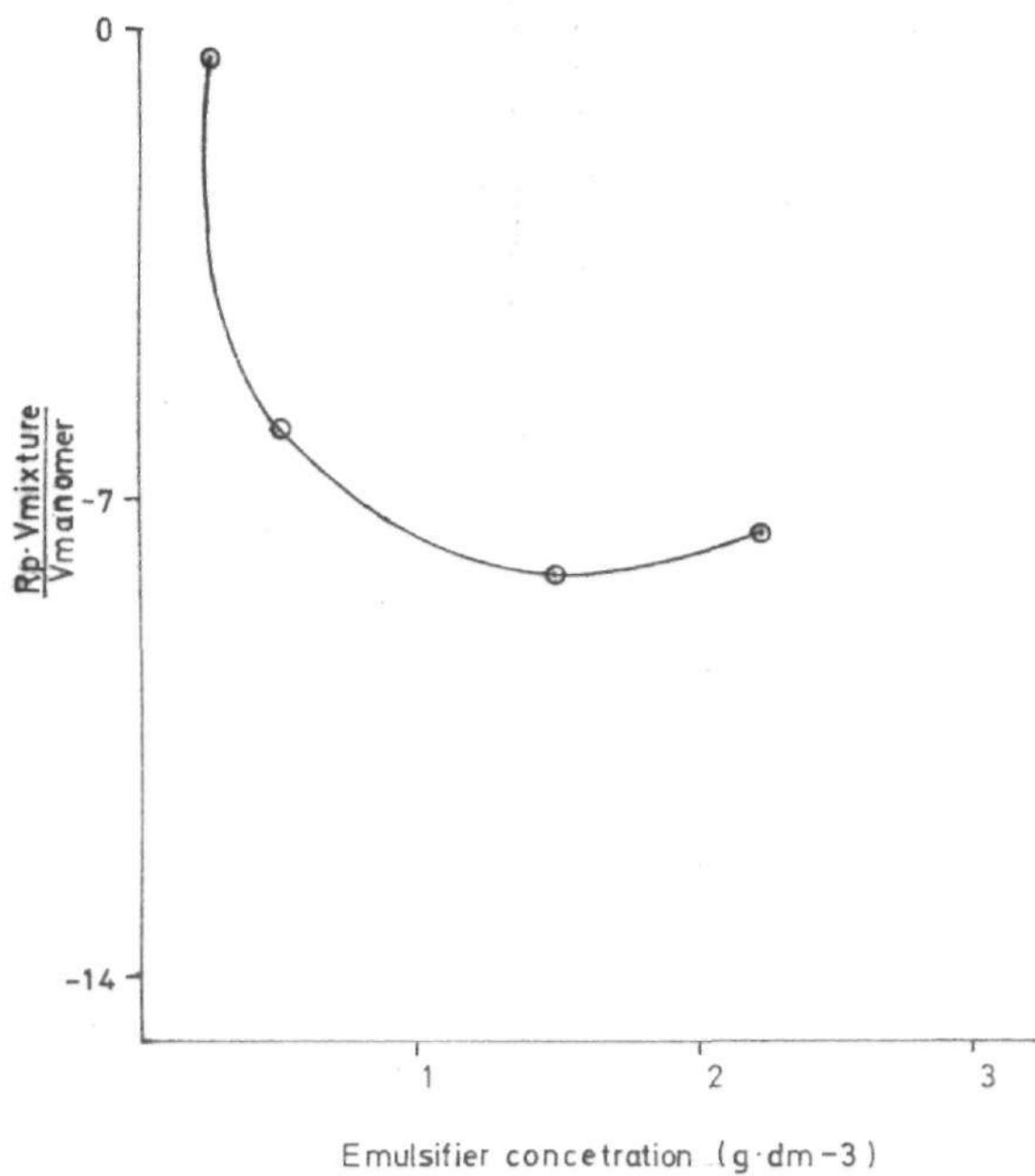


FIG. 2.8

Plots of the values of slopes of rate versus emulsifier concentrations using $1.00 \text{ g} \cdot \text{dm}^{-3}$ ($\text{K}_2 \text{S}_2\text{O}_8$)

The polymerisation rates as shown in tables 2.7 and 2.8 do not conform to that expected from Smith-Ewart (22) relations given as

$$R_p \propto N^{0.2}$$

$$R_p \propto [S_o]^{0.5}$$

$$R_p \propto [I]$$

which apply strictly to water insoluble monomers such as styrene. In these expressions:

R_p is the rate of polymerisation,

N is the number of polymer particles,

$[S_o]$ is the emulsifier concentration and

$[I]$ is the initiator concentration.

This non-conformity can be explained to an extent by the Medvedev-Sheinker (22) theory which suggested that the free radicals cannot penetrate the interior of the reaction medium and that polymerisation therefore occurs at the particle surface. Several studies in which the polymerisation rate of vinyl acetate was shown to be linearly related to the total surface area of all the particles lend support to this theory (22).

The Medvedev-Sheinker theory fits the relationship

$$R_p \propto [S_o]^{0.5}$$

From the polymerisation reactions carried out using different initiator and monomer concentrations, the rates of the polymerisation reaction varied with the exponent of the emulsifier concentrations for different monomer concentrations as shown in table 2.9. The exponents of the emulsifier concentration were arrived at by taking the slopes of the straight lines of the plots of $\log R_p$ versus $\log [S_o]$ as shown in figures 2.9 and 2.10. The relations are written in table 2.9.

TABLE 2.9

Monomer concentration (g.dm ⁻³) of mixture	Initiator concentration in (g.dm ⁻³) of mixture	
	1.50	1.00
0.931	$R_p \propto [S_o]^{0.60}$	$R_p \propto [S_o]^{0.54}$
1.455	$R_p \propto [S_o]^{0.64}$	$R_p \propto [S_o]^{0.54}$
2.095	$R_p \propto [S_o]^{0.67}$	$R_p \propto [S_o]^{0.53}$
2.851	$R_p \propto [S_o]^{0.67}$	$R_p \propto [S_o]^{0.54}$

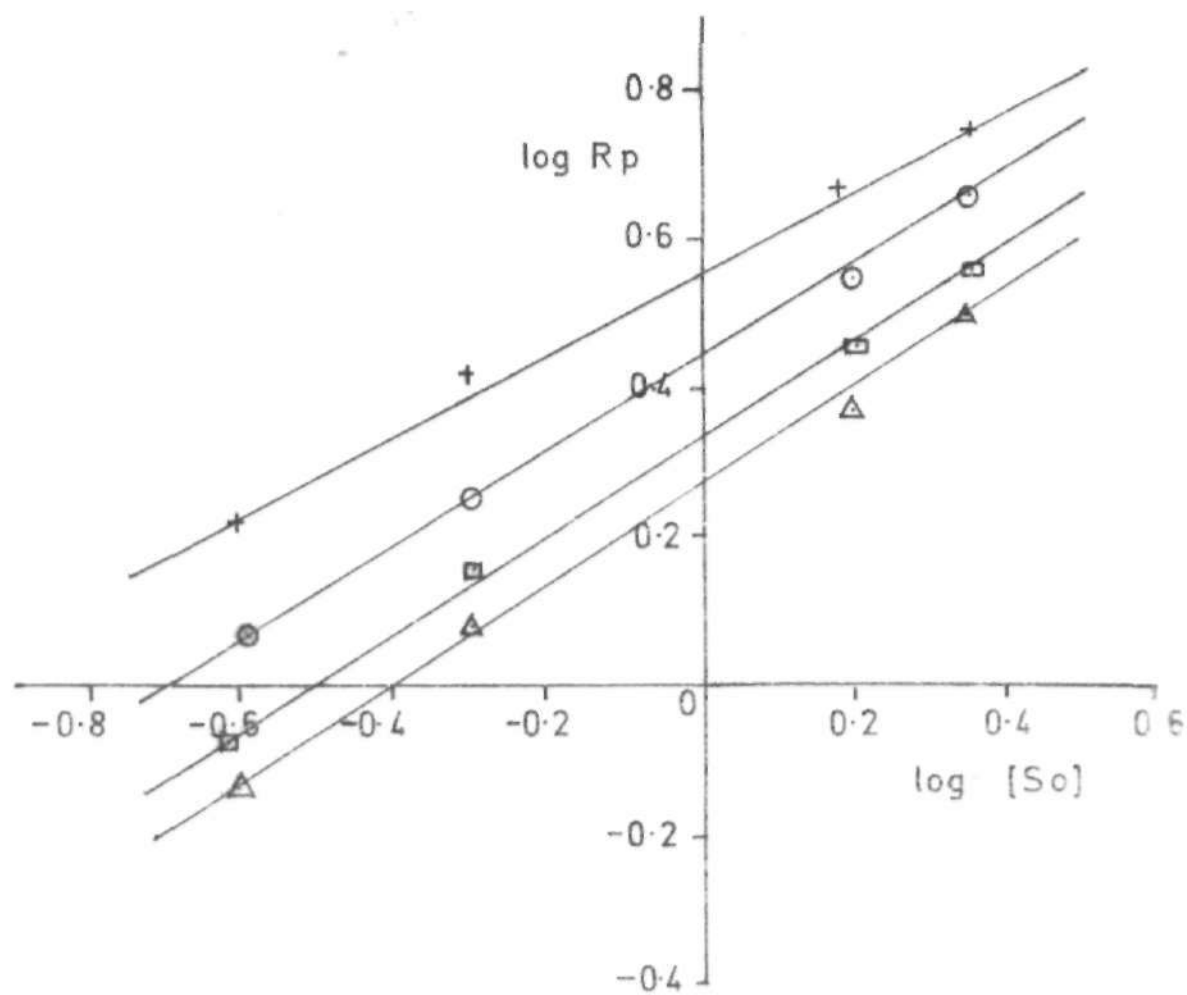


FIG. 2.9

Plots of $\log R_p$ versus $\log (S_o)$ of (+) 0.931; (⊙) 1.455; (⊠) 2.095; (Δ) 2.851 $\text{g}\cdot\text{dm}^{-3}$ of vinyl acetate and 0.25; 0.50; 1.50 and 2.25 $\text{g}\cdot\text{dm}^{-3}$ of emulsifier using 1.50 $\text{g}\cdot\text{dm}^{-3}$ of initiator.

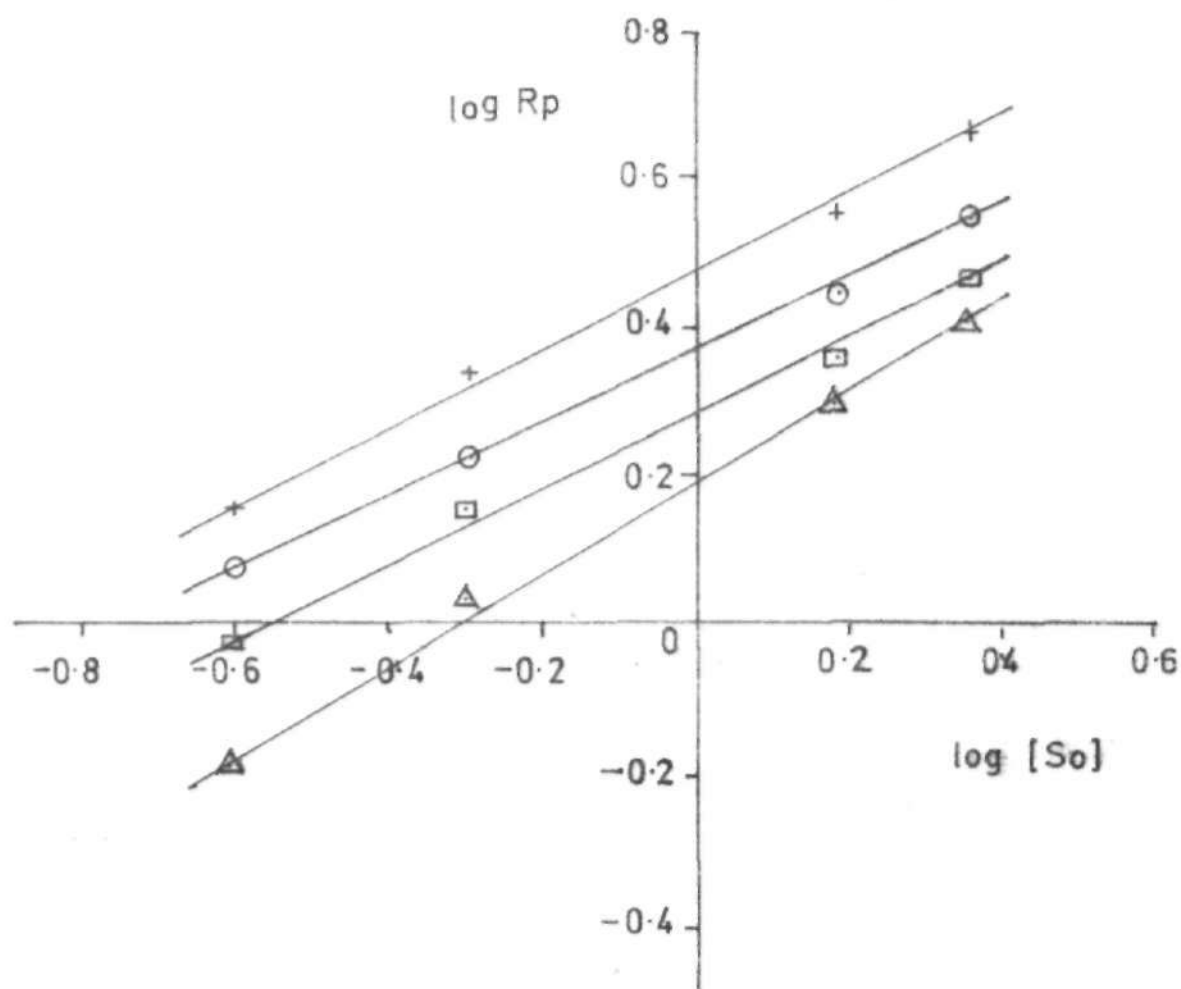


FIG. 2-10

Plots of $\log R_p$ versus $\log [S_o]$ of (+) 0.931; (⊙) 1.455; (⊠) 2.095; (Δ) 2.851 $\text{g}\cdot\text{dm}^{-3}$ of vinyl acetate and 0.25; 0.50; 1.50 and 2.25 $\text{g}\cdot\text{dm}^{-3}$ of emulsifier using 1.00 $\text{g}\cdot\text{dm}^{-3}$ of initiator.

From the results above, the value of the exponent of the emulsifier concentration increases with increase in the initiator concentration. This might be as a result of the effect of initiator on polymerisation reaction depending on the solubility of the initiator and the initiator type. In this study, potassium persulphate ($K_2S_2O_8$) used as the initiator is water soluble, it dissolves in the aqueous phase where the initiating radicals are produced. The increase in the value of the emulsifier concentration exponent with increase in the initiator concentration can thus be attributed to the initiator-surfactant interaction which appears to increase as both the initiator and surfactant concentrations increased. Consequently initiator - monomer interactions are also increased at least at the boundary between the monomer and aqueous layers.

2.2.8 DEPENDENCE OF RATE OF EMULSION POLYMERISATION OF VINYL ACETATE ON INITIATOR CONCENTRATION

The rate of the vinyl acetate polymerisation reaction determined as the slope of the straight line portion of the (%) conversion versus time curve in figures 2.1 to 2.4 was found to decrease with decrease in initiator concentration from $1.50g.dm^{-3}$ to $1.00g.dm^{-3}$ respectively. The corresponding values are as shown in tables 2.7 and 2.8.

Motoyama et al (13) indicated from their studies that the dependence of rate of emulsion polymerisation of vinyl acetate on the concentration of potassium persulphate is very complicated. They suggested that the sulphuric acid formed by potassium persulphate in the mixture probably decomposes vinyl acetate to acetaldehyde which retards the emulsion polymerisation as well as induces decomposition of potassium persulphate to a radical and sulphuric acid.

A possible explanation of the increase in rate of emulsion polymerisation of vinyl acetate with increase in the initiator concentration however, might be due to the availability of more free initiator radicals in the reaction medium with increase in the initiator concentration thereby increasing the rate of interaction between the radicals and the monomer molecules. This increases the rate at which the polymer particles are formed. This observation seems to be in order kinetically.

CHAPTER 33.0 VISCOSITY STUDY3.1 EXPERIMENTAL:3.1.1 PREPARATION OF SOLUTIONS

About 0.17g of each dried polymer sample was accurately weighed and suspended in about 30 cm³ of redistilled methanol in a 50 cm³ volumetric flask and allowed to stand for some time until it had completely swollen. It was then allowed to dissolve and was mixed by shaking. On complete dissolution, the solution was made up to the 50 cm³ mark with methanol and shaken vigorously to homogenisation. It was kept in the water bath operating at $30 \pm 0.05^{\circ}\text{C}$.

3.1.2 VISCOSITY MEASUREMENT

The relative viscosities of the polymer solutions were determined at $30 \pm 0.05^{\circ}\text{C}$ using an Ubbelohde dilution viscometer which had an efflux time of 146.5 seconds for methanol. The viscometer was cleaned by soaking it in a freshly prepared chromic acid solution for at least 24 hours. It was then washed thoroughly to remove all contaminants and finally rinsed with distilled water. It was finally allowed to dry by draining.

10 cm³ of pure methanol was measured accurately into the scrupulously clean and dry dilution viscometer. The

viscometer was placed in the water bath maintained at $30 \pm 0.05^\circ\text{C}$ to thermally equilibrate. The efflux time for methanol was determined repeatedly until reproducible to within ± 0.2 sec. The viscometer was emptied and allowed to dry. 10cm^3 of the polyvinyl acetate solution was measured accurately into the viscometer and the efflux time at $30 \pm 0.05^\circ\text{C}$ was determined as before. 5cm^3 of methanol was added to the 10cm^3 of the solution in the viscometer and the resulting solution was mixed thoroughly and carefully. The efflux time for this was determined also, as before. In step of 5cm^3 of methanol addition, four more dilutions of the polyvinyl acetate solution in the viscometer were made and their corresponding efflux times at $30 \pm 0.05^\circ\text{C}$ were determined. The above experiment was carried out for the polymer samples selected for testing.

Plots of the specific viscosity (η_{sp}/c) versus polymer concentration in g.dl^{-1} were made. The best straight lines through the experimental points were obtained by the method of least squares. The limiting viscosity number $[\eta]$, was obtained for each polymer solution as the intercept along the (η_{sp}/c) axis as calculated above. Also, the Huggins constant k' , was obtained from the slope and the $[\eta]$ of each straight line constructed.

3.2 RESULTS AND DISCUSSION

The intrinsic viscosity of a solution is a function of the molecular weight and the number average degree of polymerisation (\bar{X}_n) of the solute. These quantities are related by the empirical equation of Mark-Houwink-Sakurada (1), given as

$$[\eta] = KM_V^\alpha$$

where $[\eta]$ is the limiting viscosity,

M_V is the viscosity molecular weight,

K and α are constants for a given

polymer in a particular solvent at

a specific temperature.

For a polydispersed polymer preparation \bar{M}_V is used and is called the viscosity average molecular weight. The limiting viscosities of the different polymer samples were determined in purified methanol in an Ubbelohde viscometer at $30 \pm 0.05^\circ\text{C}$. The results are shown in tables 3.1 to 3.6.

3.2.1 DEPENDENCE OF $[\eta]$ ON (%) CONVERSION

Figures 3.1 to 3.4 show the plots of $[\eta]$ versus (%) conversion using 1.50 and 1.00g.dm⁻³ of the initiator and the four different monomer concentrations previously reported. In fig. 3.1 with 0.931g.dm⁻³ of vinyl acetate and 0.25g.dm⁻³ of the initiator, $[\eta]$ increased sharply

TABLE 3.1

Variation of $[\eta]$ and Huggins constant (k') with (%) conversion using $0.25\text{g}\cdot\text{dm}^{-3}$ (SLS) and $1.50\text{g}\cdot\text{dm}^{-3}$ ($\text{K}_2\text{S}_2\text{O}_8$).

Time of polymerisation (mins)	Vinyl acetate concentration in $\text{g}\cdot\text{dm}^{-3}$ of mixture					
	0.931			2.851		
	(%) Conversion	$[\eta]$ g^{-1}dl	Huggins constant (k')	(%) conversion	$[\eta]$ g^{-1}dl	Huggins constant (k')
30	26.70	0.83	1.1977	9.40	0.87	1.1199
35	30.14	1.16	0.255	13.54	1.14	0.2987
40	35.96	1.02	0.9305	17.44	1.02	0.5237
45	41.63	1.08	0.6898	20.71	0.75	1.4678
50	45.39	0.85	1.1122	24.45	0.87	1.0078

TABLE 3.2

Variation of $[\eta]$ and Huggins constant (k') with (%) conversion using $0.50\text{g}\cdot\text{dm}^{-3}$ (SLS) and $1.50\text{g}\cdot\text{dm}^{-3}$ ($\text{K}_2\text{S}_2\text{O}_8$).

Time of polymerisation (mins)	Vinyl acetate concentration in $\text{g}\cdot\text{dm}^{-3}$ of mixture					
	0.931			2.851		
	(%) Conversion	$[\eta]$ g^{-1}dl	Huggins constant (k')	(%) conversion	$[\eta]$ g^{-1}dl	Huggins constant (k')
20	17.27	0.95	0.7711	-	-	-
25	30.52	0.98	0.8217	8.31	0.90	0.7694
30	53.86	1.00	0.9225	12.71	0.99	0.5711
35	59.89	1.13	0.8676	19.21	1.08	0.3406
40	71.66	1.21	0.5983	25.41	1.12	0.3551
45	72.82	1.30	0.3515	33.48	0.98	0.8231

TABLE 3.3

Variation of $[\eta]$ and Huggins constant (k') with (%) conversion using 1.50 g.dm^{-3} (SLS) and 1.50 g.dm^{-3} ($\text{K}_2\text{S}_2\text{O}_8$).

Time of polymerisation (mins.)	Vinyl acetate concentration in g.dm^{-3} of mixture											
	0.931		1.455		2.095		2.851					
	(%) conversion	$[\eta]$ g^{-1}dl	Huggins constant (k')	(%) conversion	$[\eta]$ g^{-1}dl	Huggins constant (k')	(%) conversion	$[\eta]$ g^{-1}dl	Huggins constant (k')	(%) conversion	$[\eta]$ g^{-1}dl	Huggins constant (k')
20	9.15	1.14	0.2154	-	-	-	-	-	-	-	-	-
25	38.80	1.29	0.0467	7.58	1.12	0.3996	3.44	1.00	0.3887	3.31	0.90	0.6105
30	62.77	1.27	0.6325	26.33	0.91	0.9288	18.70	0.88	1.1704	13.04	1.06	0.3720
35	86.02	1.52	0.3259	40.68	1.01	0.8323	34.27	0.99	0.8152	29.99	1.07	0.3128
40	94.16	1.50	0.3266	58.10	1.23	0.4106	46.47	1.10	0.4551	29.63	1.11	0.2993
45	-	-	-	67.40	1.29	0.436	59.11	1.13	0.6562	41.12	1.50	0.0474

TABLE 3.4

Variation of $[\eta]$ and Huggins constant (k') with (%) conversion using $2.25 \text{ g}\cdot\text{dm}^{-3}$ (SLS) and $1.50 \text{ g}\cdot\text{dm}^{-3}$ ($K_2S_2O_8$)

Time of polymerisation (mins.)	Vinyl acetate concentration in $\text{g}\cdot\text{dm}^{-3}$ of mixture											
	0.931	1.455	2.095	2.851								
(%) conversion	$[\eta]$ g^{-1}dl	Huggins constant (k')	(%) conversion	$[\eta]$ g^{-1}dl	Huggins constant (k')							
15	27.00	1.01	0.9088	-	-	-	-	-				
20	58.01	1.08	0.9133	11.51	0.82	1.3176	3.77	0.86	0.9845			
25	86.35	1.31	0.6226	36.28	0.85	1.0690	19.06	0.84	0.9818	7.23	0.78	1.3677
30	96.37	1.22	0.7336	59.75	0.94	0.8901	37.55	0.81	0.8515	21.70	0.81	1.3134
35	97.99	1.32	0.6406	81.22	1.19	0.75	55.55	0.95	1.0999	38.89	0.83	1.3166
40	-	-	-	94.29	1.36	0.65	78.92	1.24	1.0045	54.54	0.84	0.9816
45	-	-	-	-	-	-	-	-	-	75.14	1.01	1.0035

TABLE 3.5

Variation of $[\eta]$ and Huggins constant (k') with (%) conversion using $0.25\text{g}\cdot\text{dm}^{-3}$ (SLS) and $1.00\text{g}\cdot\text{dm}^{-3}$ ($\text{K}_2\text{S}_2\text{O}_8$).

Time of polymerisation (mins.)	Vinyl acetate concentration in $\text{g}\cdot\text{dm}^{-3}$ of mixture											
	0.931		1.455		2.095		2.851					
	(%) conversion	$[\eta]$ g^{-1}dl	Huggins constant (k')	(%) conversion	$[\eta]$ g^{-1}dl	Huggins constant (k')	(%) conversion	$[\eta]$ g^{-1}dl	Huggins constant (k')	(%) conversion	$[\eta]$ g^{-1}dl	Huggins constant (k')
30	11.99	0.78	1.3302	9.90	0.84	0.9917	8.46	0.90	0.5104	-	-	-
40	25.05	0.87	0.7110	20.16	0.88	0.9951	16.14	0.87	0.9954	9.83	0.91	0.7385
50	41.05	0.91	0.7528	32.77	0.93	1.0306	24.92	0.88	0.4938	14.12	0.91	0.8984
60	69.41	1.12	0.6718	48.17	1.02	0.5258	34.45	0.87	0.8640	22.08	0.92	0.7740
70	81.91	1.16	0.6221	68.91	1.15	0.6077	46.13	0.97	0.5884	28.58	0.94	0.7878
80	-	-	-	-	-	-	56.36	1.09	0.4045	36.47	0.89	1.0399
90	-	-	-	-	-	-	-	-	-	48.91	0.94	0.8651

TABLE 3.6

Variation of $[\eta]$ and Huggins constant (k') with (%) conversion using 2.25 g.dm^{-3} (StS) and 1.00 g.dm^{-3} ($K_2S_2O_8$)

Time of polymerization (mins.)	0.931		1.455		2.095		2.851		
	(%) conversion	$[\eta]$ g^{-1}dl	Huggins constant (k')	(%) conversion	$[\eta]$ g^{-1}dl	Huggins constant (k')	(%) conversion	$[\eta]$ g^{-1}dl	Huggins constant (k')
20	36.87	0.99	0.9705	27.23	1.04	0.7083	-	-	-
30	82.83	1.27	0.8142	67.14	1.20	0.7555	26.63	0.98	0.6567
40	93.38	1.44	0.4716	96.25	1.33	0.6046	53.99	1.28	0.5173
50	93.78	1.38	0.6469	98.70	1.37	0.5468	84.91	1.75	0.4690
60	94.66	1.39	0.5561	99.04	1.41	0.4879	87.90	1.84	0.3490
70	96.75	1.42	0.4915	99.60	1.30	0.6351	91.18	1.85	0.2883
80	-	-	-	-	-	-	-	-	-
							99.75	1.32	0.8205

Vinyl acetate concentration in g.dm^{-3} of mixture

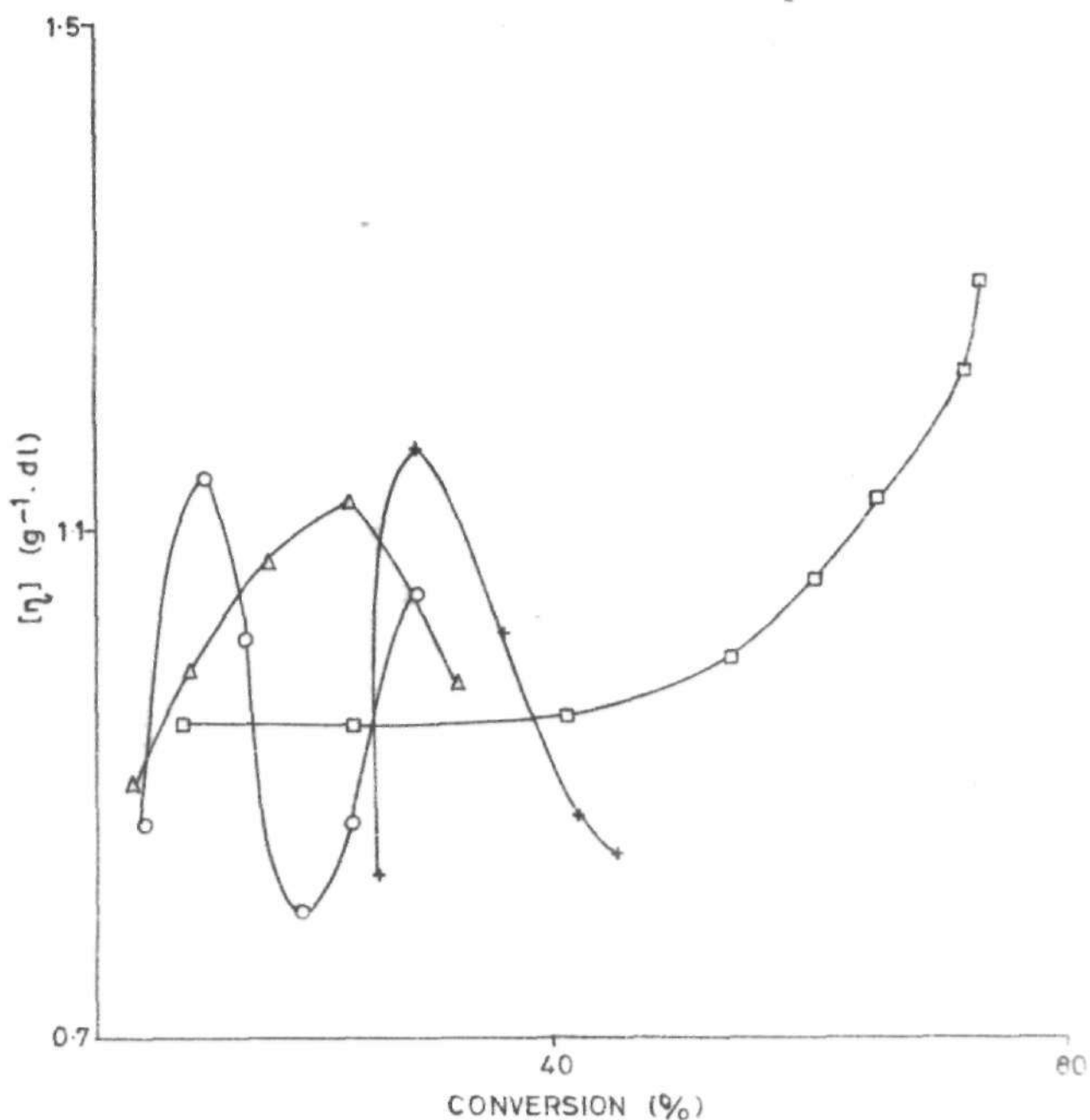


FIG.3-1 PLOTS OF $[\eta]$ VERSUS (%) CONVERSION OF POLYMER SAMPLES OBTAINED USING (+) $0.25\text{g}\cdot\text{dm}^{-3}$ (SLS) AND $0.931\text{g}\cdot\text{dm}^{-3}$ VINYL ACETATE (o) $0.25\text{g}\cdot\text{dm}^{-3}$ (SLS) AND $2.851\text{g}\cdot\text{dm}^{-3}$ VINYL ACETATE (□) $0.50\text{g}\cdot\text{dm}^{-3}$ (SLS) AND $0.931\text{g}\cdot\text{dm}^{-3}$ VINYL ACETATE AND (Δ) $0.50\text{g}\cdot\text{dm}^{-3}$ (SLS) AND $2.851\text{g}\cdot\text{dm}^{-3}$ VINYL ACETATE WITH INITIATOR CONCENTRATION AT $1.50\text{g}\cdot\text{dm}^{-3}$

to a peak at about 30% conversion and dropped sharply too at higher (%) conversion. As samples of lower conversion values were not obtained during the kinetic study, it is difficult to comment on the pattern of $[\eta]$ for conversions below about 25%. As the kinetic studies indicated, coagulation occurred at conversions above about 45%, hence results for samples with conversions above 45% are not available. In effect, a peak with a value, $[\eta]$ of 1.16 at about 30% conversion was noticed for this curve. The curve of 0.25g.dm^{-3} of (SLS) and 2.851g.dm^{-3} of vinyl acetate also showed sharp increase to a minimum at about 12.5% followed by a sharp decrease at about 21% and then an increase again in $[\eta]$ with increase in (%) conversion. For the samples obtained with 0.931g vinyl acetate and 0.50g.dm^{-3} of the emulsifier, there was a very gradual increase in $[\eta]$ with (%) conversion between about 10% to about 40% conversion, then a sharp increase followed with further increase in (%) conversion. The last curve of 0.50g.dm^{-3} of the emulsifier and 2.851g.dm^{-3} of vinyl acetate showed a decrease in $[\eta]$ after the gradual increase in $[\eta]$ with (%) conversion.

The results actually indicate that low vinyl acetate concentration with high $[S_o]$ of (SLS) at a given initiator concentration give polyvinyl acetate samples with high $[\eta]$ values. And that during the polymerisation reaction, the peak of $[\eta]$ value occurs at higher (%) conversion, or

at least, $[\eta]$ shows a tendency to increase with conversion and may not show a maximum. Lower initiator values also appear to give higher $[\eta]$ values at all conversion when $[S_o]$ and $[VAc]$ are kept constant. Hence in order to obtain polymers with high $[\eta]$ values either at low or high degree of conversion, low initiator concentration would be required.

A different pattern was obtained for the plots in fig. 3.2 when the emulsifier concentration was increased to 2.25 g.dm^{-3} while the monomer concentrations were 0.931, 1.455, 2.095 and 2.851 g.dm^{-3} . Below about 40% conversion of monomer to the polymer for all the curves, limiting viscosity appears to be fairly constant though, it varied slightly with vinyl acetate concentration. In all cases, $[\eta]$ increased sharply after the initial fairly constant value which extends to about 40% conversion.

In figs. 3.3 and 3.4, the initiator concentration was reduced to 1.00 g.dm^{-3} while two emulsifier concentrations of 0.25 and 2.25 g.dm^{-3} were used respectively in the polymerisation of vinyl acetate. The monomer concentrations remained as 0.931; 1.455; 2.095 and 2.851 g.dm^{-3} respectively. There was a common behaviour of $[\eta]$ with (%) conversion. The limiting viscosity number had a fairly constant value

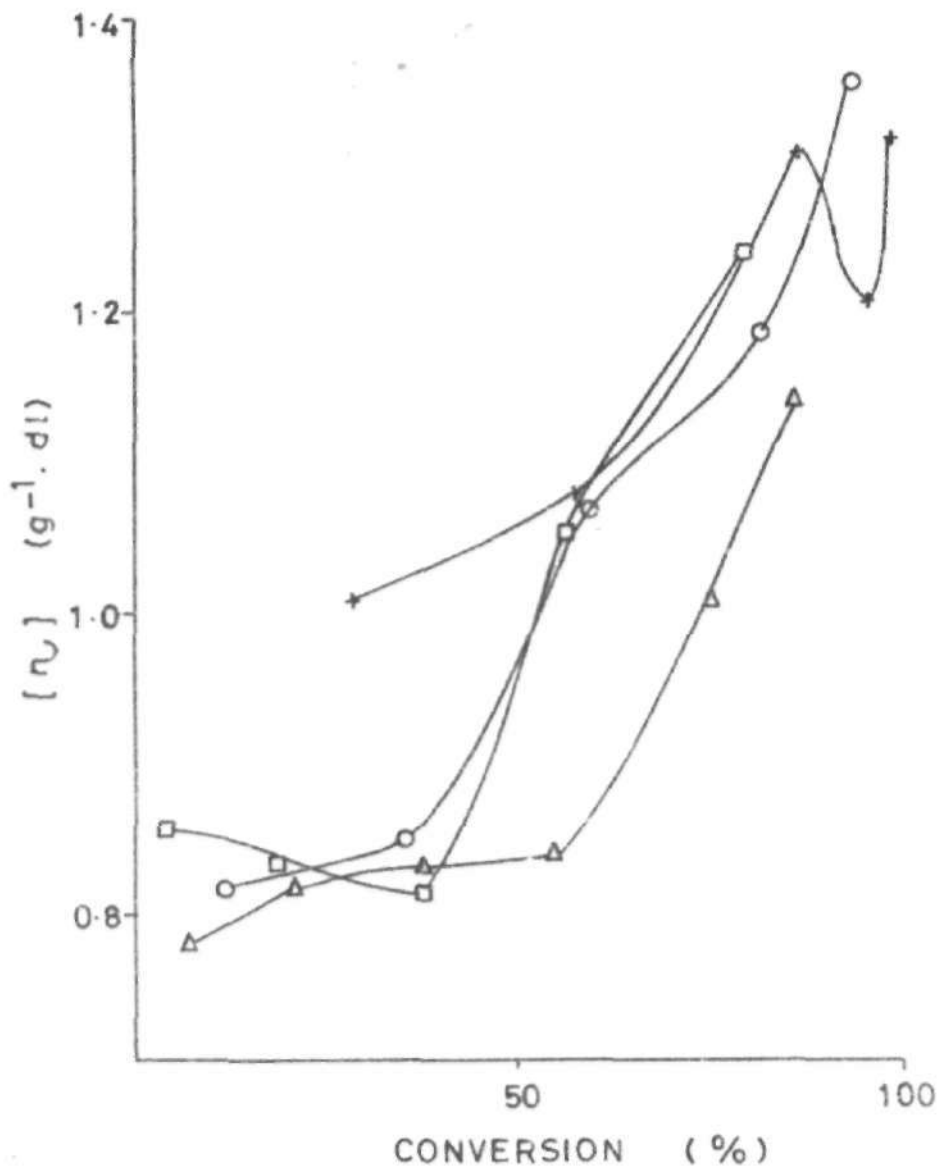


FIG. 3.2 PLOTS OF $[\eta]$ VERSUS (%) CONVERSION OF PVAc SAMPLES OBTAINED USING $2.25 \text{ g} \cdot \text{dm}^{-3}$ (SLS) AND $1.50 \text{ g} \cdot \text{dm}^{-3}$ ($\text{K}_2\text{S}_2\text{O}_8$) WITH MONOMER CONCENTRATIONS OF (+) 0.931 ; (o) 1.455 ; (□) 2.095 AND (Δ) $2.851 \text{ g} \cdot \text{dm}^{-3}$

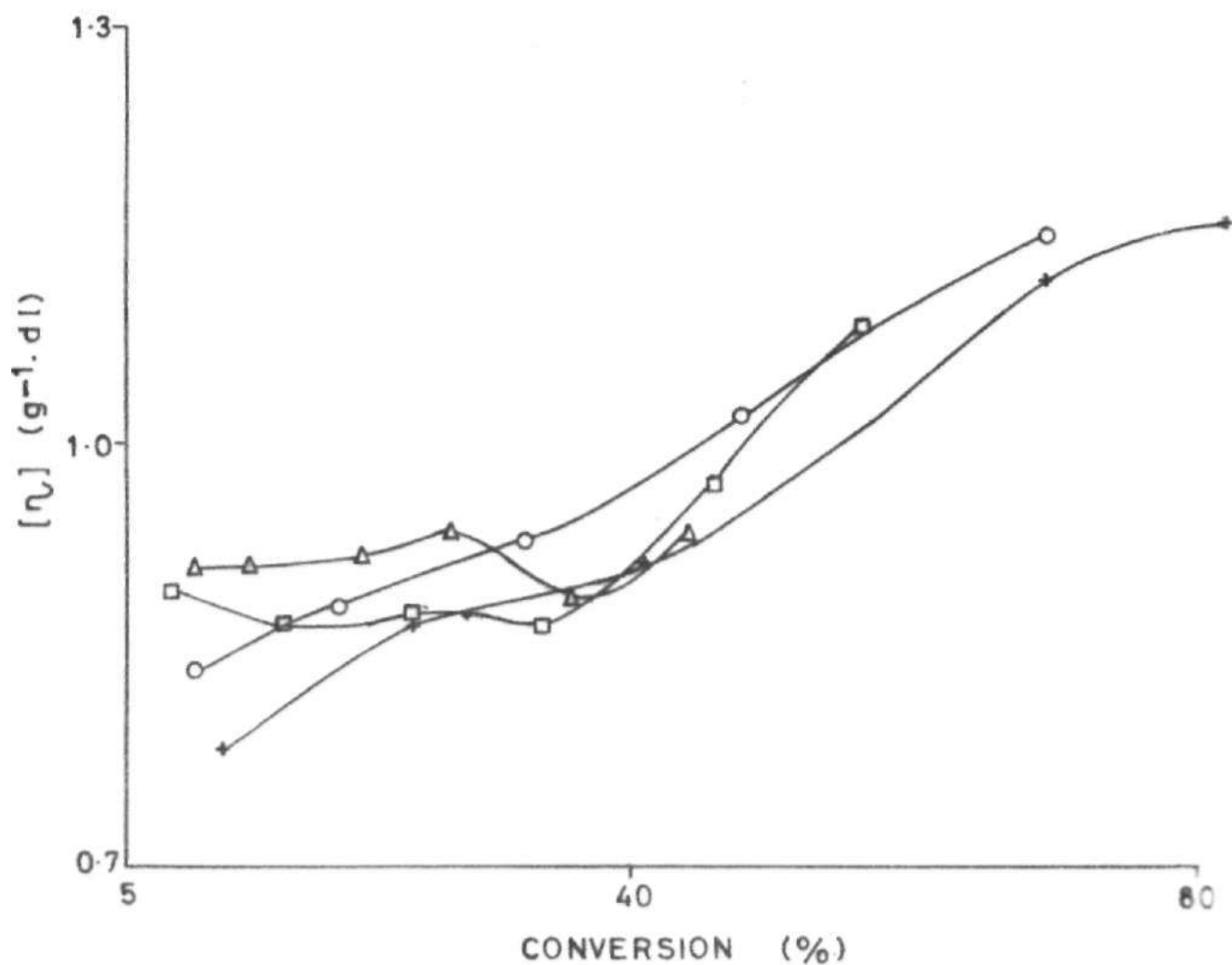


FIG. 3.3 PLOTS OF $[\eta]$ VERSUS (%) CONVERSION OF POLYMER SAMPLES OBTAINED USING $0.25\text{g}\cdot\text{dm}^{-3}$ (SLS) AND $1.00\text{g}\cdot\text{dm}^{-3}$ ($\text{K}_2\text{S}_2\text{O}_8$) WITH MONOMER CONCENTRATION AT (+) 0.931 ; (o) 1.455 ; (□) 2.095 AND (Δ) $2.851\text{g}\cdot\text{dm}^{-3}$

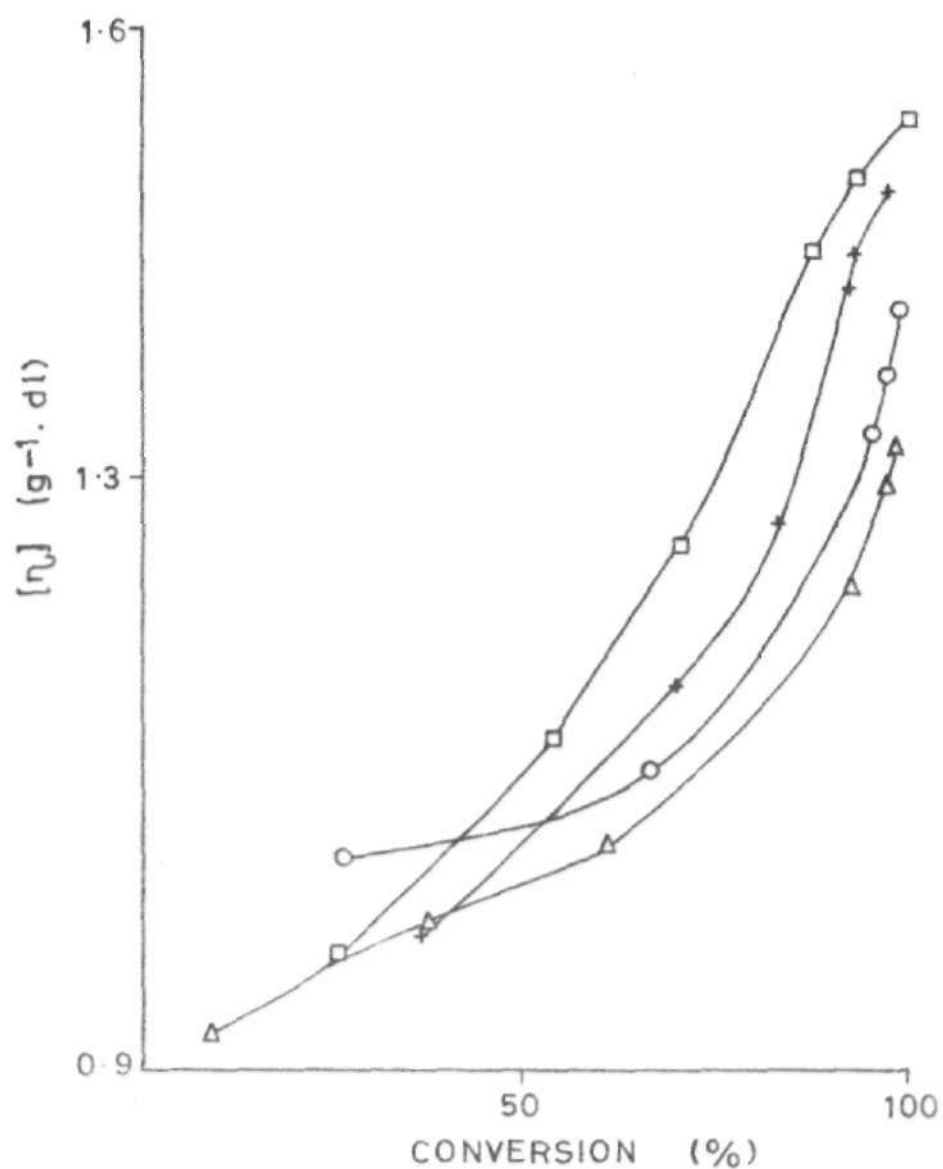


FIG. 3.4 PLOTS OF $[\eta]$ VERSUS (%) CONVERSION OF POLYMER SAMPLES OBTAINED USING $2.25\text{g}\cdot\text{dm}^{-3}$ (SLS) AND $1.00\text{g}\cdot\text{dm}^{-3}$ ($\text{K}_2\text{S}_2\text{O}_8$) WITH MONOMER CONCENTRATIONS OF (+) 0.931 , (o) 1.455 , (□) 2.095 AND (Δ) $2.851\text{g}\cdot\text{dm}^{-3}$

below about 40% conversion followed by an increase towards a maximum for each of the different curves in fig. 3.3. In fig. 3.4, the four different curves on the other hand showed an increase in $[\eta]$ with (%) conversion.

The results in figures 3.1 to 3.4, indicate that polyvinyl acetate of different average molecular parameters are obtained at different (%) conversion. The major molecular parameters that are expected to influence $[\eta]$ according to theories of polymer-solvent interactions include polymer molecular weight, its distribution and presence and extent of branching in the polymeric structure. Different values of $[\eta]$ are obtained as a result of changes in N , k_p and R_i during the course of the emulsion polymerisation of vinyl acetate. From Smith-Ewart (10) theory,

$$(\bar{X}_n) = \frac{N k_p [M]}{R_i} \quad \text{and} \quad N \propto [S_o]^{0.6}$$

where (\bar{X}_n) is the average degree of polymerisation,

$[M]$ is the monomer concentration and

$[S_o]$ is the emulsifier concentration.

Since $[\eta]$ is proportional to (\bar{X}_n) and (\bar{X}_n) is proportional to N , it follows that $[\eta]$ should be proportional to N . Hence an increase in $[S_o]$ should lead to an increase in the number of latex particles. Hence $[\eta]$ and (\bar{X}_n) should increase. The results obtained in figures 3.1 to 3.4 support the above to a reasonable extent.

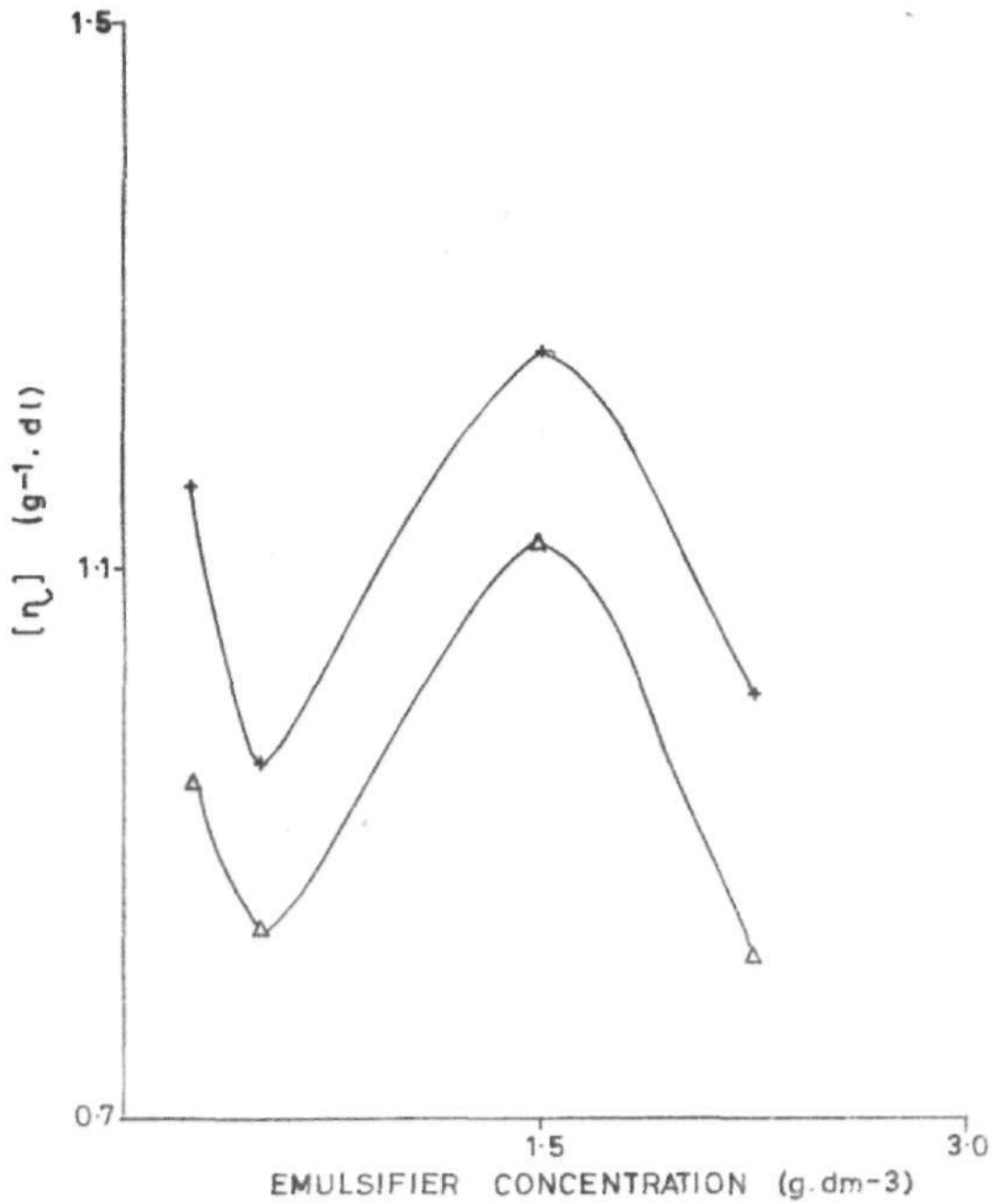


FIG. 3.5 PLOTS OF $[\eta]$ VERSUS EMULSIFIER CONCENTRATION AT 30% CONVERSION USING (+) 0.931 AND (Δ) 2.851 $\text{g} \cdot \text{dm}^{-3}$ VINYL ACETATE WITH INITIATOR CONCENTRATION AT 1.00 $\text{g} \cdot \text{dm}^{-3}$

3.2.3 THE DEPENDENCE OF HUGGINS' CONSTANT K' OBTAINED FROM THE DILUTE SOLUTION VISCOSITY OF POLYVINYL ACETATE ON THE (%) CONVERSION OF VINYL ACETATE TO POLYVINYL ACETATE

Viscosity data as a function of concentration are related by Huggins' equation:

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

where k' , the Huggins' constant is a constant for a polymer of a fixed macromolecular structure dissolved in a given solvent. The viscosity of the solution at zero concentration of the polymer in solution is obtained by extrapolation. Huggins' constant is a measure of the polymer-solvent interaction and its values for given polymer-solvent systems are not usually sensitive to molecular weight changes. The value of k' has been reported to be usually in the range of $0.3 < k' < 0.4$, in good solvents for the solvents for the particular polymer although, sometimes higher values may be observed for poor solvents (23). Also, suggestions have been made that large values of k' may indicate the presence of aggregates in the solutions (23).

Figures 3.6 to 3.9 illustrate the variation of Huggins' constant k' , with (%) conversion using different monomer, emulsifier and initiator concentrations. In fig. 3.6, the monomer and initiator concentrations remained at 0.931 and

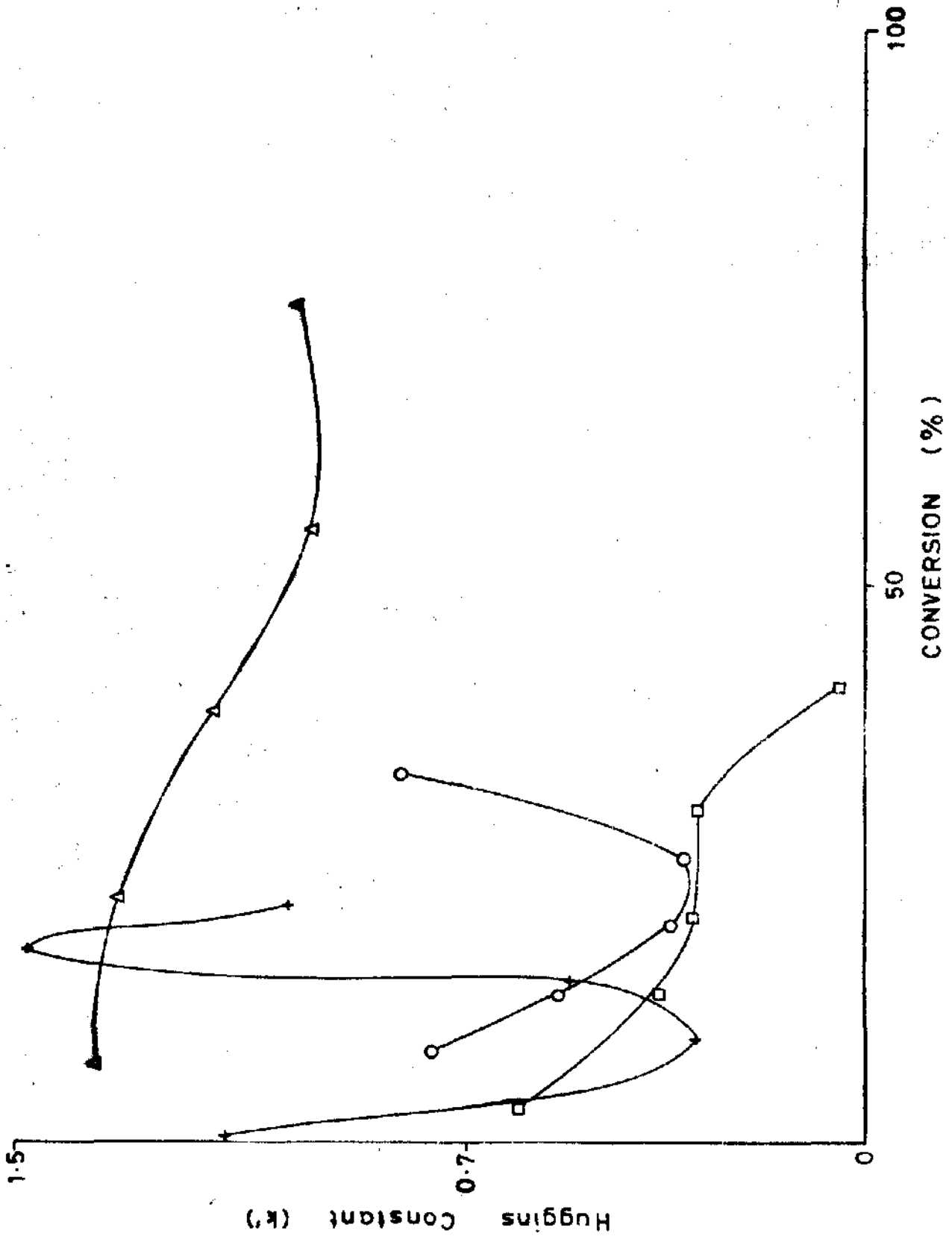


FIG. 3.7 PLOTS OF HUGGINS CONSTANT (k') VERSUS (%) CONVERSION USING 2.851g.dm⁻³ VINYL ACETATE, 150g.dm⁻³ (k₂S₂O₈) AND (+) 0.25, (o) 0.50 (□) 1.50 AND (Δ) 2.25g.dm⁻³ (SLS)

1.50g.dm^{-3} respectively for all the different curves while the emulsifier concentration was varied from 0.25 to 2.25g.dm^{-3} . The curve of 0.931g.dm^{-3} vinyl acetate and 0.25g.dm^{-3} (SLS) shows a sharp decrease followed by an increase and another decrease and then an increase in k' with increase in (%) conversion. A peak was noticed for this curve at k' of 0.93 at about 30% conversion. The curve did not exceed 45% conversion because coagulation occurred just around this value of (%) conversion. The different values of k' obtained can be as a result of the different nature of the polymers produced at different stages of polymerisation. The initial decrease in the k' value from about 1.20 to about 0.16 might be as a result of the presence of linear, flexible polymer at this conversion since the emulsifier concentration in the recipe was very low at 0.25g.dm^{-3} . Thus there is maximum interaction between the polymer and the solvent giving rise to a small k' value. The sudden increase in k' might be due to the presence of aggregates in the polymer. Hence, the polymer-solvent interaction is minimised thereby increasing the k' value. Towards the end of polymerisation, amount of monomer in the recipe is reduced, thus branching is reduced on the average per polymer molecule and therefore the polymer - solvent interaction is increased thus k' value is also reduced. The final increase in k' might be as a result of the presence of some short chain branches in the polymer leading to the coiling up of the polymer in the solvent thus

reducing the polymer - solvent interaction and hence increasing k' .

In the curve of 0.50g.dm^{-3} (SLS) and 0.931g.dm^{-3} vinyl acetate, there is a slight increase in k' from 0.77 to a maximum value of 0.91 at about 55% conversion before finally dropping to a minimum value of 0.36 at about 75% conversion. There is no distinct peak in this curve. The gradual increase in k' value from 0.77 to 0.91 could be explained in terms of the presence of some degree of branching in the polymer produced over this range of conversion. In this case too, because of the presence of some branching which can either be long or short, the polymer - solvent interaction is minimised and k' is therefore increased. The decrease in k' thereafter, towards the end of the polymerisation, can again be accounted for by the decrease in the amount of monomer in the recipe leading to a reduction in the degree of branching earlier encountered. In this wise, the polymer - solvent interaction becomes bigger and k' is thus reduced.

The curve of 0.931g.dm^{-3} vinyl acetate and 1.50g.dm^{-3} (SLS) shows a decrease in k' from 0.22 at 9% conversion to a minimum of 0.05 at about 40% conversion before increasing to the peak of 0.63 at about 65% conversion. It later dropped to a low value of about 0.33 at about 95% conversion. The initial decrease in k' might be as a result of the

reduction in the degree of branching thus the polymer - solvent interaction bigger thereby reducing k' . The high value of k' which followed could be explained in terms of the presence of bulky side chains in the polymer. The polymer in solution then tended to coil up thus, reducing polymer - solvent interaction while k' becomes large. At high conversion, monomer concentration is reduced, average degree of branching per polymer molecule is reduced, polymer - solvent interaction becomes bigger and k' value becomes smaller. This accounts for the decrease in k' towards the end of the polymerisation for this curve.

The last curve of 0.931g.dm^{-3} vinyl acetate and 2.25g.dm^{-3} (SLS) shows a decrease in k' from 0.91 to about 0.62 at about 85% conversion. The gradual increase in k' from 0.91 to about 0.93 before the sudden decrease is as a result of increase in the degree of branching in the polymer, reducing the polymer - solvent interaction thereby increasing k' . The decrease thereafter at the higher conversion might be due to inavailability of enough monomer in the recipe. Hence, degree of branching is reduced, polymer tends to be linear and polymer - solvent is maximised and k' is thus reduced.

Figure 3.7 illustrates the variation of Huggins constant k' , with (%) conversion using 2.851g.dm^{-3} vinyl

acetate and 1.50 g.dm^{-3} ($\text{K}_2\text{S}_2\text{O}_8$) with emulsifier concentration ranging from 0.25 to 2.25 g.dm^{-3} . The decrease in k' from the initial high value, might be due to the appearance of short chain branches compared to the long ones that might have limited polymer - solvent interaction thus giving rise to high k' . With short branches, polymer - solvent interaction is still favoured to a reasonable extent and k' values thus drop. The sudden increase again in k' might be explained as an increase in the degree of branching thus giving rise to a bulky polymer with restricted movement in the solvent. In this respect there is minimum polymer - solvent interaction due to the compact structure of the polymer and k' value therefore rises. The final drop in k' value might be as a result of a decrease in monomer concentration towards the end of the polymerisation reaction. With the decrease in monomer concentration, degree of branching is reduced, polymer - solvent interaction is increased and corresponding decrease is noticed in the k' value.

With the curve of 0.50 g.dm^{-3} (SLS) and 2.851 g.dm^{-3} vinyl acetate, a decrease can be noticed in k' before the occurrence of a flat portion between about 19 - 25% conversion followed by a sharp decrease in k' with increase in (%) conversion. The decrease in k' can be explained

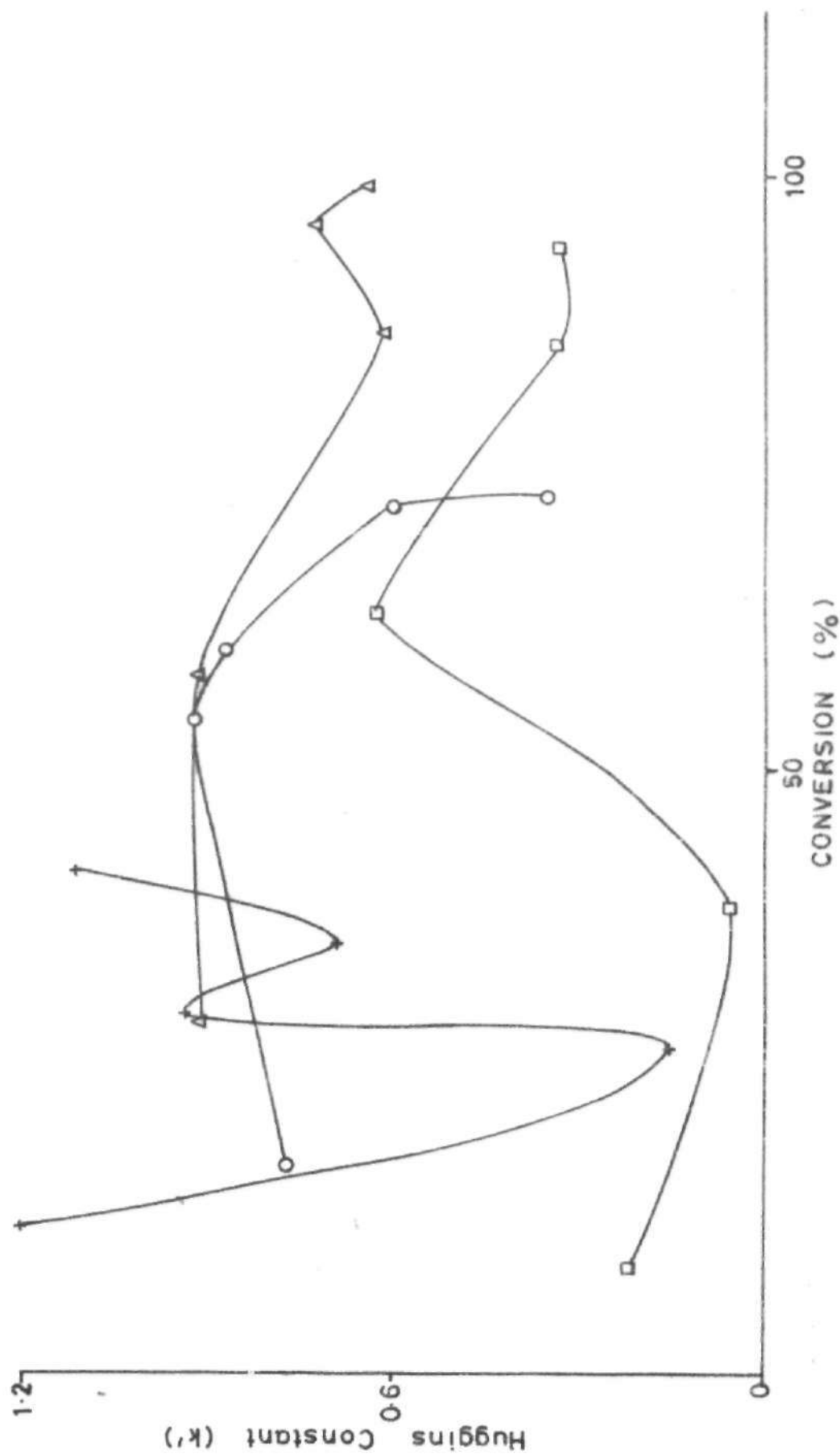


FIG. 3.6 PLOTS OF HUGGINS CONSTANT (k') VERSUS (%) CONVERSION USING $0.931\text{g}\cdot\text{dm}^{-3}$ VINYL ACETATE; $1.50\text{g}\cdot\text{dm}^{-3}$ ($\text{K}_2\text{S}_2\text{O}_8$) AND (+) 0.25 ; (○) 0.50 ; (□) 1.50 AND (Δ) $2.25\text{g}\cdot\text{dm}^{-3}$ (SLS)

in terms of bigger interaction between the polymer and the solvent probably as a result of the decrease in the degree of branching. The flat portion after the decrease in k' probably suggests that the same type of polymer was produced over that conversion range at that time of polymerisation. The increase in k' thereafter might be due to an increase again in the degree of branching in terms of replacement of short chains by long chain branches. Polymer movement in solution becomes difficult, therefore polymer - solvent interaction becomes small and a corresponding increase in k' is then noticed.

The curve of 1.50 g.dm^{-3} (SLS) and 2.851 g.dm^{-3} vinyl acetate show a decrease in k' from 0.61 to about 0.3 at 20% conversion followed by a flat portion over 20 - 30% conversion and a final decrease to a minimum of 0.05 at about 40% conversion. The initial decrease in k' is as a result of bigger interaction between the polymer and the solvent due to a reduction in the degree of branching in the polymer. The flat portion again suggests the occurrence of the same type of polymer at that time of polymerisation. The further decrease in k' might be explained in terms of the replacement of the initial long chain branches by short branches thus further increasing the polymer - solvent interaction thereby decreasing k' a little further than before.

The last curve of 2.852 g.dm^{-3} vinyl acetate and 2.25 g.dm^{-3} (SLS) shows a decrease in k' from a high value of 1.35 at about 8% conversion to about 1.00 at 75% conversion. This curve actually shows a gradual decrease in k' from a maximum value to a minimum value. The pattern of this curve can be explained in terms of the presence of long and short chain branches in the polymer. The initial high value of k' might be due to the presence of long chain branches in which case polymer - solvent interaction is a bit restricted hence the high k' value. The further decrease in k' might be as a result of the replacement of the long chain branches with short chains as the polymerisation reaction proceeds. The polymer - solvent interaction becomes bigger than before and k' is further reduced.

In figures 3.8 and 3.9, the initiator concentration was 1.00 g.dm^{-3} while emulsifier concentrations were 0.25 and 2.25 g.dm^{-3} respectively for the two graphs, for the various monomer concentrations of 0.931; 1.455; 2.095 and 2.851 g.dm^{-3} . Fig 3.8 shows the variation of Huggins' constant k' , with (%) conversion using 0.25 g.dm^{-3} (SLS) and the four different monomer concentrations previously mentioned. The curve of 0.931 g.dm^{-3} vinyl acetate shows an initial sharp decrease in k' from 1.43 to about 0.71 at 25% conversion before the gradual decrease to the minimum of 0.62 at about 82% conversion. The sharp decrease in k' might be due to the replacement of the long chain branches by short ones thus increasing polymer - solvent interaction and k' .

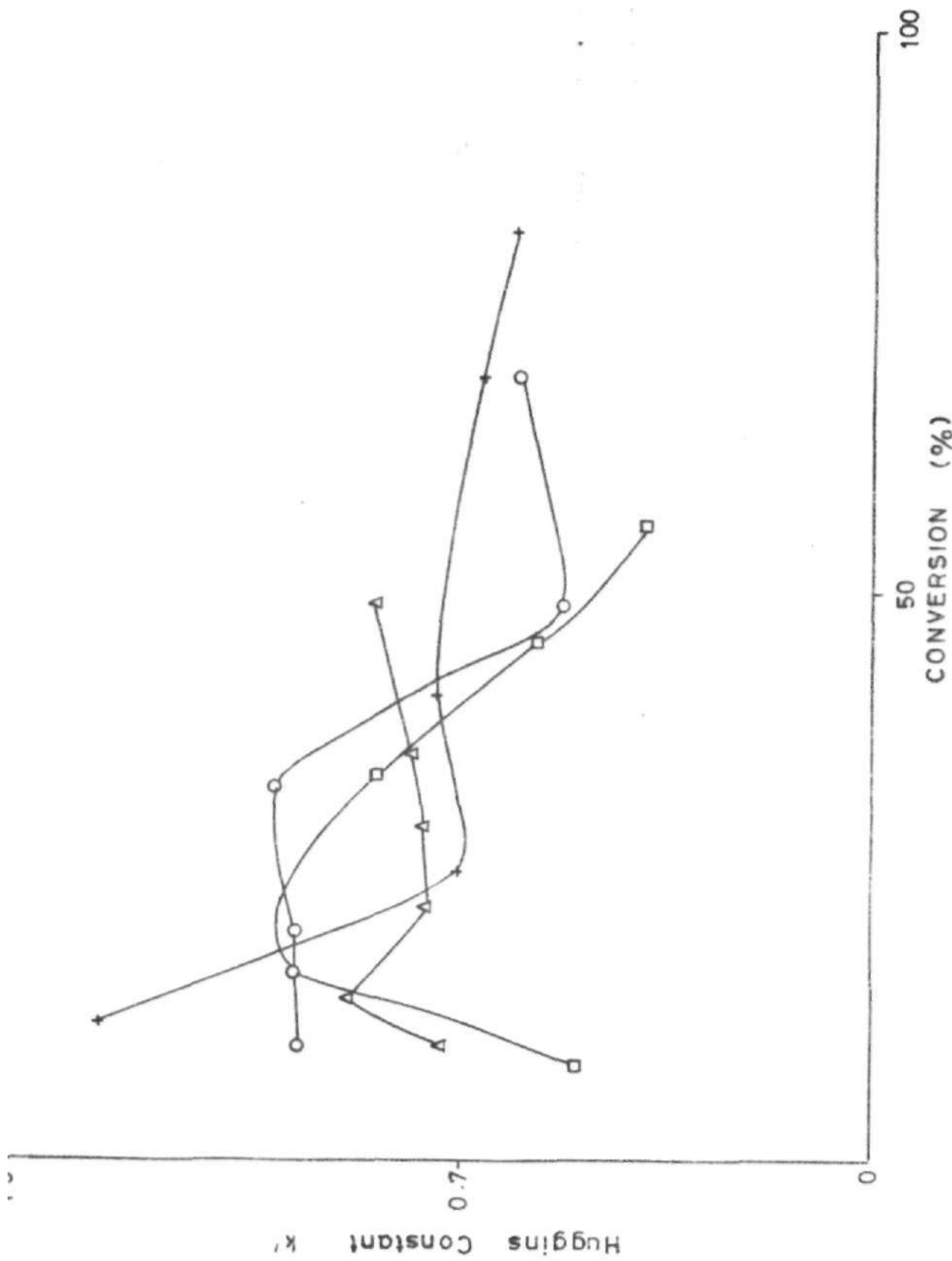


FIG. 3.8 PLOTS OF HUGGINS CONSTANT k' VERSUS (%) CONVERSION USING 0.25g.dm⁻³ (SLS); 1.00g.dm⁻³ (K₂S₂O₈) AND (+) 0.931, (○) 1.455 (□) 2.095 AND (Δ) 2.051g.dm⁻³ VINYL ACETATE

Further decrease in k' might be as a result of the reduction in the number of the short chains making the polymer tend towards being linear in which case polymer - solvent interaction is maximised and k' value is further reduced.

The curve of 1.455 g.dm^{-3} vinyl acetate shows an almost flat portion before a sharp decrease in k' from 1.03 to 0.54 at about 50% conversion, followed by a slight increase again in k' up to about 70% conversion. The initial flat portion probably indicates the presence of the same type of polymer over that conversion range. The decrease in k' might be as a result of the occurrence of maximum interaction between the polymer and the solvent whereby the polymer then exists in a flexible form. The increase in k' thereafter might be due to some degree of branching in the polymer in which case polymer - solvent interaction is reduced and k' then increases.

The curves of 2.095 and 2.851 g.dm^{-3} vinyl acetate both show an initial increase in k' before a decrease and then a slight increase again in the case of 2.851 g.dm^{-3} vinyl acetate up to about 50% conversion. The initial increase in k' might be as a result of some bulky groups attached to the polymer chain thereby limiting polymer - solvent interaction thus giving rise to a high k' . The decrease thereafter might be due to a reduction in the

bulky group in which case polymer-solvent interaction becomes bigger and k' gets smaller. The sudden rise again in k' for the curve of 2.851 g.dm^{-3} might be due to an increase in the degree of branching leading to minimum polymer solvent - interaction and therefore a high k' value.

Figure 3.9 illustrates the variation of Huggins constant k' , with 2.25 g.dm^{-3} (SLS) and 1.00 g.dm^{-3} ($\text{K}_2\text{S}_2\text{O}_8$) using 0.931 ; 1.455 ; 2.095 and 2.851 g.dm^{-3} vinyl acetate. In this graph, all the curves show the same pattern of a slight decrease in k' up to about 85% conversion followed by a sharp decrease to the minimum of different values for the various monomer concentrations studied. For the curves of 0.931 and 1.455 g.dm^{-3} vinyl acetate which continued up to about 98% conversion, a sharp increase followed the initial decrease in k' . The slight decrease in k' can be explained in terms of a gradual decrease in the degree of branching giving rise to a steady increase in polymer - solvent interaction and therefore a gradual decrease in k' . The sharp decrease in k' thereafter might be due to an almost complete disappearance of branching in which case there is an increase in polymer - solvent interaction and a corresponding decrease in k' . The sudden increase again in k' for the

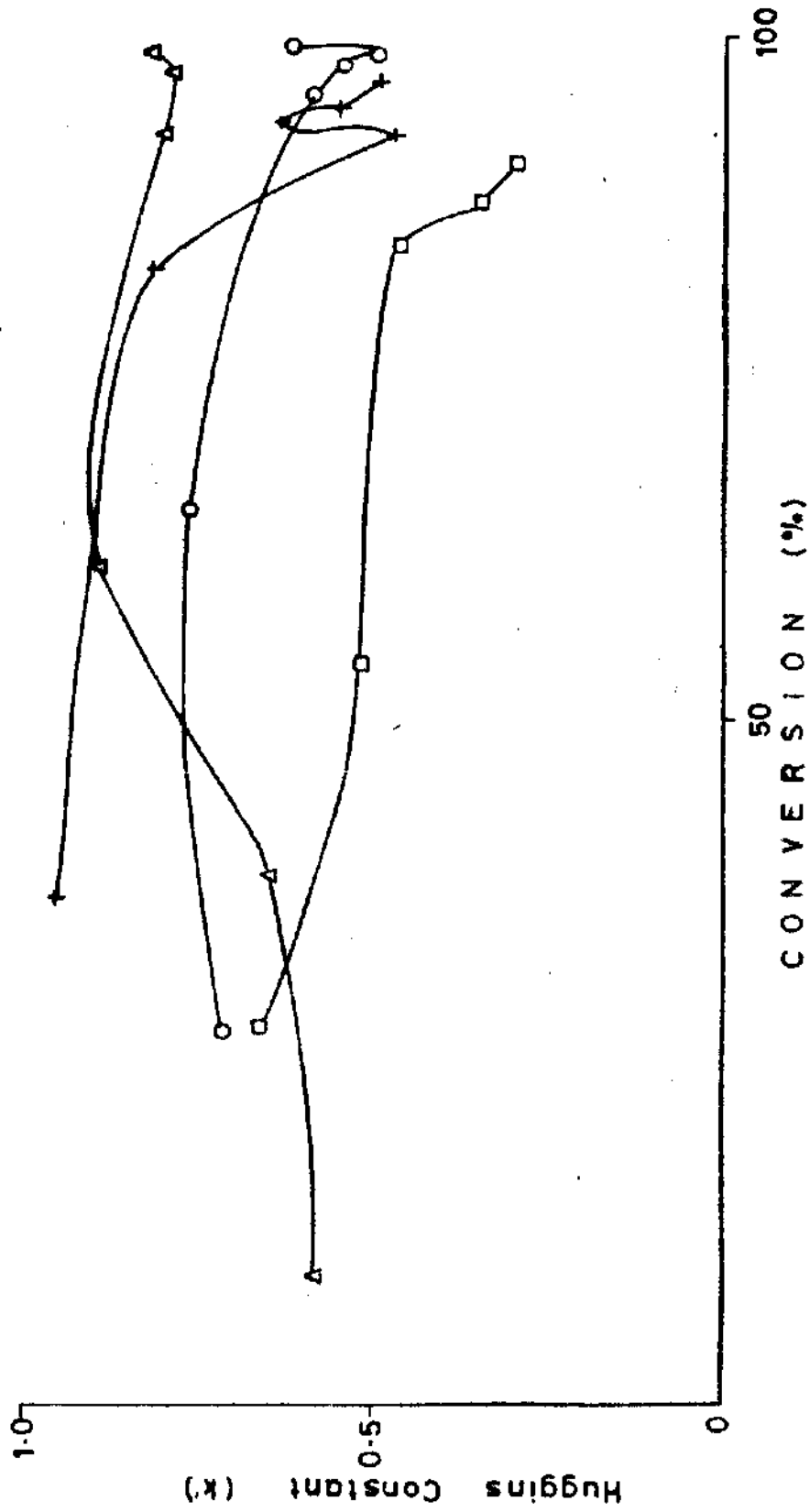


FIG. 3-9 PLOTS OF HUGGINS CONSTANT (k) VERSUS (%) CONVERSION USING 2.25g.dm⁻³ (SLS); 1.00g.dm⁻³ (M2S2O8) AND (+) 1.455 (□) 2.095 AND (Δ) 2.051g.dm⁻³ VINYL ACETATE

CHAPTER 4

CONCLUSION AND RECOMMENDATION

The kinetic study of the emulsion polymerisation of vinyl acetate shows the following;

- (i) an induction period which increases as the emulsifier concentration increases - interpreted as the time required for the proper interaction between the monomer molecules and the initiating free radicals.
- (ii) linear variation of (%) conversion with time over a range of conversion which increases as the emulsifier concentration increases, but not exceeding 20 - 80%, over which the overall rate of polymerisation is determined.
- (iii) aggregation, especially at higher (%) conversion and very low emulsifier concentration, interpreted as the inability of the emulsifier to stabilise the latex particles.
- (iv) decrease in polymerisation rate with increase in monomer concentration and decrease in initiator concentration at the particular temperature of $55 \pm 0.05^{\circ}\text{C}$ (used here).
- (v) decrease in the exponent n , of $[S_o]$ in the expression $R_p \propto [S_o]^n$ with decrease in initiator concentration.

The different values obtained for the limiting viscosity and Huggins' constant from the viscosity study show that;

(i) low vinyl acetate concentration with high $[S_0]$ of (SLS) at a given initiator concentration give polyvinyl acetate samples with high $[\eta]$ values.

(ii) polyvinyl acetate samples of different molecular parameters, as shown from the values of Huggins' constant, are produced at different times of polymerisation using different monomer, emulsifier and initiator concentrations.

RECOMMENDATION

More work should however be done on the emulsion polymerisation of vinyl acetate below the critical micelle concentration of (SLS) using higher monomer concentrations than investigated in this work. The effect of these monomer concentrations and other parameters should be studied in the characterisation of the polymer samples. The results in the present study suggest that when the monomer concentration of $[\text{monomer}]/[\text{H}_2\text{O}]$ ratio is sufficiently high, no polymerisation might be expected, or the induction time for polymerisation might be unusually long.

REFERENCES

1. Billmeyer, F.W., "Textbook of Polymer Science,"
Second Edition, John Wiley, New York, 1972.
2. Cowie, J.M.G., "Polymers; Chemistry and Physics
of Modern Materials", First Edition,
Billing & Sons Ltd., Great Britain, 1973.
3. Brydson, J.A., "Plastic Materials", Third
Edition, Newnes - Butterworths, London, 1975.
4. Rodriguez, F., "Principles of Polymer Systems,"
First Edition, McGraw-Hill Inc., New York, 1970.
5. O'Donnel, J.T., J. Polymer Sci., 1956, 28, 171
6. Bikales, N.M., "Encyclopedia of Poly. Sci., and
Tech., see "Emulsion Polymerisation", 1966, 5,
806, J. Wiley & Sons., New York.
7. Harkins, W.D., J. Am. Chem., Soc., 1947, 69,
1428.
8. Harkins, W.D., J. Poly. Sci., 1950, 5, 217.
9. Smith, W.V., J. Amer. Chem. Soc., 1948, 70,
3695.
10. Smith, W.V. and Ewart, R.H., J. Chem., Phys.,
1948, 16, 592.
11. Haward, R.N., J. Polym. Sci., 1949, 4, 273.
12. French, D.M., J. Poly. Sci., 1958, 32, 395.

13. Okamura, S. and Motoyama, T., J. Poly. Sci., 1962, 58, 221.
14. Napper, D.H., and Parts, A. G., J. Polym. Sci., 1962, 61, 113.
15. Priest, W.J., J. Phys. Chem., 1952, 56, 1077.
16. Napper, D.H. and Alexander, A.E., J. Poly. Sci., 1962, 61, 127.
17. Bikales, N.M., "Encyclopedia of Polym. Sci., and Tech." see "Polymerisation Procedures, Laboratory," 1966, 11, 304, J. Wiley, & Sons., New York.
18. Harriot, P., J. Poly. Sci., 1971, 9, A-1, 1153.
19. Baxendale, J.H. et al., Trans. Faraday. Soc., 1946, 42, 669.
20. French, D.M., J. Polym. Sci., 1958, 32, 395.
21. Lenka, S. et al. J. Poly. Sci., 1982, 20, 587.
22. Odian, G., "Principles of Polymerisation." First Edition, McGraw-Hill Inc., New York, 1970.
23. Slade, P.E. Jr., "Polymer Molecular Weights, Part II.," First Edition, Marcel Dekker Inc., U.S.A., 1975.

APPENDIX 1

Polymerisations with 0.25 g.dm^{-3} (SLS) and
 1.50 g.dm^{-3} ($\text{K}_2\text{S}_2\text{O}_8$).

Time of polymeri- sation (mins.)	Monomer concentration (g.dm^{-3}) of mixture			
	0.931	1.455	2.095	2.851
	(% Conversion)			
20	12.16	7.53	10.75	0.36
30	26.70	16.91	20.54	9.40
35	30.14	22.71	24.32	13.54
40	35.96	27.27	29.06	17.44
45	41.63	32.38	32.54	20.71
50	45.39	40.23	39.42	24.45

APPENDIX 2

Polymerisations with 2.25 g.dm^{-3} (SLS) and
 1.50 g.dm^{-3} ($\text{K}_2\text{S}_2\text{O}_8$).

Time of polymeri- sation (mins.)	Monomer concentration (g.dm^{-3}) of mixture			
	0.931	1.455	2.095	2.851
	(% Conversion)			
15	28.79	-	-	-
20	58.01	11.51	3.77	-
25	86.53	36.28	19.06	7.23
30	96.37	59.75	37.55	21.70
35	97.99	81.22	55.55	38.89
40	98.94	94.29	78.92	54.57
45	99.14	94.41	94.30	75.14
50	-	96.55	97.77	93.84

APPENDIX 3

Polymerisations with 0.25 g.dm^{-3} (SLS)
and 1.00 g.dm^{-3} ($\text{K}_2\text{S}_2\text{O}_8$).

Time of polymerisation (mins.)	Monomer concentration (g.dm^{-3}) of mixture			
	0.931	1.455	2.095	2.851
	(% Conversion)			
30	11.99	9.90	8.46	-
40	25.05	20.16	16.14	9.85
50	41.05	32.77	24.92	14.12
60	69.41	48.17	34.45	22.08
70	81.91	68.91	46.13	28.58
80	-	-	56.36	36.47
90	-	-	-	48.91

APPENDIX 4

Polymerisations with 2.25 g.dm^{-3} (SLS) and
 1.00 g.dm^{-3} ($\text{K}_2\text{S}_2\text{O}_8$).

Time of polymerisation (mins.)	Monomer concentration (g.dm^{-3}) of mixture			
	0.931	1.455	2.095	2.851
	(% Conversion)			
20	36.87	27.23	-	-
30	82.83	67.14	26.63	9.02
40	93.38	96.25	53.99	37.93
50	93.78	98.70	84.91	60.88
60	94.66	99.04	87.90	92.76
70	96.75	99.60	91.18	99.51
80	-	-	-	99.75

APPENDIX 5

Variation of $[\eta]$ with emulsifier concentration
 using 1.50 g.dm^{-3} ($\text{K}_2\text{S}_2\text{O}_8$).

Emulsifier concentration (g.dm^{-3})	Monomer concentration (g.dm^{-3}) of mixture	
	0.931	2.851
	$[\eta] \text{ g}^{-1} \text{ dl}$	
0.25	1.16	0.95
0.50	0.96	0.84
1.50	1.25	1.12
2.25	1.01	0.82