EMULSION POLYMERIZATION OF VINYL CHLORIDE

by

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ABSTRACT

The solubility of vinyl chloride monomer (VCM) in water was determined for temperatures ranging from 0 to 75^{0} C and for pressures from 1 to 6 atmospheres. VCM may be considered fairly soluble in water. The VCM solubility in potassium laurate solutions at 50^{0} C was determined for the range 0.1 to 15.0 g/l of the soap and for pressures from 1 to 6 atmospheres. It was noted that some solubilization of VCM occured even below the critical micelle concentration (cmc) of the soap and that the VCM solubility appeared to approach a limiting maximum solubility at high soap concentrations. It was observed that the solubilization effect was essentially independent of pressure.

The diffusivity of VCM in water at temperatures from 0 to 75^{0} C was also determined. In addition, VCM diffusivity in potassium laurate solutions was measured in the soap concentration range of 0.1 to 15.0 g/l and at atmospheric pressure. With increasing soap concentration there was a large decrease in VCM diffusivity when compared to that in pure water.

The cmc of potassium laurate was determined in a number of ways, the most significant of which were by means of viscosity and density measurements. The micelle number average molecular weight ($\overline{M}_N$) was also determined to be about 23,100 and the corresponding weight average molecular weight ($\overline{M}_W$) was about 33,600, yielding a polydispersity of 1.45. Hence, the number of molecules of soap per micelle was estimated to be about 120.

A polymerization reactor was designed for VCM emulsion polymerization studies. It was constructed of glass, teflon and aluminum and was capable of withstanding pressures up to 8 atmospheres. It was essentially a small batch reactor, 100 ml of emulsion were used, and auxiliary equipment was designed to permit the reactor to be operated as a calorimeter to obtain polymerization rate data.

The molecular weights of PVC polymerized in the reactor using a standard emulsion recipe appeared to be constant throughout the reaction up to a conversion of about 50%. Above this conversion the molecular weights increased rapidly. A large number of experiments were conducted varying monomer concentration as well as emulsifier and initiator concentrations. The $\overline{M}_N$ of the PVC product appeared to be directly proportional to the VCM concentration in the latex. In contrast, molecular weights appeared to be essentially independent of the initiator concentration for otherwise comparable conditions. At low emulsifier concentrations, both $\overline{M}_N$ and $\overline{M}_W$ varied as the 1/3 power of the emulsifier concentration. At high concentrations, the molecular weights became essentially independent of the emulsifier concentration. For some experiments conducted at different temperatures, both $\overline{M}_N$ and $\overline{M}_W$ appeared to increase as the reaction temperature decreased.

Samples of the latex were withdrawn from the micro-reactor during the course of the reaction to determine the rate of production and properties of the product accumulated. Calorimetric determinations for the reaction provided an essentially independent measure of the product rates, which were compared with those determined by analysis of latex samples. While for low PVC concentrations in the latex both methods gave similar reaction rates, the deviation between the rates became significant for increasing latex concentrations. The average heat of polymerization was determined to be 27.8 Kcal/mole ± 0.8 Kcal/mole. The fraction of

particles containing a radical was calculated to be much less than unity, supporting a reaction mechanism of rapid desorption and re-absorption of radicals into the particles, as proposed by Ugelstad et al (1970).

The relationship between the reaction rates and the monomer, emulsifier and initiator concentrations was determined and can be summarized by the following equation:

$$\bar{r}_p \; \alpha \; [M]^3 \; [E]^{\frac{1}{2}} \; [I]^{\frac{1}{2}}$$

This equation would be applicable for low conversions of less than 30%.

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NOMENCLATURE

a	constants in Equations 12 and 13	
b	constants in Equations 12 and 13	
c	potassium laurate concentration	g/l
cmc	critical micelle concentration	g/l
D	diffusivity	cm^2/sec
D_{12}	diffusivity of VCM in water by Equations 1 and 2	cm^2/sec
[E]	emulsifier concentration	g/l
E_a	energy of activation in Equation 15	Kcal/mole
f	initiator efficiency factor in Equation 10	
H	light scattering constant	
[I]	initiator concentration	g/l
k_d'	specific desorption rate constant in Equation 10	
k_i	initiator decomposition rate constant in Equation 10	
k_p	propogation rate constant in Equation 10	l/mole-hr
k_{tp}	termination rate constant in Equation 10	l/mole-hr
[M]	monomer concentration	g/l
m_o	monomer molecular weight	
$\overline{M}_N$	number average molecular weight	
M_p	monomer concentration in Equation 10	
$\overline{M}_W$	weight average molecular weight	
N	total number of polymer particles in Equation 10	#/liter water
N_A	Avogadro's number	
$\overline{n}$	average number of radicals per polymer particle	
pH	pH	

PVC	poly(vinyl chloride)	
R	gas constant	
r_i	rate of formation of radicals	number/l water-minute
r_p	rate of polymerization	gPVC/l water-minute
T	temperature	^oK
THF	tetrahydrofuran	
V_1	molar volume of VCM at its normal boiling point in Equations 1 and 2	l/g mole
VCM	vinyl chloride monomer	
V_p	total volume of monomer-swollen polymer particles in Equation 10	
x	solubility of VCM	mole fraction
X	conversion of VCM to PVC	
X_C	conversion above which there is no free VCM	

Greek Letters:

σ	surface tension	dynes/cm
π	osmotic pressure	cm of solution
κ	conductivity	mhos
Λ	specific conductivity	
Δn	refractive index increment	
τ	turbidity	
ρ	solution density	g/ml
η	solution viscosity	centipoises
η_{sp}	specific viscosity $(\eta - \eta_W)/\eta_W$	
μ_2	viscosity of water in Equations 1 and 2	centipoises

Subscripts:

m	micelle
s	soap
w	water

INTRODUCTION AND PREVIOUS WORK

The process for emulsion polymerization of vinyl chloride monomer (VCM) to produce polyvinyl chloride (PVC) has been used for decades, yet information concerning the monomer and the reaction mechanism has only recently begun to appear in the chemical literature. The present work was performed to add to the knowledge of VCM emulsion polymerization.

The aim of this work was to engage in a systematic study of certain variables affecting the emulsion polymerization of VCM. This investigation was commenced with a study of VCM properties such as its diffusivity in water and its solubility in water at atmospheric and higher pressures. The next phase of this investigation was the determination of aqueous potassium laurate solution properties and the effect of an increased soap concentration on the diffusivity and solubility of VCM. This study culminated with the design and operation of a polymerization reactor. Utilized as a batch reactor, the effect of the process variables - temperature, monomer concentration, emulsifier concentration and initiator concentration - upon the polymerization rate and PVC molecular weight was obtained. Operated as a calorimetric reactor, polymerization initial rate data were obtained and analyzed to obtain an insight into the polymerization kinetics of VCM.

While the solubilities of VCM in many non-aqueous solvents have been reported (Machacek and Lanikova, 1954; Saxhinov, 1962; and Hannaert et al, 1967) only a few values of VCM solubility in water have been published. Lazor (1959) quoted a value of

0.09 mole % at 20° C. Leonard (1971), quoting a Dow Chemical bulletin, reported a solubility of 0.11 gVCM/100 g water at 25° C. Peggion (1964) published a value of 0.6 ml VCM/ml water at 50° C and the saturation pressure. Utilizing his value of the saturation pressure and assuming ideal gas conditions, this corresponded to 0.00284 mole fraction. Gerrens (1967) and Vidotto (1970) reported a solubility of 1.0 g VCM/100 g water at 50° C and the saturation pressure; a mole fraction of 0.00291. Neither Lazor, Leonard, Peggion, Gerrens nor Vidotto mentioned any experimental details of the solubility determinations. Zampachova (1962 b) utilizing a static method (Zampachova, 1962 a), reported a value of 0.00280 mole fraction of VCM at 50°C and the saturation pressure of 7.8 atmospheres.

VCM, a polar compound was found to exhibit a 12% positive deviation from Henry's law at 7.8 atmospheres and 50° C compared to the solubility at 1 atmosphere. For nonpolar and even slightly polar gases it has been found that the solubilities of all gases (for a partial pressure of 1 atmosphere) appear to approach a constant molar concentration as the solvent critical temperature is approached (Hayduk and Buckley, 1971; Hayduk and Casteneda, 1973). This behaviour has been tested for gas solubilities in water, including that for vinyl chloride (Hayduk and Laudie, 1973), and the extrapolated solubility was found to be 1.40×10^{-4} at the critical temperature of water of 374.15° C. The solubility of VCM in water is large when compared to the solubility of other monomers. For example, it is about ten times that of ethylene (Bradbury et al, 1952).

To study the effect of a variation in monomer concentration upon the molecular weight of the PVC product, polymerization reactions were performed at pressures below the saturation pressure but at 50^{o} C. The VCM concentration in water and emulsifier solutions was determined by a static gas absorption method at pressures of 1, 3.06 and 6.12 atmospheres. These solubilities were then interpolated for the emulsifier concentration to determine the VCM concentration in the emulsion, the VCM concentration being changed by varying the operating pressure. It has been suggested by Peggion (1964) that the kinetics of VCM polymerization may be partly explained by taking into consideration the high solubility of VCM in water. Thus the latter experiments were considered useful in studying the polymerization kinetics.

Solubilities of VCM in water were determined at 0, 25, 50 and 75^{o} C and for each temperature, pressures from 1 to 6 atmospheres. Solubilities of VCM were also determined in potassium laurate solutions at 25, 50 and 75^{o} C and also for pressures from 1 to 6 atmospheres. The potassium laurate concentration in water was varied from 0.1 to 15.0 g/l for the above mentioned measurements.

Although the diffusivity of VCM in water has not been reported in the literature, it is important to the study of emulsion polymerization kinetics since monomer must diffuse from the monomer droplets to the reacting polymer particles. The mechanism of diffusion in liquids is only partly understood so that semi-empirical correlations, based on known physical properties of the substance under consideration, are commonly used to predict diffusion coefficients for gas-liquid systems. The most useful for prediction of diffusivities in water has been the Othmer-Thakar (1953) correlation.

$$D_{12} = \frac{14.0 \times 10^{-5}}{\mu_2^{1.1} V_1^{0.6}} \qquad (1)$$

The correlation was based on data published prior to 1950. A recent publication (Hayduk and Laudie, 1974) specifically considered the diffusivities of non-electrolytes in water. The correlation, prepared as part of this research, was determined using data published after 1950 exclusively.

$$D_{12} = \frac{13.26 \times 10^{-5}}{\mu_2^{1.14} V_1^{0.589}} \qquad (2)$$

Both correlations yield similar, but not identical, results. It was determined that an average absolute error of 6% could be expected with either correlation.

An emulsifier is used in emulsion polymerization because it is capable of forming micelles which act as the nuclei for reacting polymer particles. Micelles are formed when the soap concentration is greater than a minimum value referred to as the critical micelle concentration (cmc). In order to determine the cmc value, experiments were performed on the physical and optical properties of potassium laurate emulsifier solutions at concentrations varying from 0.1 to 15.0 g/l. In the formation of micelles, the soap molecules have been considered to align themselves in a double laminar layer as shown in Figure 1. VCM molecules tend to aggregate in the middle

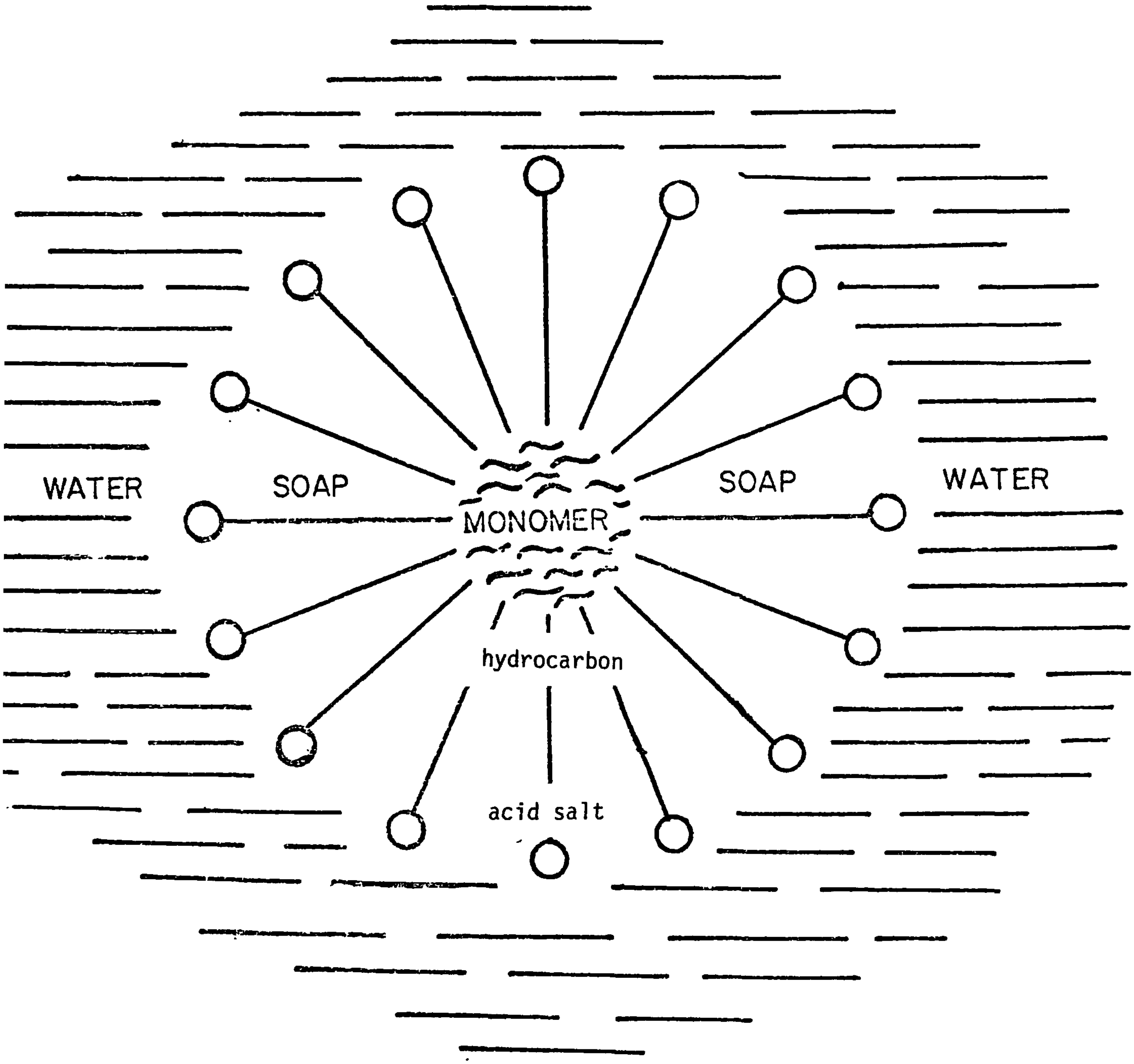


Figure 1 - Diagram of micelle with solubilized monomer.

of the micelles which contain the hydrocarbon ends of the soap molecules. Because the absorption results in the solubility of monomer in soap solutions being greater than the solubility in pure water, the phenomenon is called solubilization. From the analysis of the VCM solubilization measurements, it was determined that the optimum operating conditions for the emulsion polymerization experiments were in the concentration range of potassium laurate from 10 to 20 g/l.

An important step in the polymerization process is the transfer of monomer molecules by diffusion from free emulsified monomer droplets through the aqueous phase into the soap micelles where most of the nuclei are initiated (Harkins 1947). In this case, it has been suggested by Brooks (1971) that the reaction rate may be controlled by the diffusion rate of monomer. Of the material published on the subject of diffusivity in soap solutions, it has been determined by Stearns and Harkins (1946) and Harkins and Stearns (1946) that the diffusivity of a hydrocarbon decreases with increasing soap concentration. An analogy may be found in the biological sciences where the diffusivity of oxygen in blood was found to decrease with increasing concentration of red blood cells. According to Hershey and Karhan (1968) and Goldstick and Fatt (1970), the cells may be considered to absorb the oxygen and also to hinder the diffusion of oxygen through the heterogeneous solution. In this work, experiments were performed to determine the effect of a variation in emulsifier concentration on the diffusivity of VCM.

Before commenting on the actual emulsion system, an explanation of VCM free radical polymerization will be presented. For free radical polymerization, the initial ingredients are an initiator, I_2, and the monomer, CH_2CHCl. The initiator decomposes to produce a free radical, $R^{\cdot}$:

$$I_2 \xrightarrow{k_d} 2R^{\cdot}$$

The initiator, potassium persulfate, was chosen because it thermally decomposes readily at 50° C. During initiation a free radical interacts with a monomer molecule to initiate a growing polymer particle

$$R^{\cdot} + CH_2CHCl \xrightarrow{k_i} RCH_2C^{\cdot}HCl$$

This growing polymer particle interacts with more monomer and hence propagates the growing polymer particle

$$RCH_2C^{\cdot}HCl + CH_2CHCl \xrightarrow{k_p} RCH_2CHClCH_2C^{\cdot}HCl$$

This growing polymer particle will eventually terminate to form PVC. Because growing polymer particles are kept separate in an emulsion system, termination can occur by radical-particle termination

$$R - [CH_2CHCl]_n - CH_2C^{\cdot}HCL + R^{\cdot} \xrightarrow{k_{tc}} PVC$$

or by chain transfer to monomer

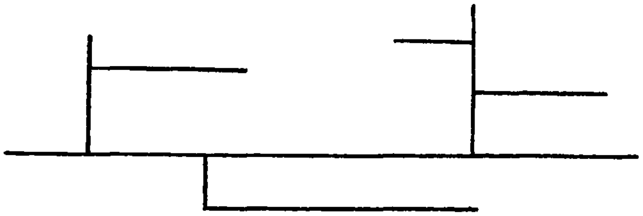
$$R - [CH_2CHCl]_n - CH_2C^{\cdot}HCl + CH_2CHCl \xrightarrow{k_{fm}} PVC + CH_2C^{\cdot}HCl$$

For VCM polymerization, chain transfer to monomer has been shown to be the major termination reaction by Friis and Hamielec (1975) and Ugelstad et al (1969).

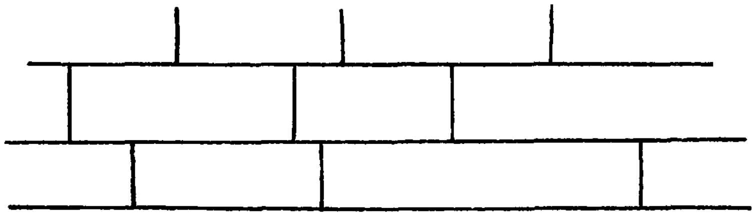
As the monomer concentration decreases with an increasing conversion, branching and cross-linking may occur. Effectively, a site for propagation can occur along the polymer chain as follows:

$$-CH_2CHClCH_2CHClCH_2CHCL- + R^{\cdot} \longrightarrow -CH_2CHClCH_2C^{\cdot}ClCH_2CHCl- + RH$$

New monomer can be added in the middle of the chain to form branching, with a schematic structure as follows:



In addition, for almost complete conversion of monomer, cross-linking may occur between a growing polymer particle and PVC to give a schematic structure as follows:



The process in which polymer molecules become bound together into essentially giant polymer molecules is known as gel formation. This occurs at very high conversions. It is possible, that the growing polymer chain will coil within the particle. This chain entanglement produces a compact PVC molecule rather than an elongated molecule. The physical compaction of the molecule can effect the end uses of the polymer produced.

It should be noted that all polymerization experiments reported herewithin, with one exception, were performed to an overall VCM conversion of approximately 30%. At this low conversion, little branching, cross-linking or chain entanglement are expected to occur.

The single exception was a set of experiments performed to determine the entire molecular weight versus conversion history of a VCM polymerization.

At this point it is convenient to define the molecular weights used in this study. The number average molecular weight is defined as

$$\overline{M}_N = \frac{\Sigma n_i M_i}{\Sigma M_i} \qquad (3)$$

and was determined from osmotic pressure measurements. The weight average molecular weight is defined as

$$\overline{M}_W = \frac{\Sigma n_i M_i^2}{\Sigma n_i M_i} \qquad (4)$$

and was determined from viscosity measurements by the use of the Freeman-Manning correlation (1964)

$$[\eta] = 1.63 \times 10^{-5} \, (\overline{M}_W)^{0.766} \qquad (5)$$

This has been confirmed by Bromfield (1973) to apply for PVC of low polydispersity ($\sigma \leqslant 2$). As polydispersity and branching increases, the index value (0.766) would be expected to decrease. Since the polydispersity of the PVC produced in the present work is low, the Freeman-Manning correlation is expected to be a reliable function from which to obtain $\overline{M}_W$.

Emulsion polymerization systems are thought to consist of a dispersion of soap micelles, polymer particles and monomer droplets in an aqueous medium as shown in Figure 2. Harkins (1947, 1950)

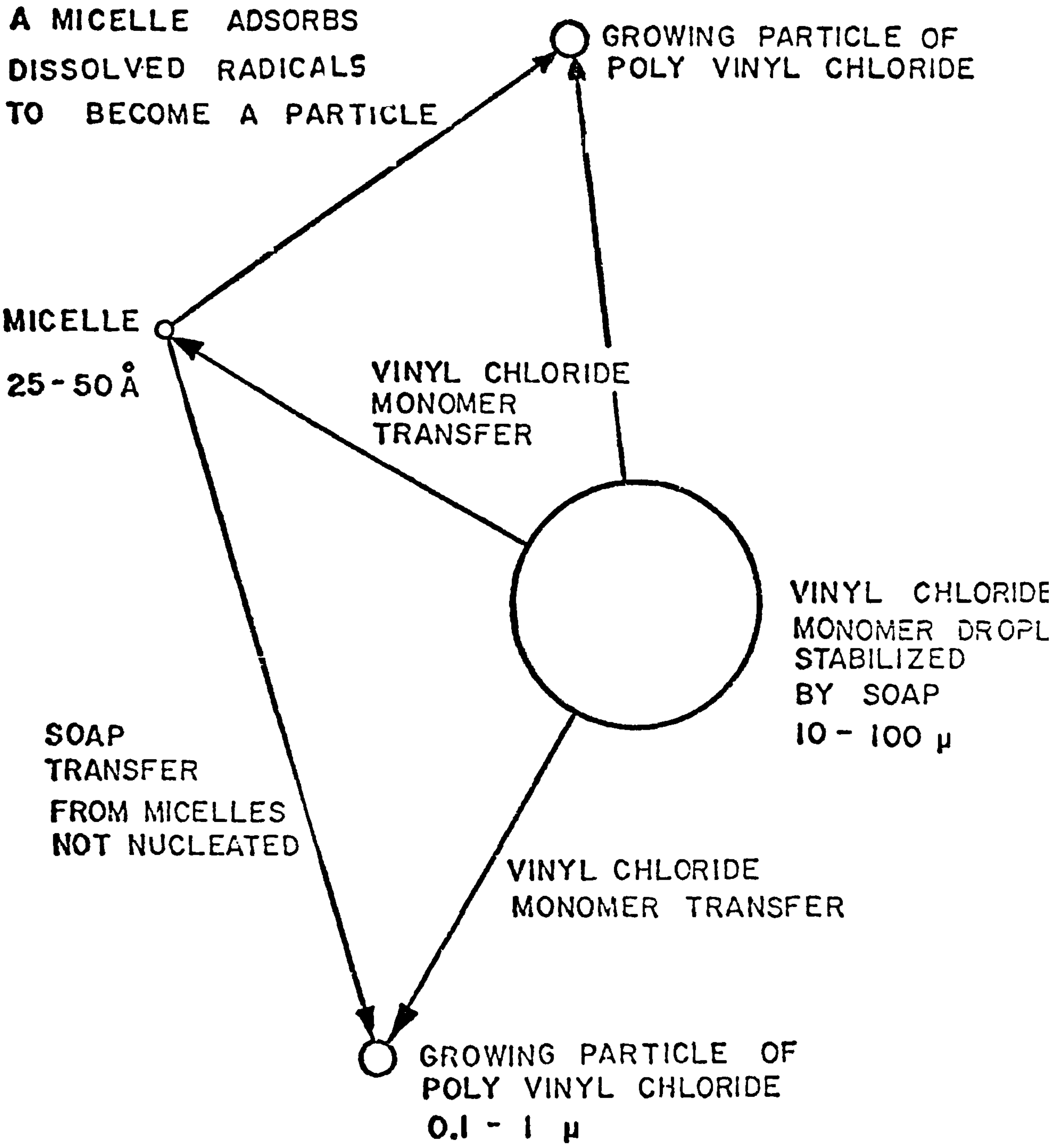


Figure 2 - Emulsion polymerization process.

suggested that the micelles which are swollen with monomer, serve as a locus for particle nucleation and subsequent growth. The micelles also contribute soap to help stabilize growing polymer particles in the later stages of growth. Micelles, which contain no polymer are eventually absorbed by other growing particles. The monomer droplets serve as reservoirs and supply monomer by diffusion to growing particles.

Gardon (1968 a,b,c,d,e,f) divided the batch isothermal emulsion polymerization process into three intervals. It was suggested that initially the monomer can be found in three locations, dissolved in water, absorbed by micelles, and dispersed as a separate phase in droplets. At the beginning of the reaction (interval 1), new latex particles are formed and their number increases. These latex particles absorb monomer and are swollen by it. After a certain number of particles are formed, their number remains constant in intervals 2 and 3. Interval 2 begins when all soap micelles have either become growing particles or have been absorbed by growing particles. In intervals 1 and 2 the conversion is still sufficiently low so that some unreacted monomer is present in the form of droplets. In interval 3 the conversion is sufficiently high so that all monomer droplets have disappeared; hence the monomer is present only in monomer-swollen particles or dissolved in the water. In this latter stage cross-links and branches are formed in increasing numbers.

The emulsion polymerization of VCM has been the subject of many investigations which have appeared in the literature, all of which have agreed that VCM polymerization does not follow the general Smith-Ewart mechanism for emulsion polymerization. The Smith-Ewart theory of emulsion polymerization assumed that the polymer is soluble in its own monomer, that the polymerization takes place execusively in the interior of the micelles, that any polymer particle will be actively growing half of the time and dormant the other half of the time, and the total number of particles is small, less than 10^{18}. In effect, the Smith-Ewart polymerization theory utilizes the following relationships:

$$r_p \; \alpha \; [N][I]^{2/5} \; [E]^{3/5} \tag{6}$$

$$N \; \alpha \; [I]^{2/5} \; [E]^{3/5} \tag{7}$$

It has been noted that VCM polymerization does not follow these relationships. The difference has been attributed to water-phase polymerization (Giskehaug, 1966), degradative chain transfer (Gerrens et al, 1965) or to the high water solubility of VCM and the low solubility of PVC in VCM (Peggion et al, 1964). It has been observed by the above mentioned authors that with the emulsion polymerization of VCM the number of latex particles, N, varies strongly with the emulsifier concentration, E, and is independent of initiator concentration, I. It has also been observed that the rate of reaction, r_p, increases with increasing initiator concentration and that conversion is autocatalytic. In these respects, VCM emulsion polymerization is similar to VCM bulk polymerization.

VCM emulsion polymerization has been noted to follow the relationships of Medvedev-Sheinker (Odian, 1970) as follows:

$$r_p \propto [N]^{1/5} [E]^{\frac{1}{2}} [I]^{\frac{1}{2}} \tag{8}$$

$$N \propto [E]^3 [I]^0 \tag{9}$$

This theory requires that the polymer be insoluble in its own monomer, that the site of reaction is the surface of the particles, the number of particles be large ($>10^{18}$), and the number of radicals per particle is much less than unity ($<10^{-2}$).

On the basis of recent studies of VCM emulsion polymerization, Ugelstad et al (1967,1969,1970) proposed a model based on rapid absorption and desorption of radicals by the growing polymer particles. Assuming that the desorption rate constant was a function of the polymer particle radius, the average number of radicals per polymer particle was small (10^{-4}), and the rate of desorption of radicals from a particle was proportional to the total number of radicals in the particle, Ugelstad and Mork (1970) proposed the following equation supported by experimental measurements:

$$r_p = \frac{k_{p.} [M]}{N_A} \; 2(fk_i [I])^{\frac{1}{2}} \left\{ \frac{V_p N_A^{\;2}}{2k_{tp}} + \frac{N^{1/3} \; V_p^{\;2/3}}{2k'_d} \right\}^{\frac{1}{2}} \tag{10}$$

Details of the derivation of Equation 10 may be found in Ugelstad and Mork (1970). The important features of Equation 10 that relate to this work are that the rate of polymerization is proportional to the square root of the initiator concentration, $[I]^{\frac{1}{2}}$, provided that the initiator is 100% efficient, and to the 1/6 power of the particle concentration,

$N^{1/6}$ for small particles, that is, $V_p N_A^2/2k_p << N^{1/3} V_p^{2/3}/2k_d'$. Friis and Hamielec (1974) have quoted values of the power of N to be between 0.05 and 0.20. The dependence of rate of reaction upon emulsifier concentration is not explicitly stated but can be determined by assuming a relationship between N and the emulsifier concentration as yet undetermined. Similarly, the dependence of the rate upon monomer concentration requires a knowledge of the relationship between the saturated monomer and emulsifier concentrations which could be made from solubility measurements.

Friis and Hamielec (1974) further interpreted Equation 10 as indicating that the polymerization rate should increase in the interval $0 < X < X_c$ where X_c is the conversion at which the separate monomer phase disappears. X_c was determined to be about 0.7. The polymerization was considered to be autocatalytic up to the conversion X_c. Presumably a maximum in the rate is reached at X_c and following that, the rate decreases. This is similar to bulk polymerization as described by Horie et al (1968).

In this case, the rate constant, k_p, is not considered to be truly constant but instead to be affected both by the diffusion rate for the monomer and for the polymer radicals. At lower conversions, k_p, is dependent upon the radical concentration; at higher conversions it is dependent upon the diffusion of monomer so that the reaction type changes to one which is diffusion controlled. As the reaction proceeds toward completion, the viscosity of the latex increases, while the effective viscosity inside the particles is also very high (Brooks, 1971). Hence the reduced monomer diffusion rate has the effect of reducing the reaction rate.

Friis and Hamielec (1974) also determined the molecular weights of the PVC product. Their paper may be consulted for mathematical details. It was determined that the number average molecular weights ($\overline{M}_N$) and the weight average molecular weights ($\overline{M}_W$) were constant up to the conversion X_c. Beyond that conversion, both $\overline{M}_N$ and $\overline{M}_W$ as well as the degree of branching increased rapidly. Also, the molecular weight of the polymer produced was considered to be independent of particle number, N, and particle size, as well as initiator concentration.

In this work, the effects of variations of monomer, initiator (potassium persulfate) and emulsifier (potassium laurate) concentration upon the PVC molecular weights were experimentally determined. Because of the corrosive nature of VCM, a reactor constructed of glass, aluminum and teflon was designed. Polymerizations were conducted at 50^o C and the VCM saturation pressure of 7.8 atmospheres. Auxiliary equipment for temperature control for the reactor was similar to that used by Anderson (1966, 1969) for calorimetric studies of the emulsion polymerization of styrene. Polymerization experiments were performed at 50^o C with VCM concentration varying from 1 atmosphere up to the saturation pressure.

Initiator concentration was varied from 0.7 to 11 g/l. Emulsifier concentration was varied from 0.3 to 24 g/l, the lower value being below the cmc of potassium laurate. Some polymerizations were also performed at 25, 30 and 40^o C, and some calorimetric experiments were performed at 50^oC. Analyses were performed by osmometry, and viscometry, to determine $\overline{M}_N$, and $\overline{M}_W$, respectively. As a result of these experiments, a greater insight into the variables affecting the emulsion polymerization of VCM has been achieved.

PROPERTIES OF MATERIALS

Polymerization grade VCM having a minimum specified purity of 99.9 mole %, was purchased from Matheson of Canada Limited. VCM was shipped as a liquid containing a phenolic inhibitor. This inhibitor was removed by scrubbing the gaseous VCM at 20 psig with a saturated sodium hydroxide solution. Subsequent drying removed vaporized water. The gaseous VCM was condensed again at 0^{o} C by means of ice water circulating around the VCM collection tube. Some of the physical properties of VCM found useful in this work may be found in Table 1. Some of these properties were taken from the literature of Dana et al (1927). The thermodynamic properties of VCM have been determined by Banerjee (1958).

Potassium laurate emulsifier, having a specified purity of 95-98% was purchased from K and K Laboratories. The initiator used was potassium persulfate of 99.5% purity. To prevent the coagulation of the emulsion latex, potassium hydroxide was added to keep the pH of the emulsion between 10 and 10.5. According to Enomoto (1960), during polymerization some of the VCM is split into HCl^{+} and $CHCH^{-}$ and the higher the conversion, the more HCl that is formed. At 30% conversion, sufficient HCl would have formed to lower the emulsion pH to 7. In a neutral or acid medium, the emulsion latex would coagulate. To compensate for the HCl produced, potassium bicarbonate was added as a buffering agent. These latter three chemicals were purchased from Fisher Scientific. All solutions were made using distilled water, boiled to remove traces of carbon dioxide.

The basic polymerization recipe used in this research was:

VCM (liquid)	50-60 ml
Water	55 ml
Potassium laurate	14.55 g/l mixture
Potassium persulfate	3.64 g/l mixture
Potassium bicarbonate	1.82 g/l mixture
Potassium hydroxide	pH 10-10.5

The potassium laurate and potassium persulfate concentrations were varied by factors of two about this standard recipe. The ratio VCM/Water was kept close to 1/1 so as to approximate the industrial recipes given by Hardie (1966) and Leonard (1971).

The molecular weights of PVC were determined from PVC solution osmotic pressure and viscosity. The solvent used for dissolving the PVC samples was tetrahydrofuran (THF). The procedures used to obtain $\overline{M}_N$ and $\overline{M}_W$ were the same as those described by Bromfield (1973) (Appendix I).

TABLE 1

Properties of Vinyl Chloride Monomer

Temp °C	Vapor Pressure Atm.	Liquid Density g/ml	Liquid Heat Capacity cal/g °C	Vapor Heat Capacity cal/g °C	Latent Heat of Vaporization cal/g
-13.6	1.00	0.9697	0.284	0.184	78.2
0	1.72	0.9471	0.298	0.190	76.0
25	3.90	0.9014	0.329	0.203	71.2
50	7.83	0.8517	0.360	0.215	66.4
75	13.87	0.7974	0.391	0.228	61.6
100	22.82	0.7401	0.442	0.240	56.8

Molecular weight	62.50
Critical temperature	156.5 °C
Critical pressure	55.05 atmospheres
Heat of polymerization	-25.3 ± 0.5 Kcal/mole (Leonard, 1971)

EXPERIMENTAL EQUIPMENT AND PROCEDURE

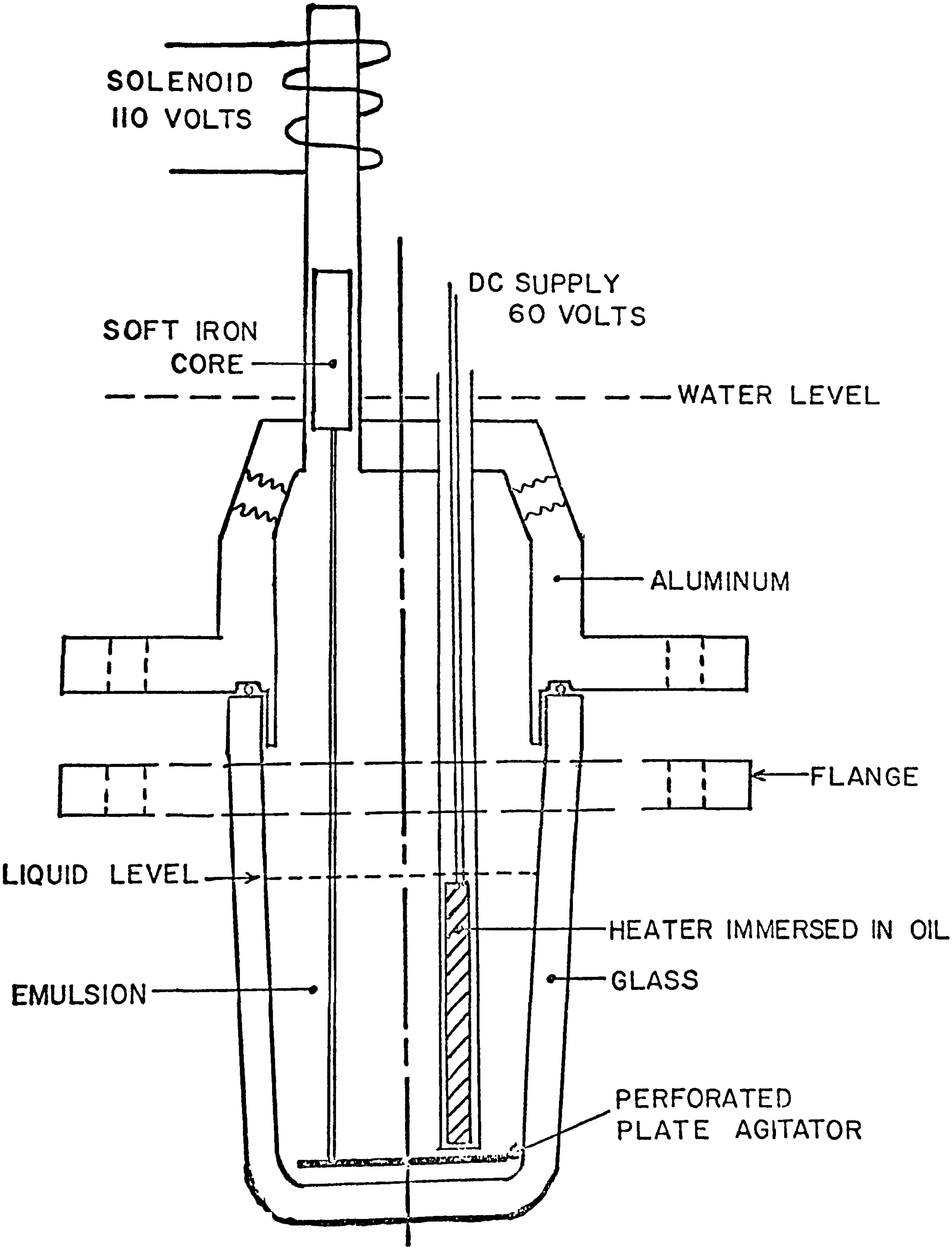
The solubility apparatus used to determine the solubility of VCM in water and in soap solutions at atmospheric pressure was essentially of the same design as that described by Buckley (1971). It required measuring the dry gas needed to saturate a stream of degassed liquid flowing down an absorption spiral at a known flow rate. Equipment details and operating procedures have been published by Hayduk and Buckley (1971).

The solubility apparatus used to determine the solubility of VCM in water and in soap solutions above atmospheric pressure was especially designed for this work. It was based on the measurement of the gas volume required to saturate a known amount of degassed liquid, at constant pressure. For the solubility calculations, due consideration was given to the compressibility of VCM, which was measured by means of the solubility apparatus modified for this purpose. The compressibility measurements are included for reference in Appendix A. Equipment details and the operating procedure have been published by Hayduk and Laudie (1974).

VCM diffusivities in water and soap solutions were determined using equipment that was essentially identical to that described by Buckley (1971). Equipment details, operating procedure and the associated mathematical analysis for the diffusivity cells have been published by Malik and Hayduk (1968) and Hayduk and Buckley (1972).

The physical properties of the soap solutions at 50°C were determined with a variety of laboratory devices. Solution viscosities were determined with calibrated Cannon-Fenske viscometry tubes. These were also used to measure the viscosities of the PVC solutions to determine $\overline{M}_W$. Solution densities were determined with an Anton Paar Model DMA 02C digital precision densitometer. The instrument utilized a vibrating reed, the frequency of which was a function of the density of the fluid in which it was immersed. The densitometer required calibration with two fluids of accurately known density, usually dried air and distilled water (Hayduk and Laudie, 1974). Electrical conductivities were measured with a Yellow Springs Instrument Company Model B conductivity meter. Solution surface tension was determined with a calibrated Precision Scientific tensionmeter. The solution pH was measured using a calibrated Corning Model 12 Research pH meter. The osmotic pressure of the soap solutions was determined with a Hewlett-Packard Model 501 Automatic Osmometer using an aqueous type B25 membrane. From the osmotic pressures, the micelle $\overline{M}_N$ was calculated. The osmometer was also used to determine the osmotic pressures of PVC solutions for the calculation of the polymer $\overline{M}_N$. Solution refractive indices were measured with a calibrated Brice-Phoenix differential refractometer. Solution turbidities were determined with a Brice-Phoenix Model 200 Light-Scattering Photometer. The refractive indices and turbidities were used to calculate the micelle $\overline{M}_W$. The same equipment was used with PVC solutions providing data for the calculation of polymer $\overline{M}_W$.

The polymerization reactor was specifically designed to carry out emulsion polymerization of vinyl chloride. Because of the high activity of VCM, the reactor construction materials were glass, aluminum, stainless steel and teflon. The main body of the reactor shown in Figure 3, consisted of a 2-inch diameter QVF glass end buttress, topped by a machined aluminum cover. The two pieces were bolted together using flanges, with an O-ring forming the seal. The reactor was tested and found capable of withstanding pressures up to 8 atmospheres. There were



Polymerization reactor details.

two teflon valves from O.H. John's Scientific, threaded into the aluminum top. These valves facilitated filling the reactor with the emulsion mixture, purging of the reactor, adding liquified VCM as well as initiator solution.

Agitation of the emulsion was performed by means of a stainless steel perforated plate agitator connected by a stainless steel rod to a soft iron core. This soft iron core, housed in a ¼-inch diameter stainless steel sheath, was moved up and down by means of an external solenoid connected to a timer operating at 1 cycle per second. Thus the agitator was essentially a churn with the force for the downward stroke provided by the weight of the plunger. Initial trial runs determined that this agitation rate was sufficient for forming and maintaining an emulsified mixture in the reactor. A ¼-inch diameter stainless steel thin-wall tube immersed in the emulsion, served as a heater sheath. A Sunbeam Type 24136 commercial heating element of about 330 ohms resistance was inserted in the sheath partially filled with oil to increase the heat transfer rate from heater to sheath. An additional 1/8-inch diameter stainless steel sample tube, capped by a third teflon valve, was fixed in the reactor head with its interior end located near the bottom of the reactor to obtain latex samples during polymerization. Provision was also made in the reactor top for the insertion of a thermistor probe and for a copper-constantan thermocouple.

The reactor itself was immersed in a vessel containing water at a constant temperature as shown in Figure 4. Water at 46^{0} C was pumped through a rotameter and into the bottom of the vessel. The water flowed up and around the reactor and overflowed back into the constant temperature

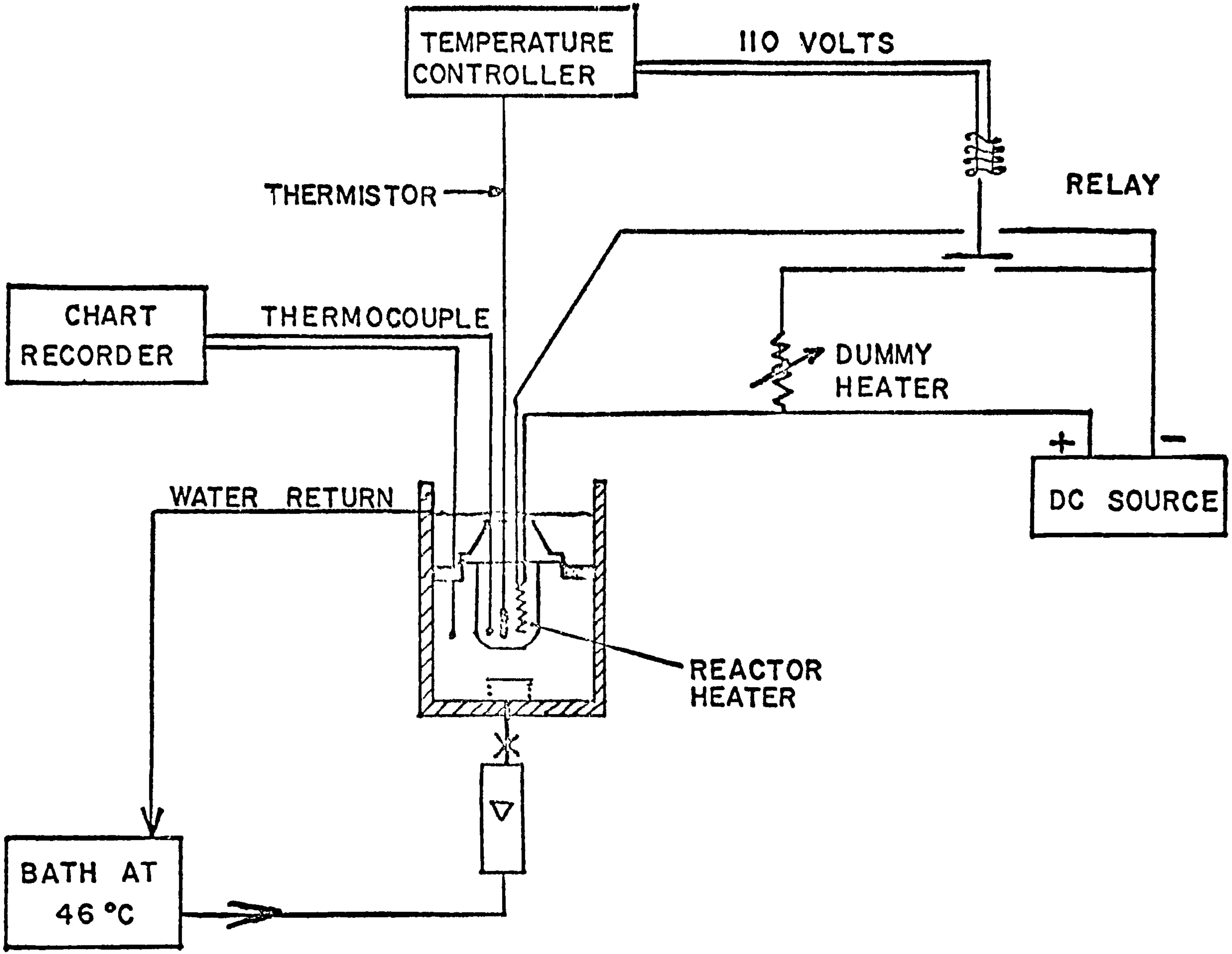
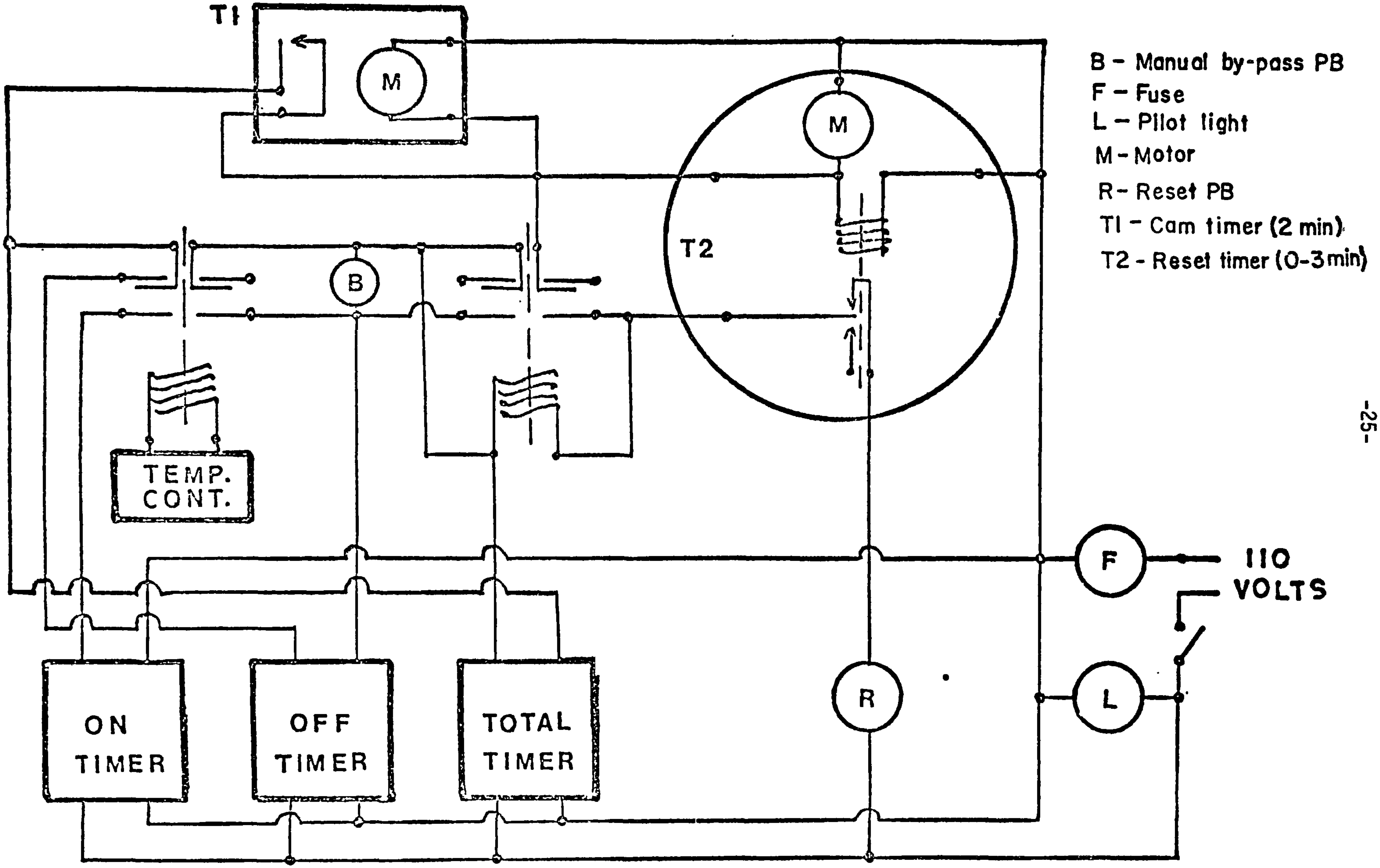


Figure 4 - Schematic of reactor temperature control circuit.

bath. This arrangement assured a constant external heat transfer coefficient at the reactor wall. The thermister probe was connected to a Bayley Model 245 ON-OFF temperature controller which was calibrated to a setpoint of 50^{o} C. The electrical output of the controller, which normally would have been connected to a heating element, was instead connected to the solenoid coil of a relay. When the solenoid coil was energized the relay connections were made so as to connect the internal heating to a 60 volt DC source. The DC source was in fact a rectifier and voltage regulating device purchased from Tygron Electronics. The combination of heat produced by the heater and by the reactor kept the reaction mixture exactly at 50^{o} C. When the controller was off, the DC current was directed through a dummy heating circuit which was balanced so as to have the same resistance as that of the internal heater. This arrangement prevented current surges in the heating element circuitry. The line was always fully loaded. In addition, a system of timing clocks was arranged to measure the internal heating element's "on" time and "off" time in 2-minute intervals. The circuit for the clocks was similar to that originally reported by Anderson (1966, 1969). The circuit is shown in Figure 5. Two calibrated copper-constantan thermocouples, connected so that the voltages generated were opposing, always measured the temperature difference between the reaction mixture in the reactor and the external bath temperature nominally 4.0^{o} C.

The calorimetric equipment consisted of the polymer reactor combined with a timing scheme similar in design to that used by Anderson (1966). The clock time of 2 minutes used by Anderson (1966) was determined to be too small an interval for this work and hence 5 consecutive time periods were combined to give a time interval of 10 minutes



B - Manual by-pass PB
F - Fuse
L - Pilot light
M - Motor
R - Reset PB
T1 - Cam timer (2 min)
T2 - Reset timer (0-3 min)

Figure 5 - Schematic of electrical timing circuit.

duration.

The amount of heat supplied by the heater to keep the reaction mixture at the required temperature, without reaction, was determined as an initial base line heat requirement, W_D. When the reaction was started, heat was supplied from two sources - the internal heater, W_H and the reaction, W_R. The sum of the two was considered to be equal to W_D. From calibration experiments it was determined that the heater efficiency decreased with increasing monomer conversion, probably because the fluid viscosity had increased and the heat transfer characteristics changed. Consequently a linear correction was applied to W_D throughout the experiment to account for the changing heating characteristics. Since the heat supplied by the heater was determined from the power supplied and the amount of time it was operated, the heat from the reaction could be calculated. This heat from the reaction, in watts, was related to polymer production rate by the following equation:

$$\bar{r}_p = \frac{C\ M_o W_R}{\Delta H_p} \tag{11}$$

where C 14.33, conversion from watts to calories/minute

M_o 62.5, molecular weight of VCM

ΔH_p is the heat of polymerization in cal/g mole

$\bar{r}_p$ is average rate of polymerization in gPVC/minute

The total amount of PVC produced was weighed at the end of the reaction. The cumulative amount of PVC produced during the 10 minute intervals was summed over the total reaction time. These two values were substituted into Equation 11 and the heat of polymerization calculated.

VCM is normally stored as a liquid at its saturation pressure of about 4 atmospheres with an inhibitor in it to prevent polymerization. To remove the inhibitor vaporized VCM was scrubbed by bubbling it at 4 atmospheres through a glass column containing saturated sodium hydroxide. The VCM was then dried with anhydrous copper sulfate and collected by condensing it at 0^{o} C and about 2 atmospheres in a glass high pressure chromatographic column.

The high pressure column consisted of a jacketed tube, capable of withstanding up to 20 atmospheres, and could be isolated from the scrubbing system by the use of teflon needle valves. The column was purchased from O.H. John's Scientific. A centimeter scale attached to the column enabled an accurate measurement of the liquid VCM collected.

Prior to the polymerization experiment, the reactor was assembled and tested for leaks by pressurizing the submerged reactor with compressed nitrogen. After the pressure was released, measured quantities of potassium laurate and potassium bicarbonate solutions were charged. The reactor was purged and subsequently pressurized with gaseous VCM. A measured quantity of liquified VCM, about 50 ml, was introduced and the reactor immersed in the controlled temperature vessel. The agitator was started and the temperature observed by means of the recorded temperature. When the reaction mixture rose to 46^{o} C the heater system was activated and the temperature of the reaction mixture increased to 50^{o} C.

The fraction of time the heater was "on" gave a base-line determination for later calorimetric calculations. To start the reaction, a measured quantity of potassium persulfate solution, thermostated to 50° C, was added by means of a pressure buret. The time of introduction for the initiator was taken as the "time zero" for the reaction.

During the course of the polymerization, the "time-on" and "time-off" periods of the clocks were recorded. Samples of latex were withdrawn when required. The temperature difference between the reaction mixture and the temperature bath was continuously recorded. A rapid initial reaction or other irregularity could be observed on the temperature chart recorder.

A series of experiments was performed at 50° C utilizing only gaseous VCM at pressures below saturation as shown in Figure 6. A jacketed, ½-inch diameter, high pressure chromatographic column was used as a reservoir of liquid VCM. It was connected to the reaction vessel by means of a flexible 1/8-inch diameter polyethylene tube. After the reactor was purged, the purge tube was connected to a Statham Model PA 822 pressure transducer. A Statham Model SC1001 meter was used to determine the pressure in the reactor. A connecting valve was opened, thus allowing gaseous VCM to be supplied from the reservoir. Because the temperature in the VCM reservoir was kept constant, lower than the 50° C of the reactor, the polymerization was allowed to proceed at a constant pressure lower than the VCM saturation pressure as determined by the temperature in the reservoir. The VCM concentration corresponded to pressures of 1, 3.06 and 6.12 atmospheres (15, 45 and 90 psia) as measured by means of the pressure transducer. To obtain a VCM pressure of 1 atmosphere the reservoir was kept at a temperature above the VCM normal boiling point, while the pressure in the reactor was kept at 1 atmosphere by means of a constant pressure regulator in the connecting line.

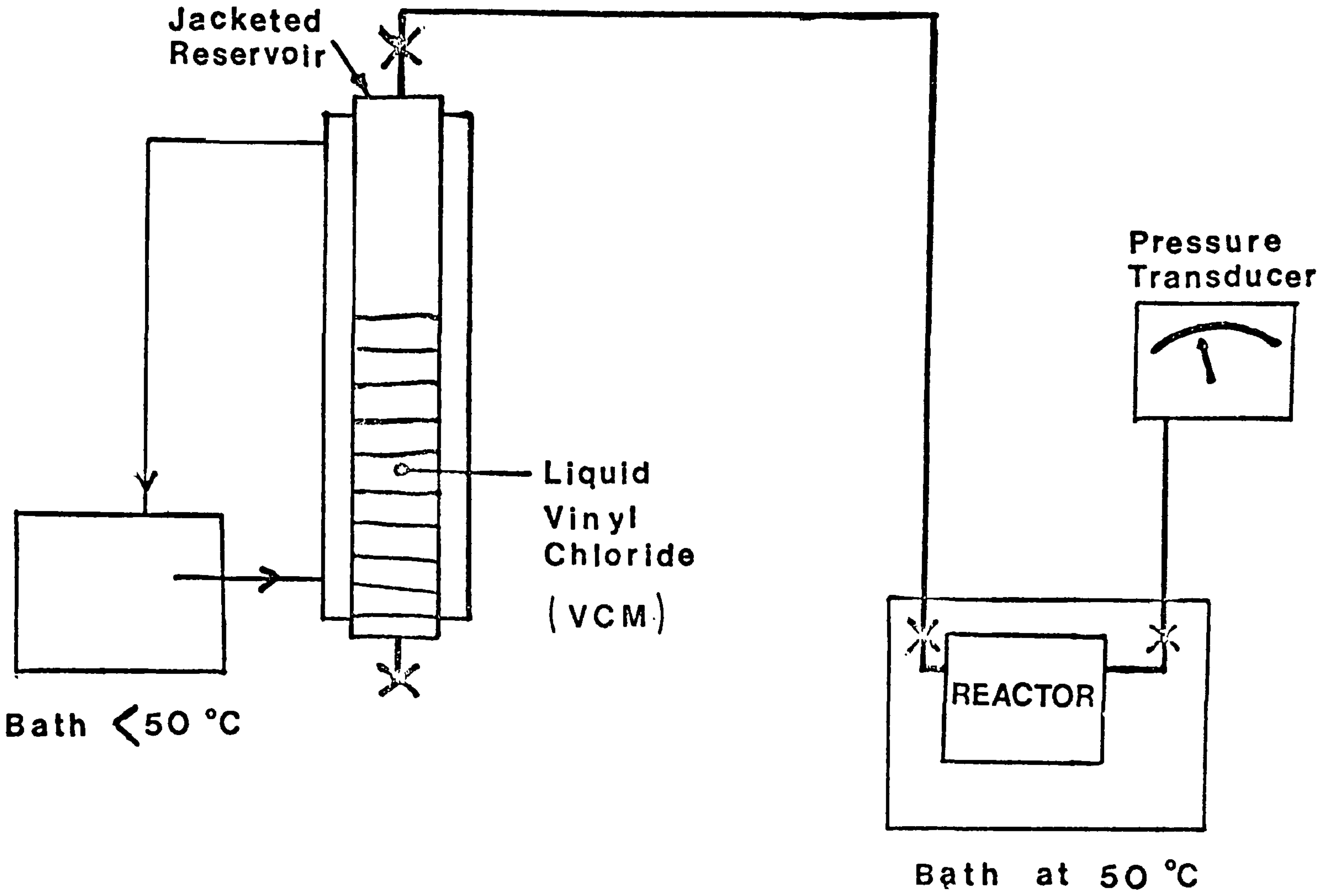


Figure 6 - Schematic of experimental equipment required to operate the reactor below the VCM saturation pressure.

When an experiment was completed, the reactor was removed from the temperature bath and the excess VCM vented into an exhaust line. The reactor was dismantled and latex coagulated by the addition of sodium chloride. The PVC product was thoroughly washed with hot water and filtered to remove the sodium chloride and other chemicals. The PVC was then dried at 50° C for 24 hours, cooled, weighed and the amount produced recorded. The PVC product varied in texture from lumps to a fine powder. Measurements made with both textures of PVC from the sample produced approximately equivalent molecular weights, the texture apparently depending on the coagulation procedure.
Some PVC solutions were precipitated with non-solvent, washed, dried, and redissolved in tetrahydrofuran for re-measurement. Again equivalent molecular weights were obtained. Hence it was considered that the washing process of purifying the PVC product essentially removed all soap, initiator or other soluble impurities.

The PVC was dissolved in tetrahydrofuran so that an analysis of its solution could be used to determine the PVC molecular weight. The $\overline{M}_N$ of the PVC was determined from osmotic pressure measurements made with a Hewlett-Packard Model 501 automatic osmometer using S & S 08 membranes at 25° C. The $\overline{M}_N$ determination was an absolute method. The intrinsic viscosity of the PVC solutions was determined from viscosity measurements at 25° C made with Cannon-Fenske calibrated viscosity tubes. The $\overline{M}_W$ was determined from the intrinsic viscosity by the Freeman-Manning (1964) correlation. Details of these methods and the mathematical analysis associated with them may be found in the thesis of Bromfield (1973) (Appendix I).

RESULTS AND DISCUSSION

The presentation and discussion of the experimental results has been separated into three categories: properties of VCM in aqueous and soap solutions, the determination of the cmc for aqueous potassium laurate solutions and from an analysis of these two sections, the third section, the emulsion polymerization of VCM.

The solubilities of VCM in water at 1 atmosphere are shown in Figure 7. The solubilities compare favorably with those obtained by Zampachova (1962 b) but the results of the present work extend over a wider temperature range. The log x-log T relation is non-linear which is typical for polar solvents such as water as discussed by Hayduk and Laudie (1973). It has been speculated by Garrett (1972) that in polar solvents hydrogen bonding or association appears to have the effect of excluding solvent molecules. The slope of the log x-log T diagram has been shown to be related to the entropy of solution for the dissolving gas (Hayduk and Castaneda, 1973). It is apparent therefore, that the entropy of solution for VCM in water is not constant. VCM has a relatively high solubility in water, comparable to that of carbon dioxide and acetylene. Hardie (1964) noted that dry VCM will not attack metals, but wet VCM will corrode iron and steel. Leonard (1971) quoted the existence of a water-VCM azeotrope. Both of these phenomena would suggest the possibility of a chemical reaction between VCM and water. The reactions of carbon dioxide and water are well documented. Hiraoka (1954) suggested the possibility of acetylene hydrate to account for the high acetylene solubilities in water. Although a larger molecule, a VCM hydrate formation could possibly

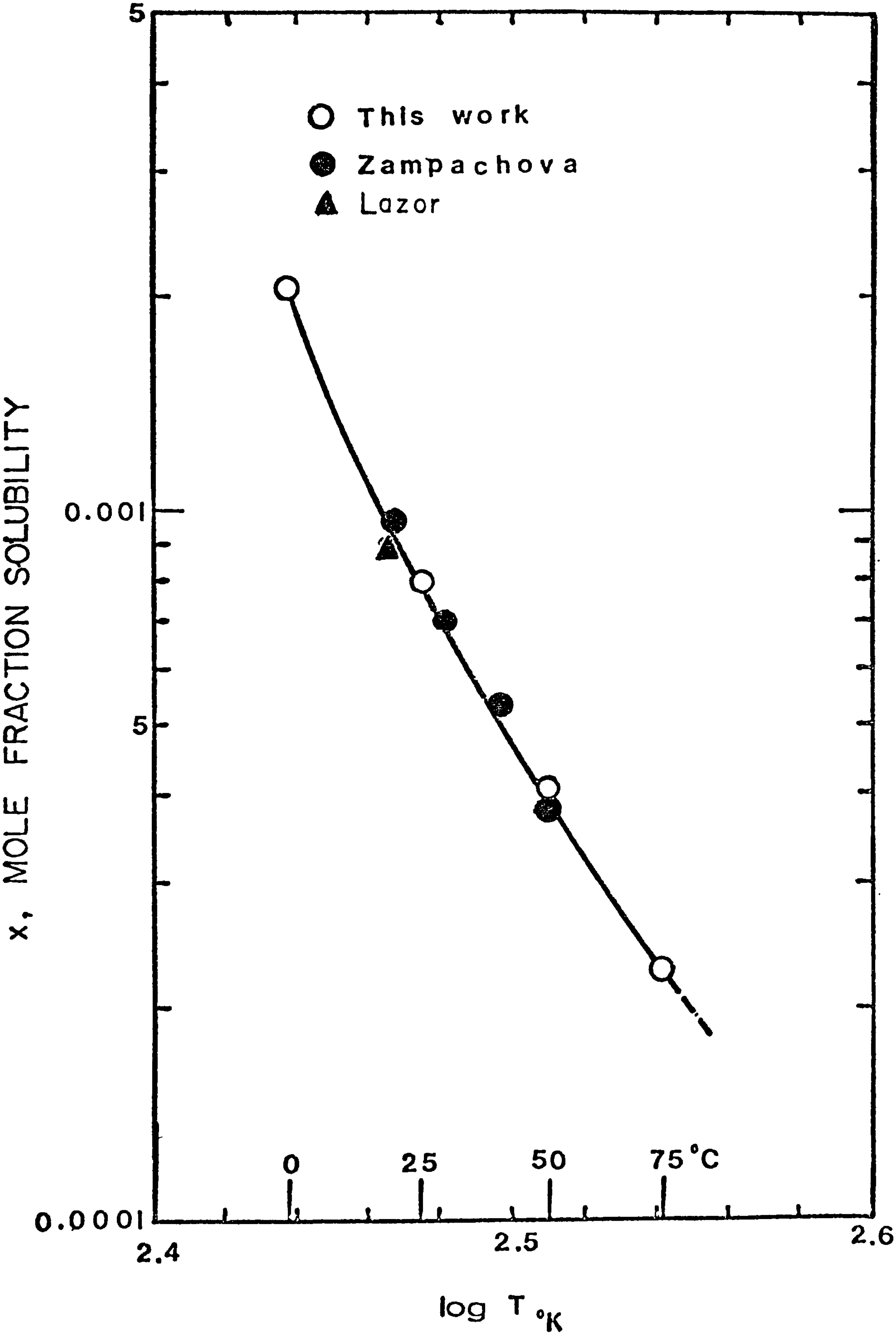


Figure 7 - Solubility of VCM in water at atmospheric pressure.

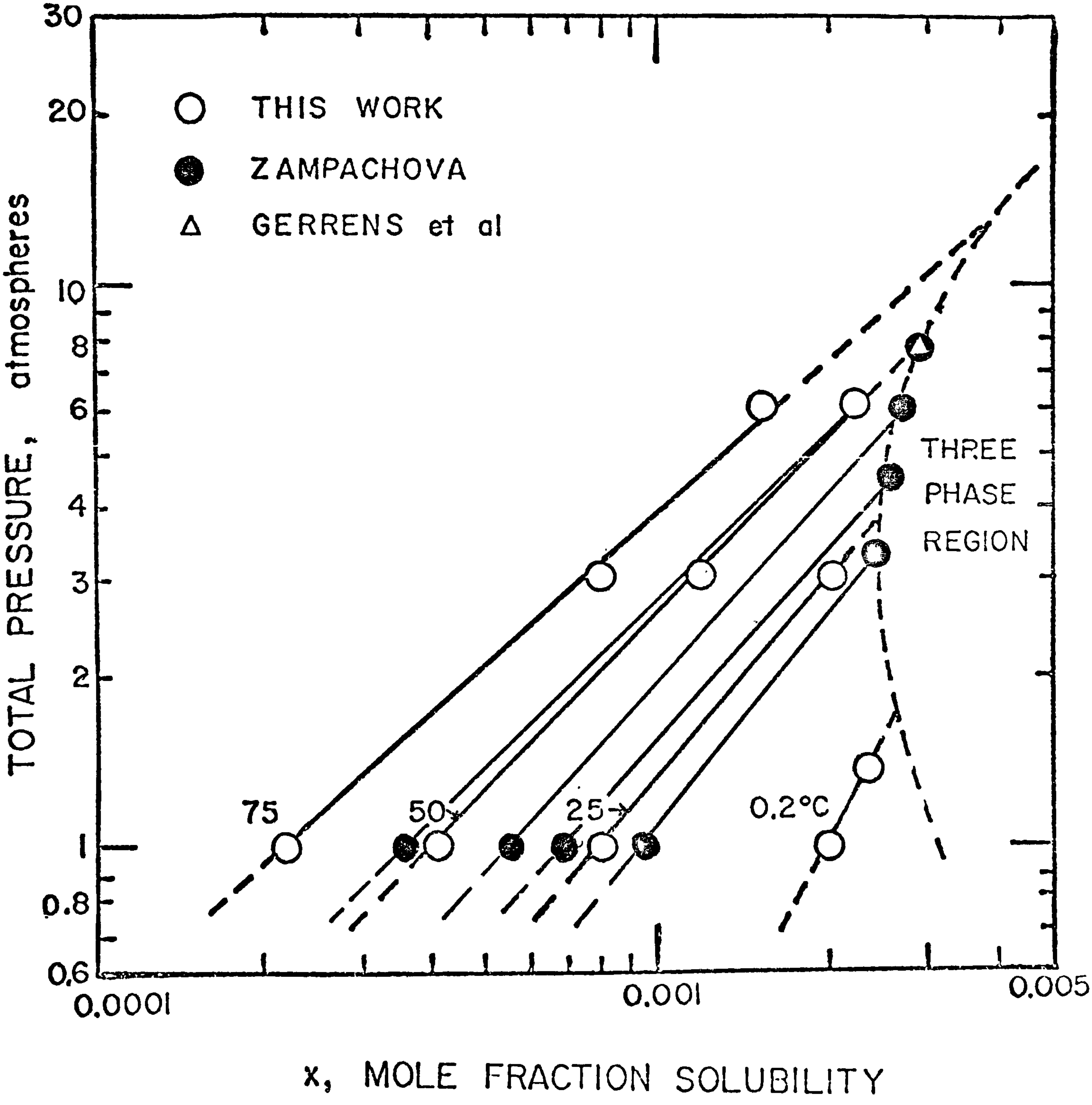


Figure 8 - Solubility of VCM in water from atmospheric to the saturation pressure.

increase the solubility in water.

Of more potential value to polymerization studies is the VCM solubility in water above atmospheric pressure. These results are shown in Figure 8. The solubility of VCM at 50° C and the saturation pressure as reported by Gerrens et al (1967) appear consistent with the results obtained here. Similar linear extrapolations to the saturation pressure for the other temperatures indicate the probable limit of the three-phase region. The three phases consist of gaseous VCM, liquid VCM and liquid water. Some of Zampachova's (1962 b) data in this region have been plotted in Figure 8 for comparison. The log solubility - log pressure plot is typical in form to that for other hydrocarbon gas-water solutions.

The diffusivity of VCM in water is given in Table 2, along with the values from the correlations of Othmer and Thakar (1953) and Hayduk and Laudie (1974). A complete analysis of the diffusivity data for a wide range of substances in water may be found in the literature (Hayduk and Laudie, 1974). The diffusivity of VCM was similar to that for other substances with similar liquid molar volumes at the normal boiling point.

TABLE 2

Diffusivity of VCM in Water as compared to recent correlations (% error in brackets $[(D-D_{expt})/(D_{expt})] \times 100$) at atmospheric pressure.

T		Diffusivity x 10^5	(cm^2/sec)
°C	Expt.	Othmer-Thakar	Hayduk-Laudie
0	0.70	0.60 (-14.3)	0.59 (-15.7)
25	1.33	1.30 (- 2.3)	1.30 (- 2.3)
50	2.43	2.22 (- 8.6)	2.26 (- 7.0)
75	3.67	3.33 (- 9.3)	3.44 (- 6.3)

A number of physical properties of potassium laurate solutions were measured at 50° C to determine the cmc. All solutions in the concentration range from 0.1 to 15.0 g/l were clear at 50°C, although at lower temperatures a precipitate was formed. It was been determined by Bury and Parry (1935) that dilute acidic solutions of potassium laurate have a tendency to deposit the acid of the soap. To prevent this deposition, fresh solutions were prepared when required and were kept stoppered to limit carbon dioxide absorption. The solutions when freshly made were slightly basic. Three cmc's have been reported by Sata and Tyuzyo (1953) and by Hess et al (1939). The first corresponds to a change from dilute homogeneous molecular solution to one containing soap clusters or disordered micelles, the second corresponds to the change to an ordered micelle structure, and the third corresponds to the start of the micelle crowding. In this work, only the first cmc was considered to be of importance because of the solubilizing effect of the micelles for VCM even at relatively low soap concentrations.

The viscosities of potassium laurate solutions were thoroughly investigated by Kurzmann (1914) but at that time no attempt was made to determine the cmc probably because the micelle theory had not yet been advanced. The values of cmc, at 50° C considered most reliable were obtained from a reduced viscosity versus concentration plot as shown in Figure 9. The unusual shape of the plot has been noticed with other soaps in other recent work by Ekwall et al (1971). The contention that the first cmc is the concentration of the peak of the reduced viscosity plot and the second cmc is the concentration at the curve's minimum, results in the values for the cmc, from

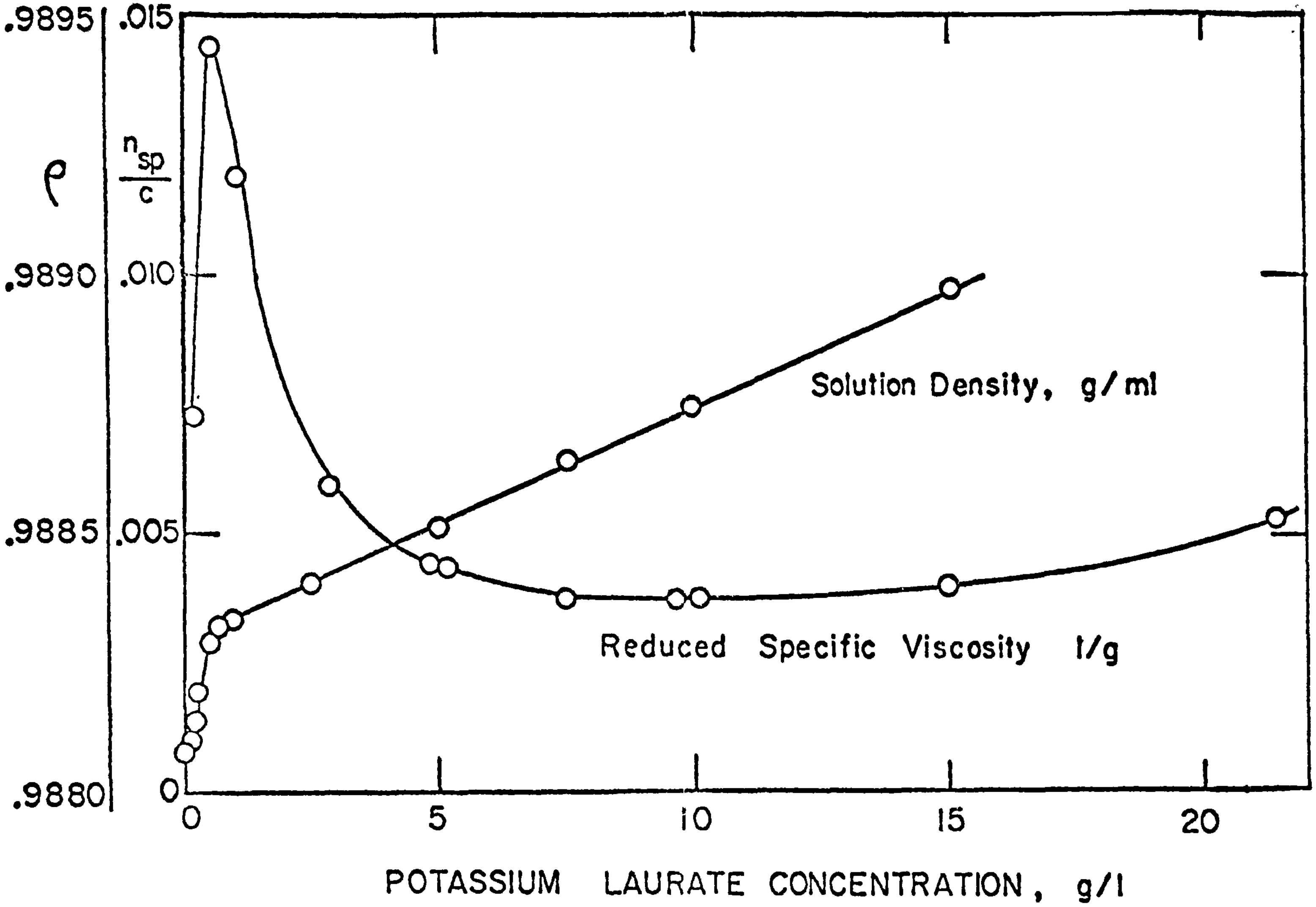


Figure 9 - Physical properties of potassium laurate solutions at 50°C.

this work, as follows:

T °C	cmc 1 g/l	cmc 2 g/l	cmc (Klevens) g/l	cmc (Bury) g/l
25	0.2	-	6.0	9.0
50	0.5	8.5	7.8	6.5
75	1.2	12.0	11.8	-

The second cmc values are in approximate agreement with the literature values as reported by Klevens (1947) and by Bury and Parry (1935) and determined using refractive index, interferometer, and x-ray analysis. The data for the cmc analysis are available in Appendix D.

The densities of potassium laurate solutions were measured at 50° C and are also shown in Figure 9. The density was found to increase very rapidly up to a concentration of 0.5 g/l. Above this concentration the increase was less rapid. The breakpoint in the curve was considered to be the cmc. Other measurements of physical properties of potassium laurate solutions as discussed below were obtained which also indicated an abrupt change in properties at a concentration of 0.5 g/l at 50° C. Hence this cmc value was taken as the minimum emulsifier concentration that would be reasonable for the emulsion polymerization experiments at 50° C.

Experimental results for osmotic pressure and light scattering measurements of potassium laurate solutions are in Appendix D. The results of these measurements are only semi-qualitative, but are useful in estimating the approximate size of micelles. Osmotic pressure measurements were used to estimate the number average molecular weight of the micelles and hence the number of soap molecules per micelle (Coll, 1970). A reduced osmotic pressure versus concentration plot was drawn as normally required for estimating average molecular weights, but because the π/c versus c data were non-linear, it was difficult to estimate accurately the intercept at $C = 0$. Extrapolating the two higher concentrations to the π/c intercept, a micellar number average molecular weight of 23100 was obtained. This corresponded to a value of approximately 100 potassium laurate molecules per micelle at 50^{0} C. Turbidimetric data obtained by light scattering have been used to obtain the weight average molecular weights of micelles by Uko and Venable (1971), Ekwall et al (1971) and Debye and Anacher (1951). A reduced turbidity versus concentration plot yielded an approximate value for the micellar weight average molecular weight of 33600. The corresponding value for the number of molecules of potassium laurate per micelle at 50^{0} C was approximately 140. The ratio of the two molecular weights yields a micelle polydispersity of approximately 1.45. Coll (1970) reported that micelles were expected to be generally fairly monodispersed, the polydispersity varying from 1.06 to 1.25. Potassium laurate micelles would appear to be somewhat more polydispersed. While the uncertainty in both the above measurements may be as large as 25%, an approximate size of potassium laurate micelles would appear to correspond to roughly 120 molecules. The number of molecules per micelle has been reported in the literature from 50 to 150. Harkins et al (1947) reported a value of 76 molecules per micelle for potassium laurate at 25^{0} C as determined from x-ray analysis. The somewhat higher value obtained in this work is corroborated by two measurements. Molecular weight analyses are in Appendix H.

The solubility of VCM is increased in the aqueous soap solutions above that obtained with pure water. The ratio of solubility at 50^{o} C in soap solution, x_s, to that in water, x_w, versus soap concentration is represented in Figure 10. It may be observed that the effect of pressure on the extent of solubilization is small and that the distribution of VCM between the water and the micelles is relatively independent of pressure. This phenomenon was reported by Zampachova (1962 b) for the solubilization of VCM in mersolate and for other gases in other soap solutions (Ross and Hudson, 1967 and McBain and Soldate, 1942). Contrary to liquid hydrocarbon solubilization in water, gaseous VCM appeared to be solubilized at a soap concentration below the cmc. This was evident in the increase in VCM solubility in the dilute soap solutions at 0.1 g/l. It has been suggested by Nakagawa (1967) that because they are small the gaseous hydrocarbon molecules are adsorbed by the individual soap molecules, or by small clusters of soap molecules which are below micellar size. Also from Figure 10 it may be observed that there appeared to be a limiting solubilizing effect as the soap concentration is increased. It is postulated that at high soap concentrations even though more soap is added, fewer additional micelles are formed and hence there is only a little increase in solubilization. The upper limit to solubilizing measurements is limited by the solubility of the soap itself. Mukerjee (1971) in quoting the work of several authors analyzed solubilization by analogy to the adsorption process proposed by Langmuir. It was supposed that the amount of VCM in a micelle, $x_m = x_s - x_w$, is related

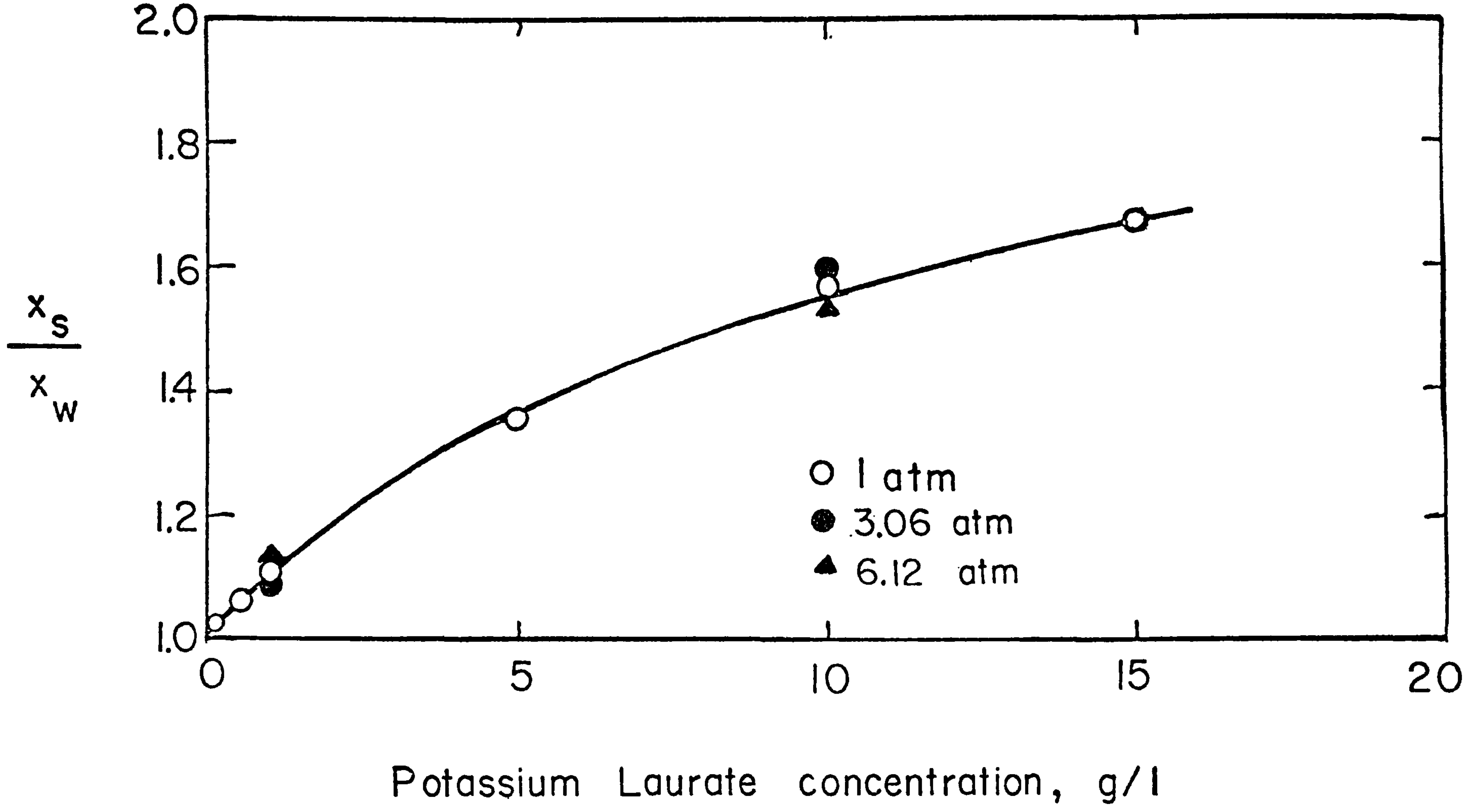


Figure 10 - Solubilization of VCM in potassium laurate solutions.

to the number of micelles, or amount of soap, c g/l, by an equation of the form

$$x_m = \frac{ac}{b+c} \tag{12}$$

This would imply that a plot of c/x_m versus c would be linear. This linearity was obtainable from an analysis of the solubility data obtained in this work as well as the solubilization of other gases as reported in the literature. The equation would be most applicable only to relatively high soap concentrations since gas solubilities at low soap concentrations are relatively difficult to measure accurately and x_m values are subject to a large scattering. Representative values of a and b obtained from this work are given below for use in Equation 12:

Temp °C	a	b
25	1.06×10^{-4}	0.86
50	4.35×10^{-4}	8.70
75	7.14×10^{-4}	23.75

The VCM solubility in soap solution data are in Appendix B.

The diffusivity of VCM in soap solutions was substantially reduced with increasing soap concentration. This is shown in Figure 11 where the ratio of diffusivity in soap solutions to that in water is plotted versus soap concentration. Recent theories proposed by

Navaii et al (1971) and Jalan et al (1972) to predict the diffusion of gases in protein and polymer solutions have been based on the assumption that no chemical interaction or association occurred between the gas and the solution. Since VCM was strongly absorbed by the micelles, these theories failed to predict the diffusivity of VCM in soap solutions. A recent review by Rogers and Machin (1972) considered the concentration dependence of diffusion coefficients for the case where the diffusing molecules were immobilized in solution. Assuming a Langmuir adsorption mechanism the equation postulated was:

$$\frac{D_s}{D_w} = \frac{a}{(1 - bc)^2} \tag{13}$$

Diffusivities obtained for VCM in aqueous potassium laurate were fitted to Equation 6. It was assumed that the concentration of micelles was directly proportional to the amount of soap in the solution. For Equation 13 values of $a = 1.0$ and $b = -0.075$ were obtained by a linear fit of $\sqrt{D_w/D_s}$ versus c. This empirical correlation is also drawn in Figure 11. If it was assumed that the VCM molecules solubilized in the micelles were completely immobile and only the VCM in the water could diffuse with complete mobility, it might be expected that the fractional diffusivity, D_s/D_w, should be equal to the fraction of the free VCM in the water, x_w/x_s. This simple premise is shown to be in error in Figure 12. It appears possible that the micelles hinder the diffusion of VCM even if

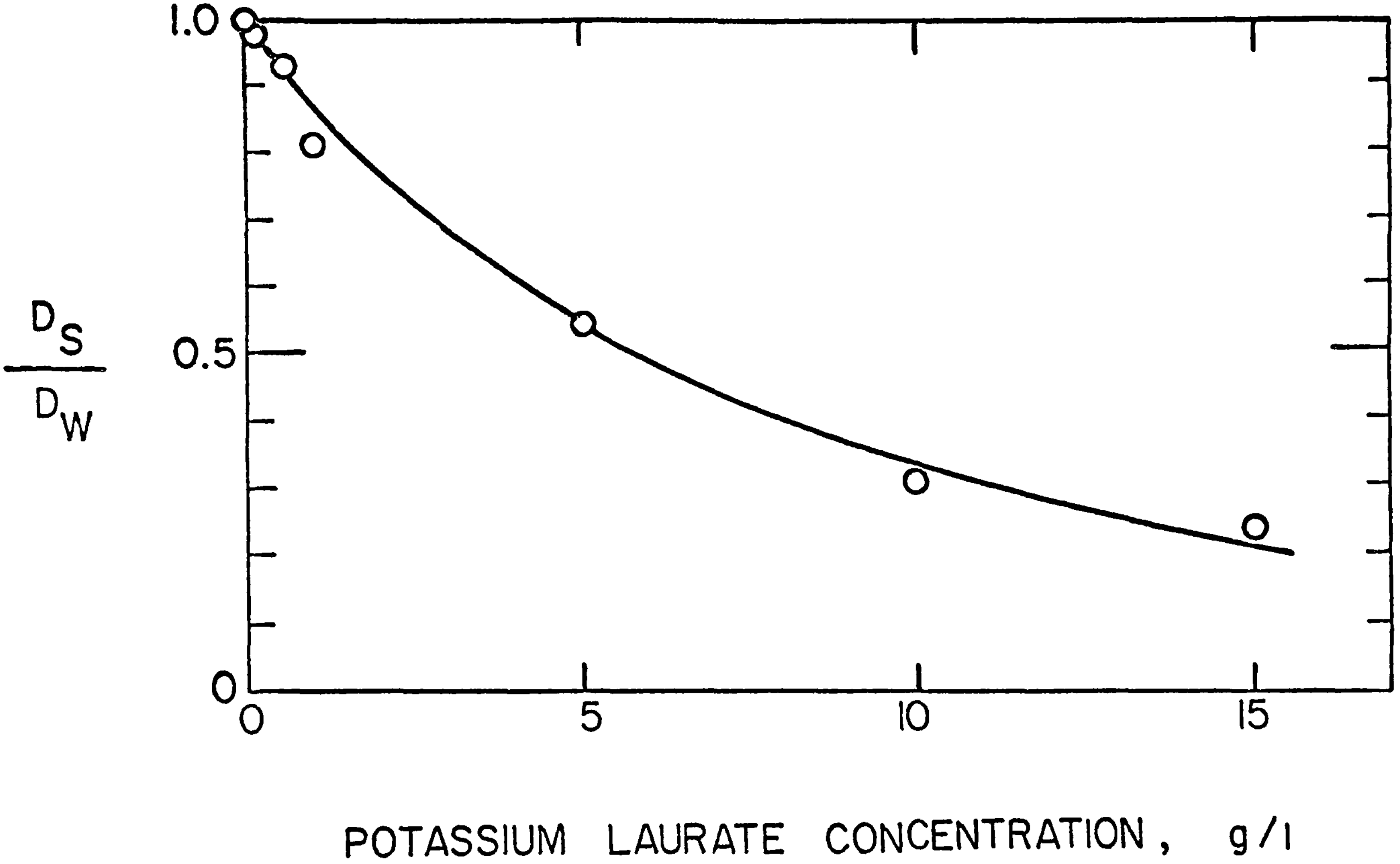


Figure 11 - Diffusivity of VCM in potassium laurate solutions.

the VCM is not directly absorbed within the micelles. At higher soap concentrations, the ratio D_s/D_w appears to approach zero when extrapolated using Equation 13. Hence, it is suggested that if the solution is packed with micelles saturated with VCM, no VCM could diffuse through it. The maximum solubility of potassium laurate in water at 50^o C is 670 g/l (ICT, 1929). Substituting this value into Equation 12 to get x_m, the limiting solubility of VCM in this solution can be calculated to be $x_w/x_s = 0.48$. This point is also shown in Figure 12 and appears to be a reasonable extrapolation of the D_s/D_w versus x_w/x_s data. The presence of micelles appears to hinder the diffusion of VCM. As the micelles increased in number, less of a free path is open to diffusion in the solution.

No published data for the diffusion of hydrocarbon gases in soap solutions can be found in the literature. Experiments by Harkins (1947) were reported in which the diffusion of an oil into polymer and into polymer-monomer latex indicated similar diffusion rates in both liquids. If it is assumed that polymer particles behave in a manner similar to micelles, then it may be assumed that VCM diffusivities in latices are comparable to those in soap solutions. In the emulsion polymerization process, the VCM droplets act as reservoirs for VCM. The VCM must diffuse from a droplet through a soap solution into a growing polymer particle where the VCM reacts or into a micelle where the VCM awaits initiation. It would be expected that VCM diffusion would be an important step in the reaction mechanism particularly when the VCM droplets were near depletion.

VCM transport by micellar diffusion was expected to be small. Using an estimated density of the micelles of approximately 0.625 g/ml as reported by Debye and Anacker (1951) and the measured value of molecular weight of approximately 23100, the diffusivity of the micelles could be estimated to be 0.05 x 10^{-5} cm^2/sec by means of Equation 2. This assumes no interaction of the micelles. Since micelles are charged they would be expected to repel one another and hence their actual diffusivity would be expected to be less than the value estimated with consideration for their size alone. Diffusivity data are available in Appendix C.

Having obtained the essential data about VCM and potassium laurate solutions, it was possible to interpret some of the emulsion polymerization experiments subsequently performed. The process variables studied included time of reaction, VCM concentration, reaction temperature, initiator concentration, and emulsifier concentration. Calorimetric experiments were conducted to obtain initial rate data and the heat of polymerization.

Several identical reaction recipes were polymerized for different reaction time periods to determine the variation of PVC molecular weight during the course of polymerization. Molecular weights of the PVC products, corresponding to the different conversions achieved, were measured. As shown in Figure 13, the molecular weights (both $\overline{M}_N$ and $\overline{M}_W$) were found to be reasonably constant for the initial stages of the reaction, up to about 50% conversion. Corresponding to an increasing conversion, the latex thickened and eventually turned semi-solid, while the molecular weights continued to increase. This

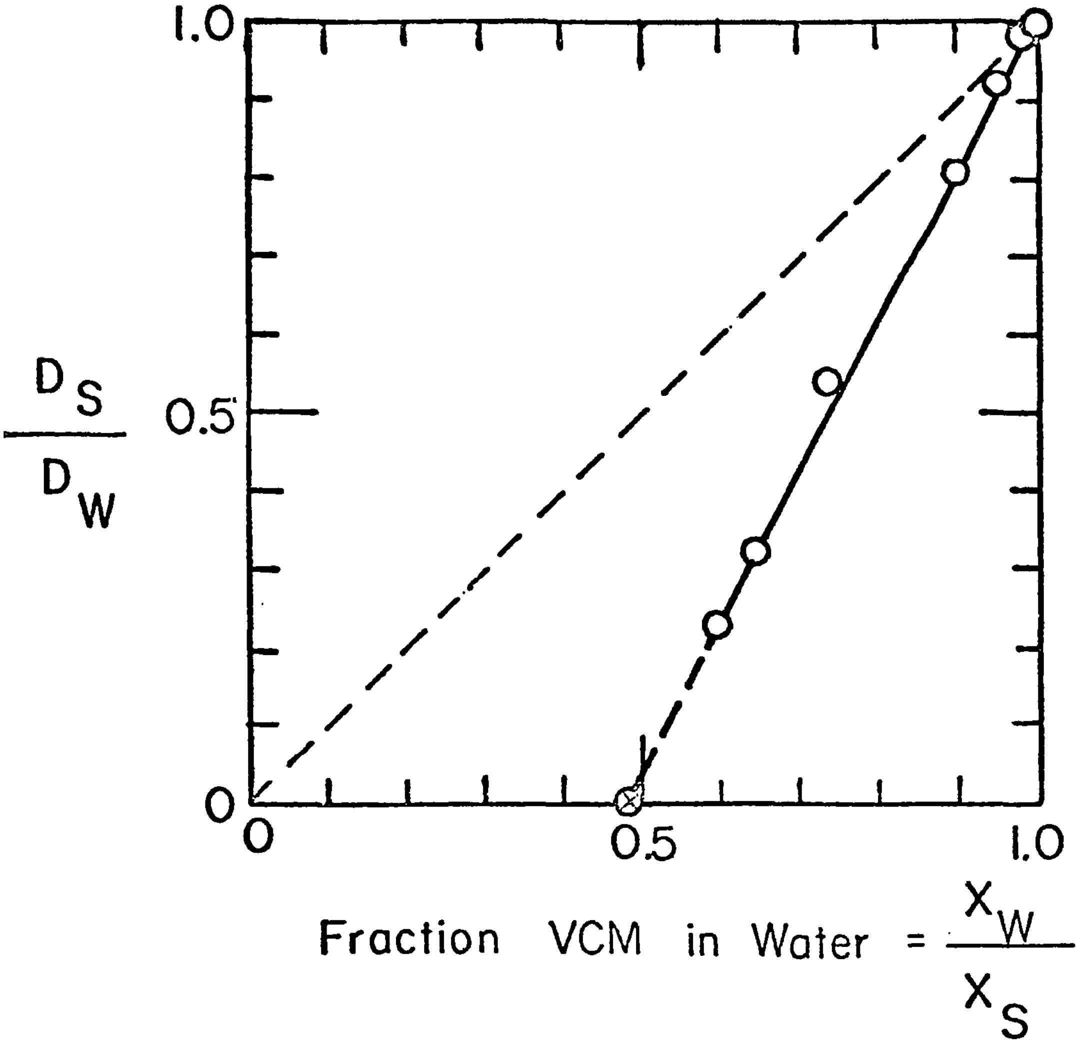


Figure 12 - Diffusivity of VCM in potassium laurate solutions.

was the result of the formation of branches and cross-links on polymer molecules previously formed, because of the reduced rate of monomer transfer resulting from a low VCM diffusivity as the viscosity of the latex increased. The presence of gel-like polymer was postulated by the rapid increase in $\overline{M}_W$ and polydispersity relative to the increase in $\overline{M}_N$.

Although Figure 13 does not show the actual reaction times, it may be noted that in the initial 60 minutes of reaction about 10% conversion was obtained while about 30% conversion was obtained in the following 40 minutes. This autoacceleration in PVC production, indicating an increase in the reaction rate, is typical of VCM polymerization. It has been postulated by Ugelstad and Mork (1971) that this autoacceleration could be interpreted as reaction within, and also on the actual polymer particle surface. They also indicated that a very rapid desorption and re-absorption of radicals by the particles would result in a low fraction (about 10^{-4}) of latex particles which would contain an active radical chain. It has been suggested by Friis and Hamielec (1974) that autoacceleration may also occur because the polymer particles grow larger and incorporate a larger quantity of monomer as the reaction proceeds.

The description of the latex condition as given in Figure 13 was based on visual observations and should be considered as qualitative only. Meaningful experiments as to the effect of other variables on the PVC molecular weights could be made only if

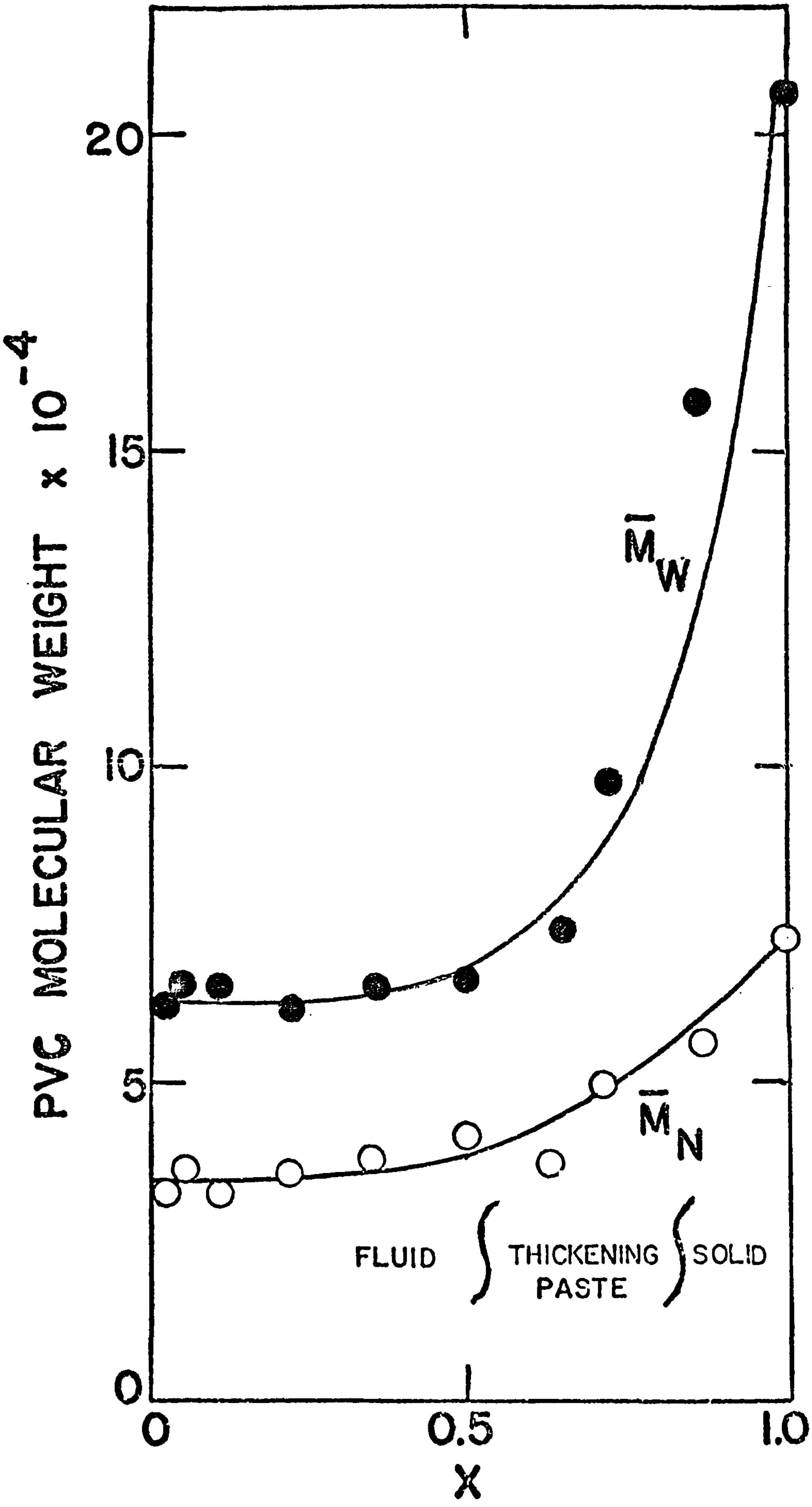


Figure 13 - Molecular weights of PVC during polymerization, at constant initiator and emulsifier concentrations.

the reactor contents remained fluid so that for most of the polymerization experiments the conversion was kept to low values, up to a maximum of about 30%. An initiator concentration of 3.64 g/l and an emulsifier concentration of 14.55 g/l, yielded a reaction time of about 100 minutes and a conversion of approximately 30%. The conversion was estimated during the reaction both from the reaction time and by visual observation of the change in volume of the latex. The conversion was subsequently determined exactly by weighing the washed and dried PVC product.

Figure 14 shows results of experiments to determine the effect of variation in temperature upon the molecular weights of PVC for otherwise identical reaction conditions and conversions. The classical emulsion theory could predict that molecular weights would depend on the polymerization variables as follows:

$$\overline{M} = \frac{k_p\ [M]N}{2r_i} \tag{14}$$

where $\overline{M}$ is the polymer molecular weight

k_p is the propagation rate constant

$[M]$ is the monomer concentration

N is the number of particles

r_i is the rate of initiation

The propagation rate constant, k_p, can be represented by an Arrhenius type equation of the form $k_p = K_p \exp(-E_p/RT)$. An

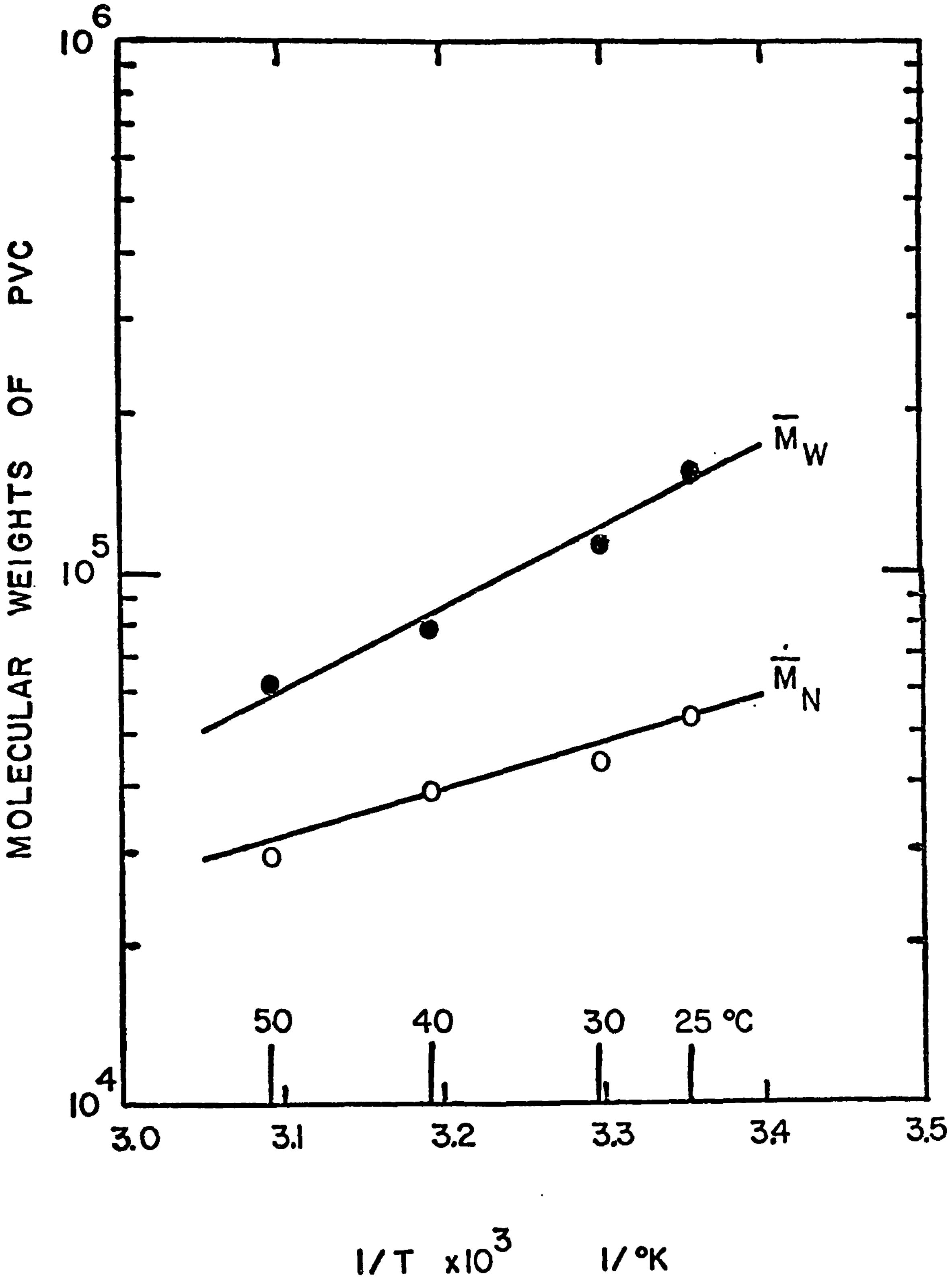


Figure 14 - Effect of a variation in temperature upon PVC Molecular weight, at constant initiator and emulsifier concentrations and conversion of 30 ± 5%.

analysis of the solubility data of Figure 8 indicated that the VCM solubility effect was relatively small. Hence, [M] could be considered essentially constant. All experiments were performed at the saturation pressure and from 50 to 25^{o} C for which VCM solubility decreases by only 15%. The temperature effect on the number of particles, N, should be constant, being related to the emulsifier concentration. The rate of initiation, r_i, can be given by $r_i = k_d[I]$ where the initiator decomposition constant, k_d, is given by an Arrhenius type equation, $k_d = K_d \exp(-E_d/RT)$. An analysis of the relative magnitude of the constants (Billmeyer, 1962) indicated that as temperature decreased, the molecular weight increased because the activation energy for initiator decomposition was larger than the other terms. Equation 14 can also be expressed as an Arrhenius type function by substituting values of k_p, k_d into it. Hence it is suggested

$$\overline{M} = K\, e^{-Ea/RT} \qquad (15)$$

A plot of log molecular weights versus reciprocal temperature shown in Figure 14, was approximately linear yielding a net energy of activation of 4, and 7 Kcal/mole for $\overline{M}_N$ and $\overline{M}_W$, respectively. This decrease in molecular weight with increasing temperature is consistent with commonly observed behaviour.

The results of experiments in which the VCM concentration was varied, i.e., the effect on the PVC molecular weights, are shown in Figure 15. The VCM concentration was controlled by supplying the VCM to the reactor at a controlled pressure. Because the initiator and emulsifier concentrations as well as temperature were held constant, it may be deduced from Equation 14, that the PVC molecular weights would be proportional to the first power of VCM concentration, [M]. This result was experimentally demonstrated for $\overline{M}_N$ values but not for $\overline{M}_W$ as shown in Figure 15. It may also be noted that by reducing the VCM concentration, the polydispersity of the PVC was also reduced. This relation may be qualitatively explained. It may be assumed that a growing polymer particle will grow for an average of t seconds from initiation to termination. During this time period, the higher the VCM concentration, the more probable the polymer particle will react with more VCM rather than another free radical and hence a higher $\overline{M}_N$ may be expected. For a similar reason lower molecular weights and less branching could be expected at lower VCM concentrations since an active polymer radical is more likely to react with a free radical and terminate in the absence of monomer. Also any growing branches would be short as they would terminate before much monomer is added. The overall conversions for these experiments was about 30%. This was determined by weighing the PVC produced. The VCM concentrations as shown in Figure 15 were based on the high pressure solubility data assuming that the reaction mixture was saturated with VCM at the saturation pressure. The data for these experiments are given in Table 17 of Appendix F.

Although it is not apparent from Figure 15, the polymerization rate was also affected by a variation in the monomer concentration. These results are shown in Figure 16. Average reaction rates were determined

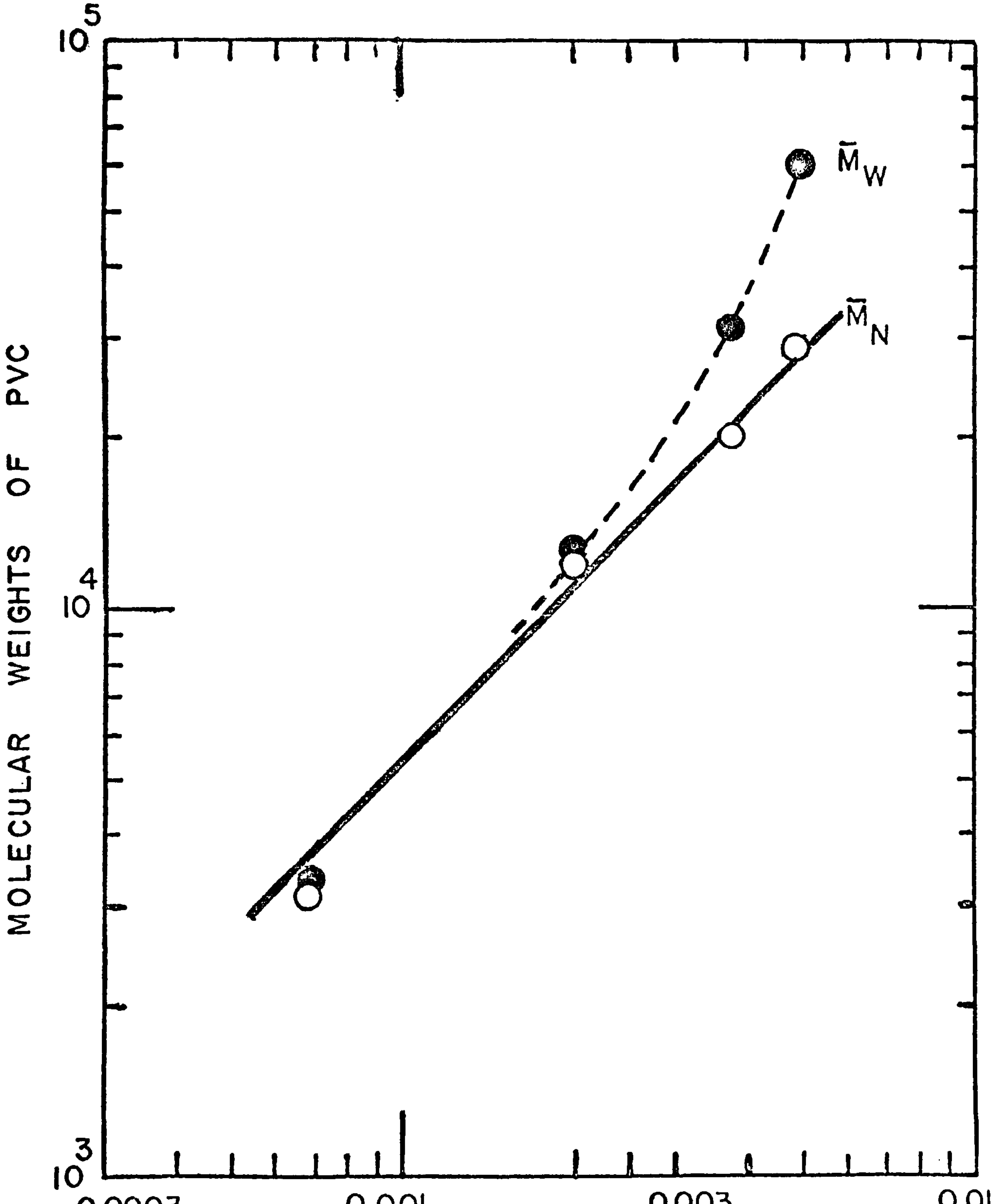


Figure 15 - Effect of a variation of VCM concentration upon PVC molecular weights.

over the reaction period to determine the effect of VCM concentration upon $\overline{M}_N$ and $\overline{M}_W$. Assuming that the rate was slow so that any autocatalytic effect was negligible, the rate was taken as the total PVC produced during the total reaction time, both of which were easily measured. Under these circumstances, the monomer concentration was the concentration of VCM in the soap solution, that is, [M] was equal to x_s corresponding to the actual pressure used. The rate of PVC production versus x_s is shown in Figure 16. From the slope which was found to be 3, it follows that

$$\overline{r}_p \; \alpha \; [M]^3 \tag{16}$$

It is recognized that this result is quite different from the common assumption with regard to the effect of monomer concentration. However, few experiments have actually been performed for the sole purpose of investigating this variable. It had simply been assumed to apply. The work of Ugelstad et al (1969) in which VCM pressures were varied during a portion of the polymerization period qualitatively verifies the above. A plausible explanation for this unexpected behaviour might be that prior to the reaction several molecules actually allign themselves along an axis that is to become the polymer backbone in a normal reaction. Hence, when the reaction begins it is very rapid only if the molecules are already in proper alignment for polymerization. This supposition is contrasted with the one in which single molecules must move sequentially to the polymerization site. The first power dependence of rate upon monomer concentration is based

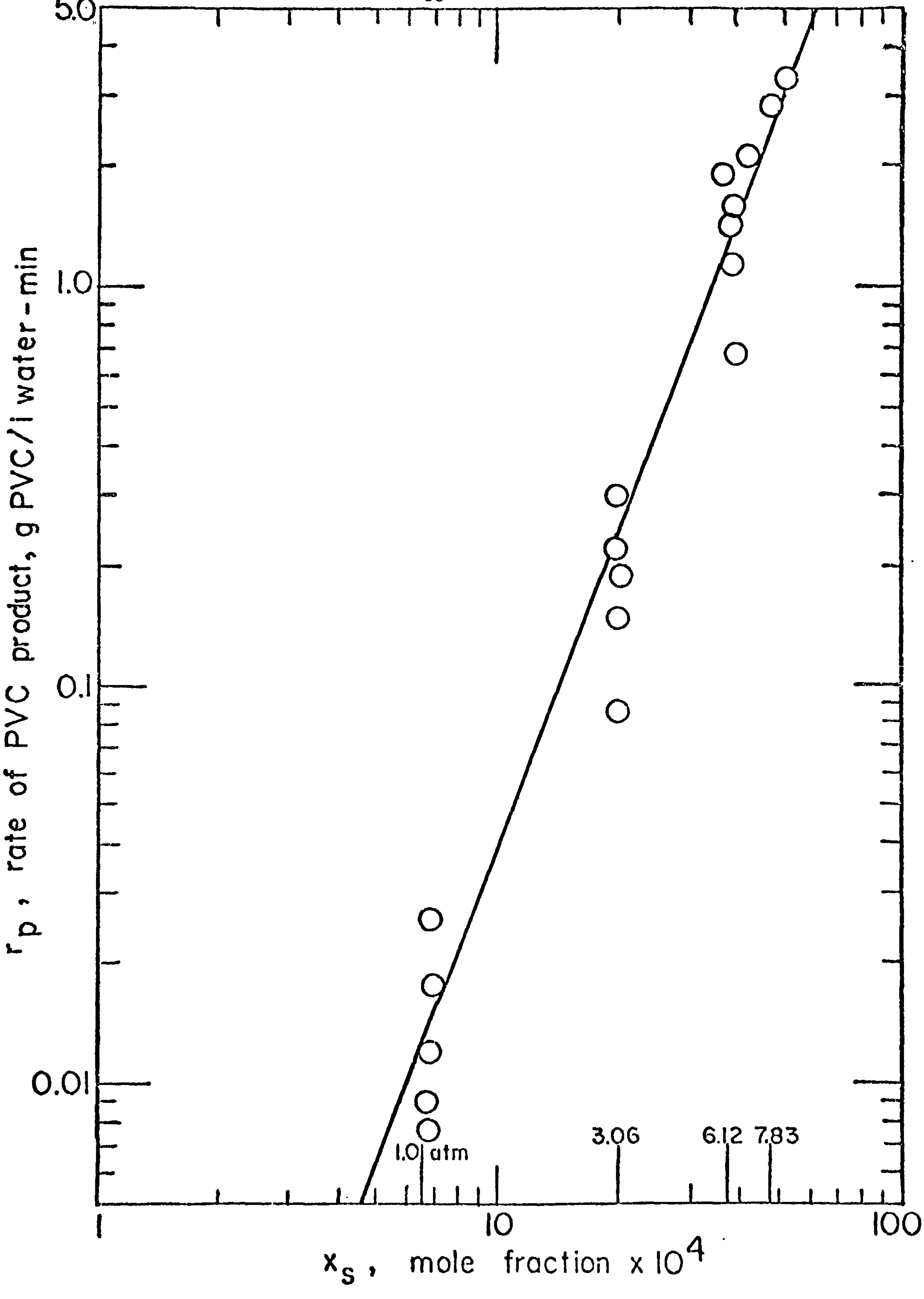


Figure 16 - Rate of Polymerization versus monomer concentration.

on the assumption that the monomer and the polymer are miscible which is not true for PVC in liquid VCM. The experimental method in the present work and in the work of Ugelstad et al (1969) forced the VCM/water mass ratio to be small, less than 0.01, as opposed to the normally used ratio of about 1.0 in other experiments. This small reacting volume ratio may also account for the noted results in the fact that depleted monomer could not be replaced as quickly so that the effective VCM concentration is lower than measured in a non-reacting system.

As an aid to interpreting results involving the monomer and emulsifier concentrations, the solubility data for VCM in potassium laurate solutions at 50^{o} C have been replotted in Figure 17 expressing the relationship between x_s and [E]. Considering the data above the cmc only, it was determined that the monomer concentration [M] could be expressed as

$$[M] = x_s \alpha [E]^{1/6} \tag{17}$$

Substitution into Equation 16 yielded

$$\bar{r}_p \alpha [E]^{\frac{1}{2}} \tag{18}$$

indicating that the PVC reaction rate varied as the ½ order of emulsifier concentration. It should be understood that substitution of Equation 17 into Equation 16 is valid only if the only effect of changing the soap concentration was to change [M].

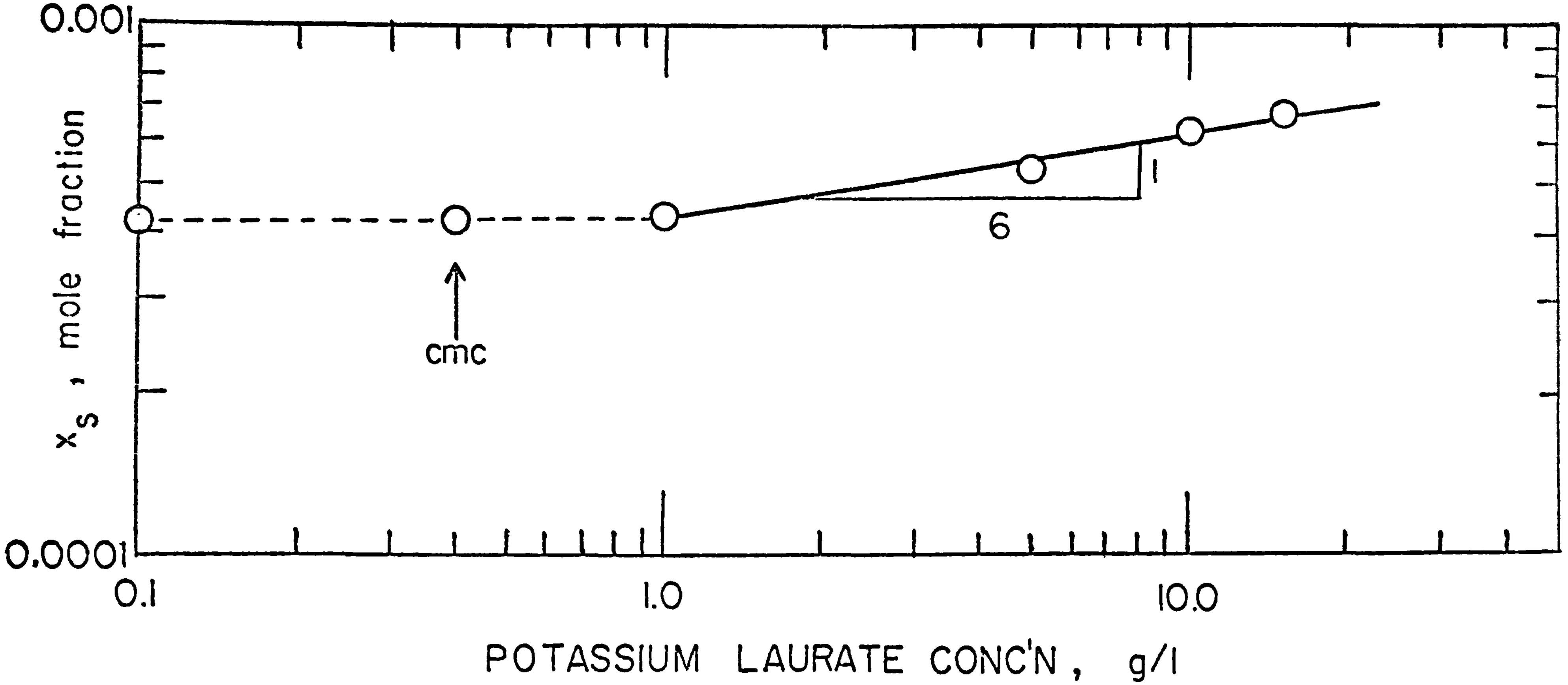


Figure 17 - Monomer concentration versus emulsifier concentration at 50^oC.

Figure 18 demonstrates the results of experiments to show the effect of variation in emulsifier concentration upon PVC molecular weights while the other variables were held constant. The molecular weights increased with increasing soap concentration up to about 10 g/l potassium laurate. At higher soap concentrations, both $\overline{M}_N$ and $\overline{M}_W$ were found to be approximately constant. This phenomenon can be partly explained by the effect of VCM concentration upon molecular weights. From solubilization experiments it was determined that [M] increased with increasing soap concentration and appeared to reach an upper limit value in a micellar soap solution. Hence the results are in qualitative agreement with Equation 14 insofar as the effects of monomer concentrations are concerned.

Figure 19 depicts the effect of various emulsifier concentrations upon VCM conversion during the course of the reaction. The conversions were determined by withdrawing latex samples for analysis. For a particular reaction time conversion can be seen to increase with an increasing emulsifier concentration. Although the number of particles in the PVC latex was not measured in this work, it is well known that the N increases with emulsifier concentrations, as described for example by Ugelstad et al (1969) and Gerrens et al (1967). These authors have also shown that there is not a simple relation between soap concentration and reaction rate. However, in qualitative terms, consistent with previous work, increasing the emulsifier concentration increased the number of micelles available for initiating. As a result the larger number of particles resulted in an increased reaction rate and a larger PVC conversion during the same reaction time. Whereas the polymer concentrations are shown as a function of reaction time in Figure 19, the reaction rates could be determined by differentiation,

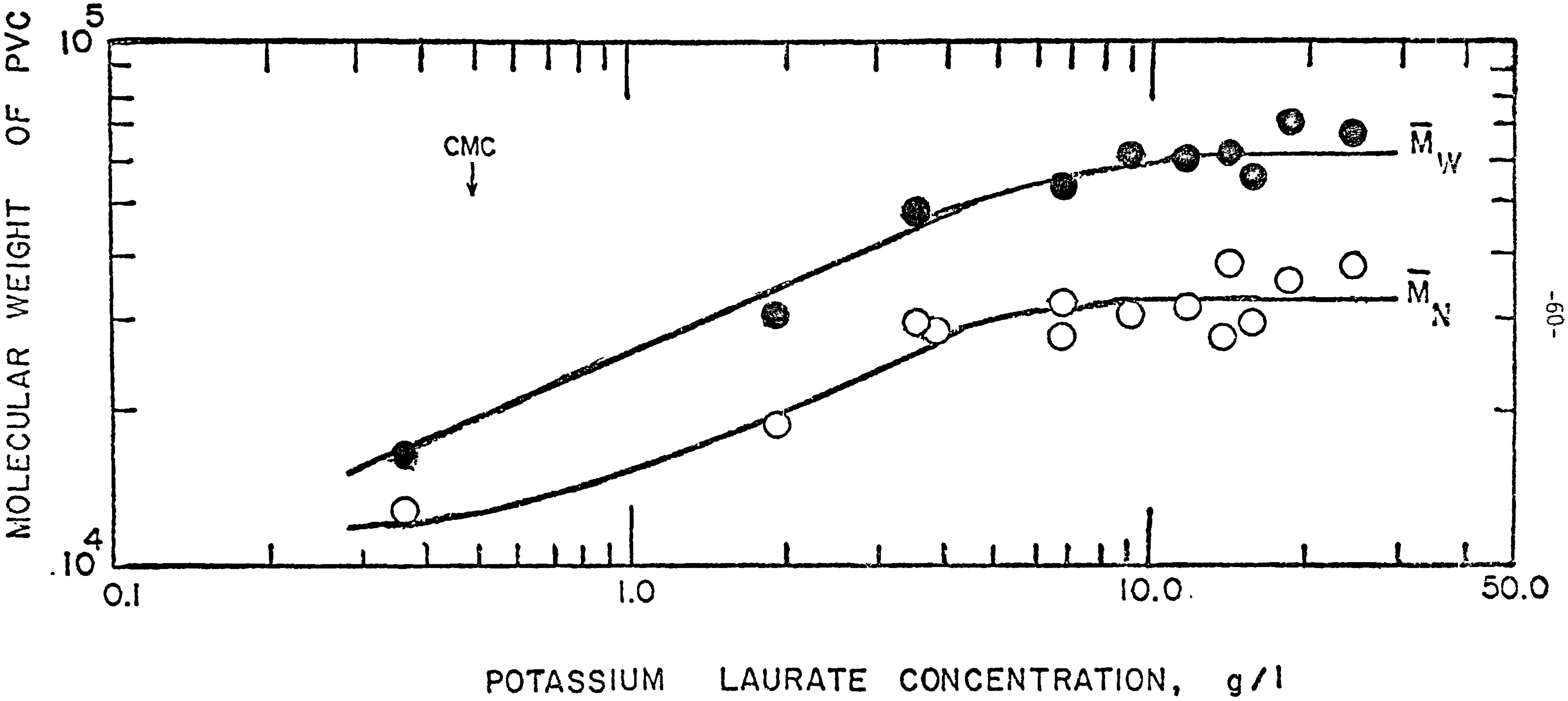


Figure 18 - Effect of a variation in emulsifier concentration upon PVC molecular weight, at constant initiator concentration and conversion of 30 ± 5%.

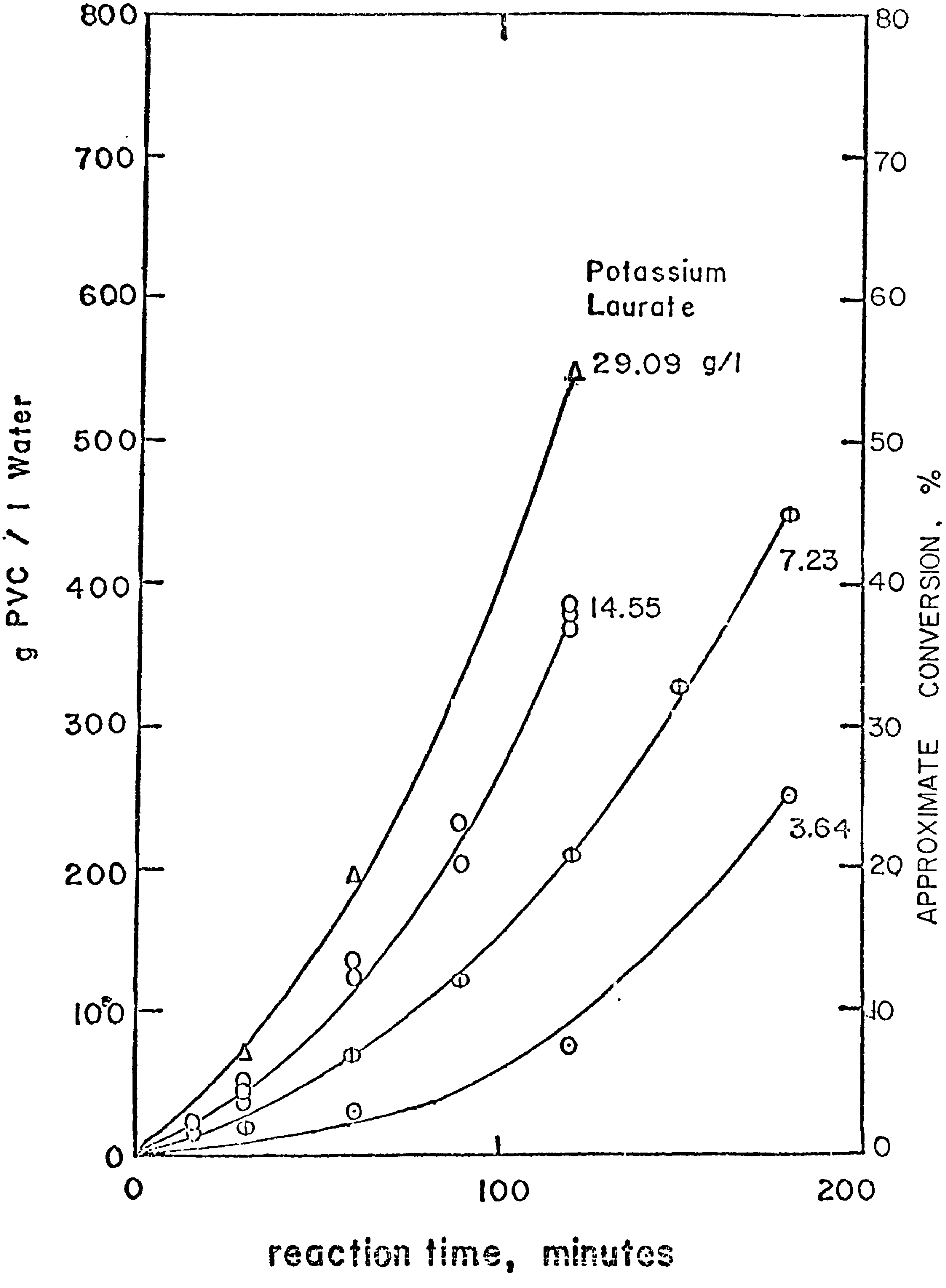


Figure 19 - Effect of a variation in emulsifier concentration on the cumulative mass product of PVC, at constant initiator concentration.

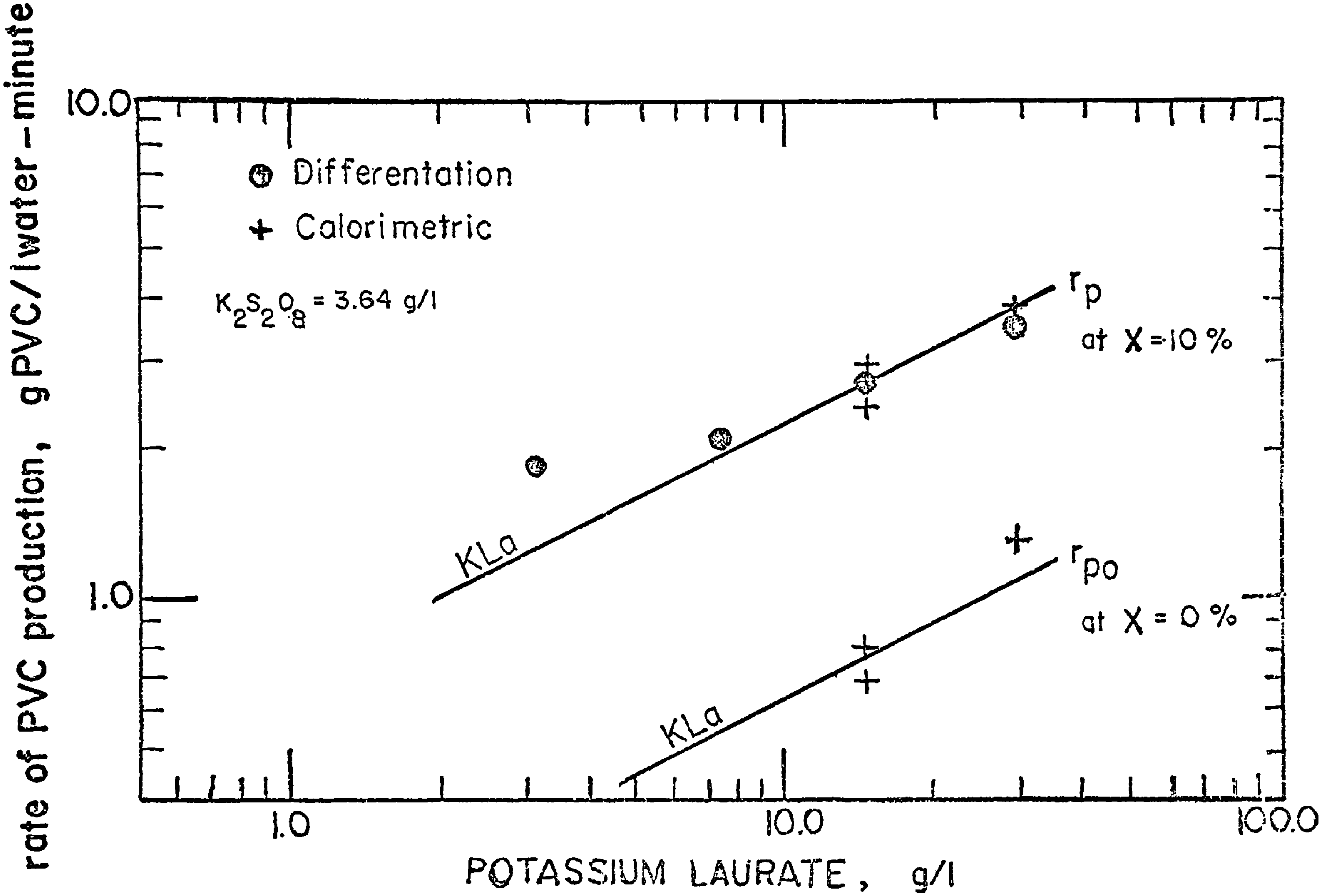


Figure 20 - Effect of a variation in emulsifier concentrations upon the rate of PVC production at constant initiator concentration.

by taking tangents to the curves at a set value of PVC concentration, such as for example, 100 g PVC/l water. This procedure was followed to obtain comparable polymerization rates which in turn could be compared with those obtained from the calorimetric measurements as shown in Figure 20. It may be observed that the rate of reaction increases with increasing emulsifier concentration to approximately the half-order, that is, $\overline{r}_p \alpha [E]^{\frac{1}{2}}$. This may be compared with an exponent of 0.6 obtained by Gerrens et al (1967) for [E] greater than 10 g/l or with an exponent of 0.1 to 0.3 obtained by Peggion et al (1964) for [E] above the cmc.

A number of experiments to study the effect of a variation in initiator concentration for otherwise constant polymerization conditions were performed. The effect on PVC molecular weight is shown in Figure 21. It can be noted that $\overline{M}_N$ was found to be relatively independent of initiator concentration, a result which differs significantly from the general Smith-Ewart theory of emulsion polymerization. It has been observed by Peggion et al (1964) as well as Ugelstad et al (1969) however, that the number of polymer particles remained constant for conversions greater than 5-10% and that the number of particles was also essentially independent of the initiator concentration. If the additional premise that the fraction of the particles containing a radical is very small, is considered valid, then an explanation for the observed behaviour is possible. The predominant mechanism for termination may not be by radical-radical interaction but by desorption of radicals, especially for PVC where transfer to monomer is known to take place (Ugelstad and Mork, 1970; Ugelstad et al, 1971). Assuming that the reaction time for those few particles containing active radical chains is similar, it might be expected that PVC molecular weights would likewise be similar and independent of initiator concentration. One may also observe from Figure 21 that $\overline{M}_w$ increased slightly with increasing initiator concentration. This increase may indicate the onset of cross-linking or chain-transfer to polymer even though the overall conversion was less than 30%.

The anticipated effects of initiator concentration upon PVC reaction rate and conversion are shown in Figures 22 and 23. For otherwise similar conditions, the amount of PVC produced increases with increasing initiator concentration. As with varying emulsifier concentration, the curvature of the conversion-time relation shown in Figure 22 would indicate the typical autoacceleration characteristic of emulsion polymerization of PVC. Polymerization rates determined both by taking slopes (differentation method) at a conversion of 100 g PVC/l water, and by actual rates obtained by calorimetry are shown in Figure 23. The PVC reaction rates increase with increasing initiator concentration as expected. The estimated relation between rate and initiator concentration is to the half-order, that is, $\overline{r}_p \propto [I]^{\frac{1}{2}}$. This compares with a range of orders obtained by other workers using different emulsifiers. Peggion et al (1965) reported 0.6 to 0.7, Giskerhaug (1966) 0.5, Gerrens et al (1967) 0.8, while Ugelstad et al obtained an order of 0.5. It is apparent that the emulsifier used, as well as the conversion achieved has some bearing on the effect of initiator concentration.

The rates of PVC production at the constant conversion of 100 g/l, as well as the initial rates, versus the emulsifier and initiator concentrations are plotted in Figures 20 and 23 respectively.

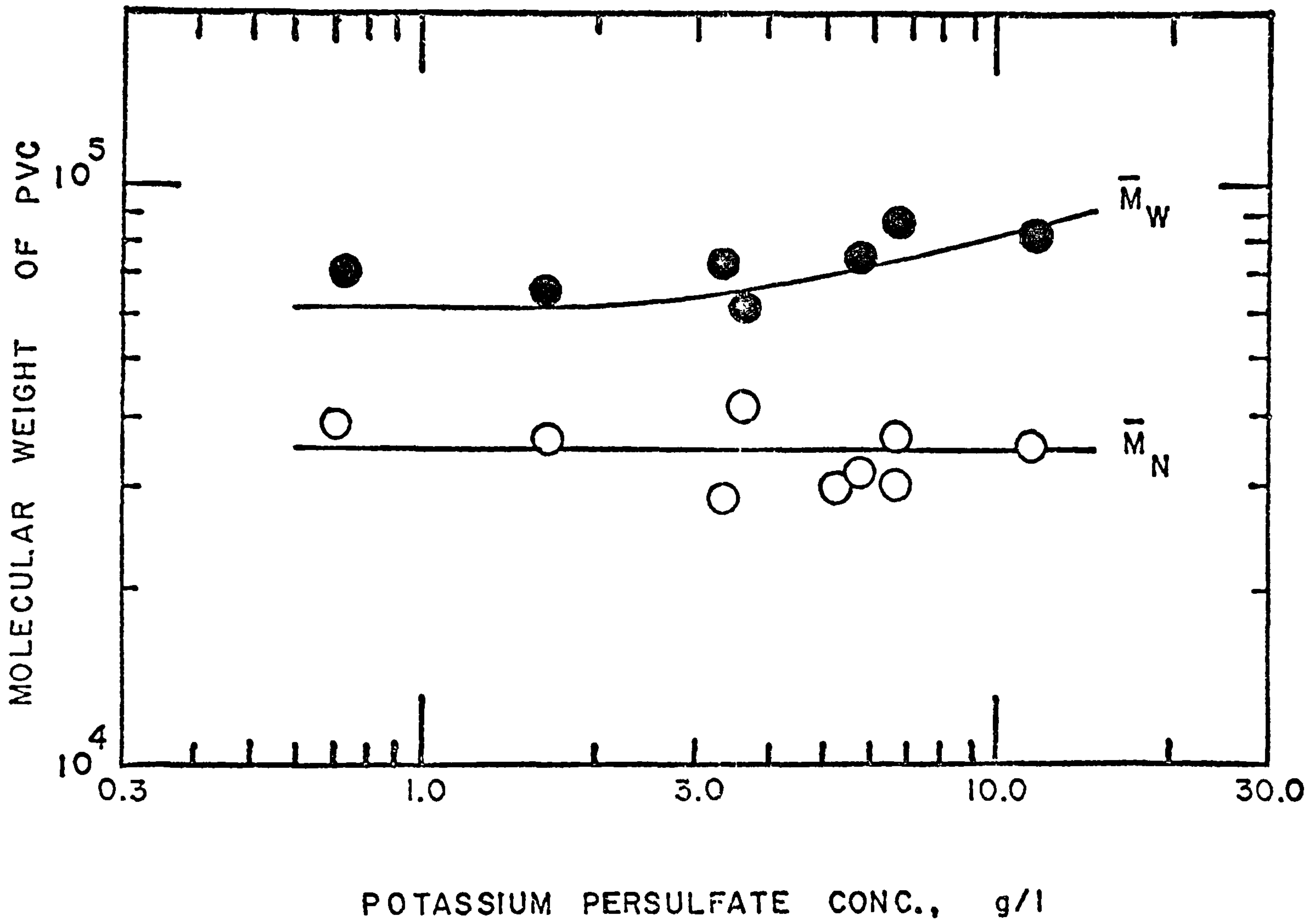


Figure 21 - Effect of a variation in initiator concentration upon PVC molecular weight, at constant emulsifier concentration and conversion of 30 ± 5%.

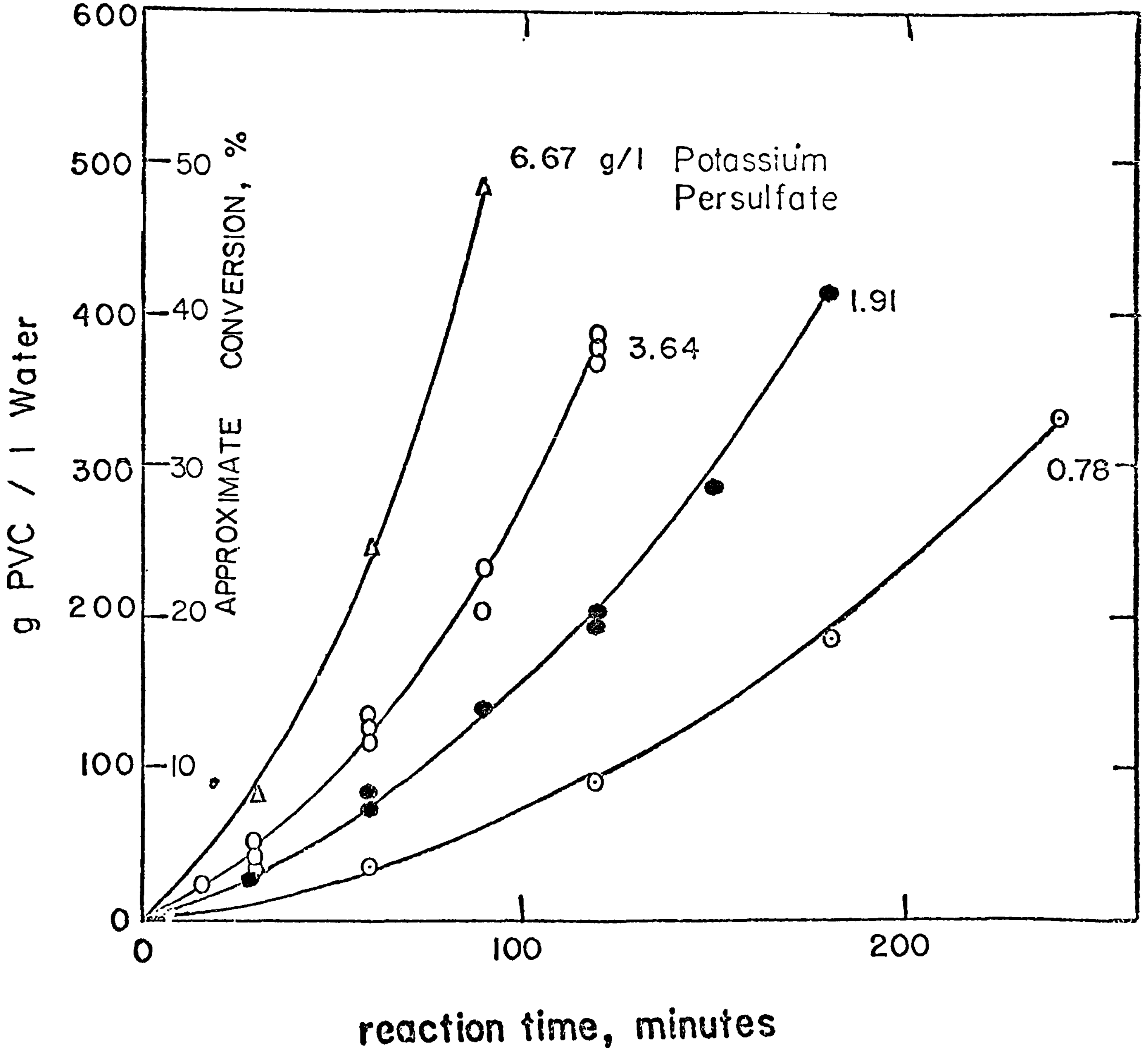


Figure 22 - Effect of a variation in initiator concentration on the cumulative mass product of PVC, at constant emulsifier concentration.

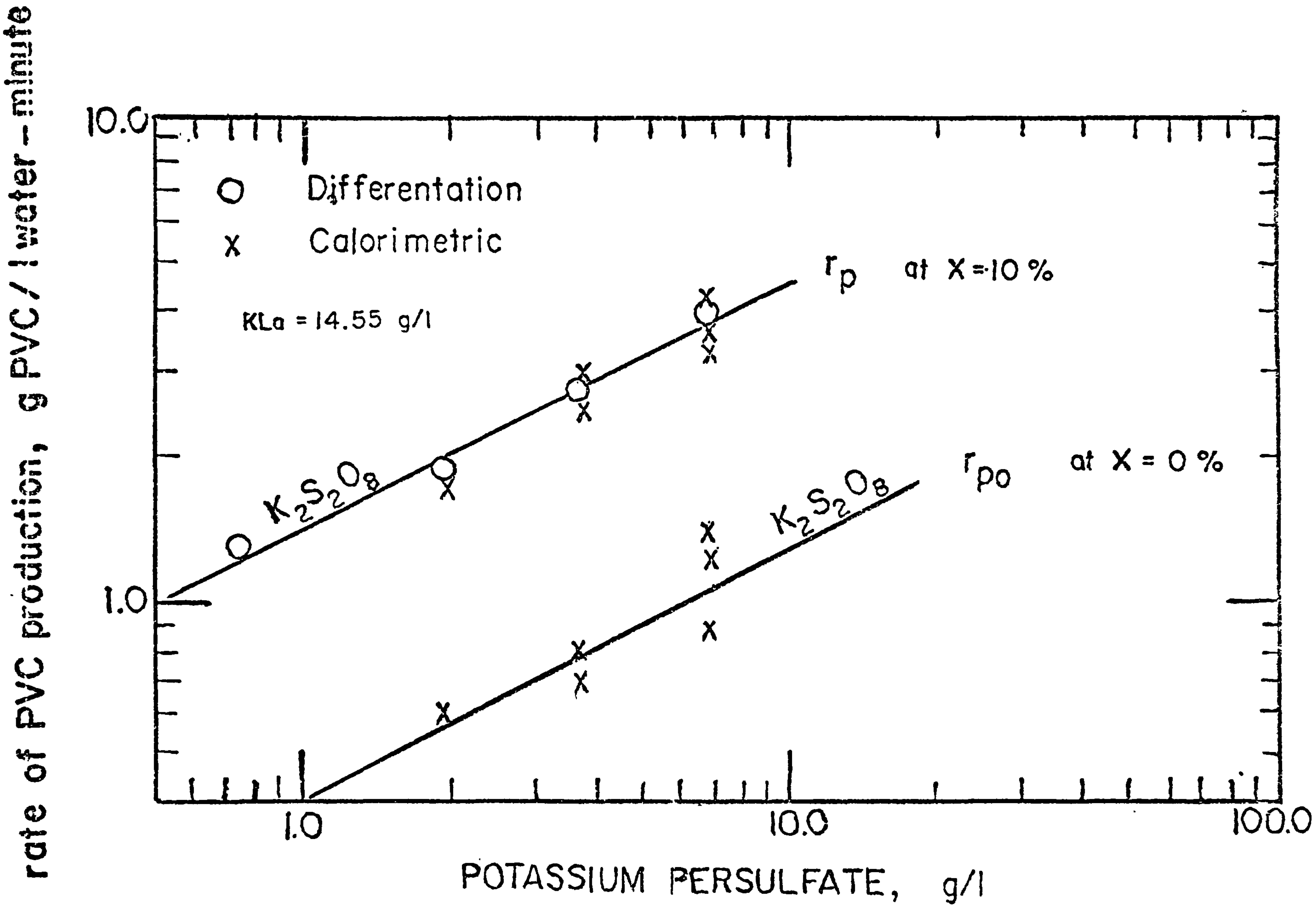


Figure 23 - Effect of a variation in initiator concentration upon the rate of PVC production at constant emulsifier concentration.

The rate was found to be approximately proportional to the ½ power of the initiator concentration. Assuming that the initiator efficiency is constant, the ½ order is compatible with that given by Ugelstad and Mork (1970) in Equation 10. The rate was also found to be approximately proportional to the ½ power of the emulsifier concentration. The dependence of rate upon emulsifier concentration cannot be stated directly from Equation 10 as the relationship between emulsifier concentration, E, number of particles, N and particle volume, V_p is not explicitly stated but would probably depend on the soap used. Experiments by Ugelstad et al (1969) have shown that the order of reaction lies between 0.3 and 0.5 with respect to V_p, and between 0.05 and 0.15 with respect to N.

For the purpose of reactor control the heat of polymerization for PVC is of great interest, especially since it is considered to be the highest of all the common polymers. A range of heats of VCM polymerization may be found in the literature corresponding to the experimental difficulties involved. Leonard (1971) reported a value of 25.8 Kcal/mole. Matthew (1972) quoted a value of 22 Kcal/mole from one author but stated that the best value is approximately 30 Kcal/mole. From the present calorimetric studies, the calculated heats of polymerization appear to decrease with increasing conversion indicating perhaps that a linear correction should be applied to the heat base line to correct for changing heat transfer characteristics of the latex. A linear plot of the heat of polymerization versus final conversion was extrapolated to a ΔH_p corresponding to zero conversion. This plot, shown in Figure 24, yield an extrapolated value of 27.8 Kcal/mole ± 0.8 Kcal/mole.

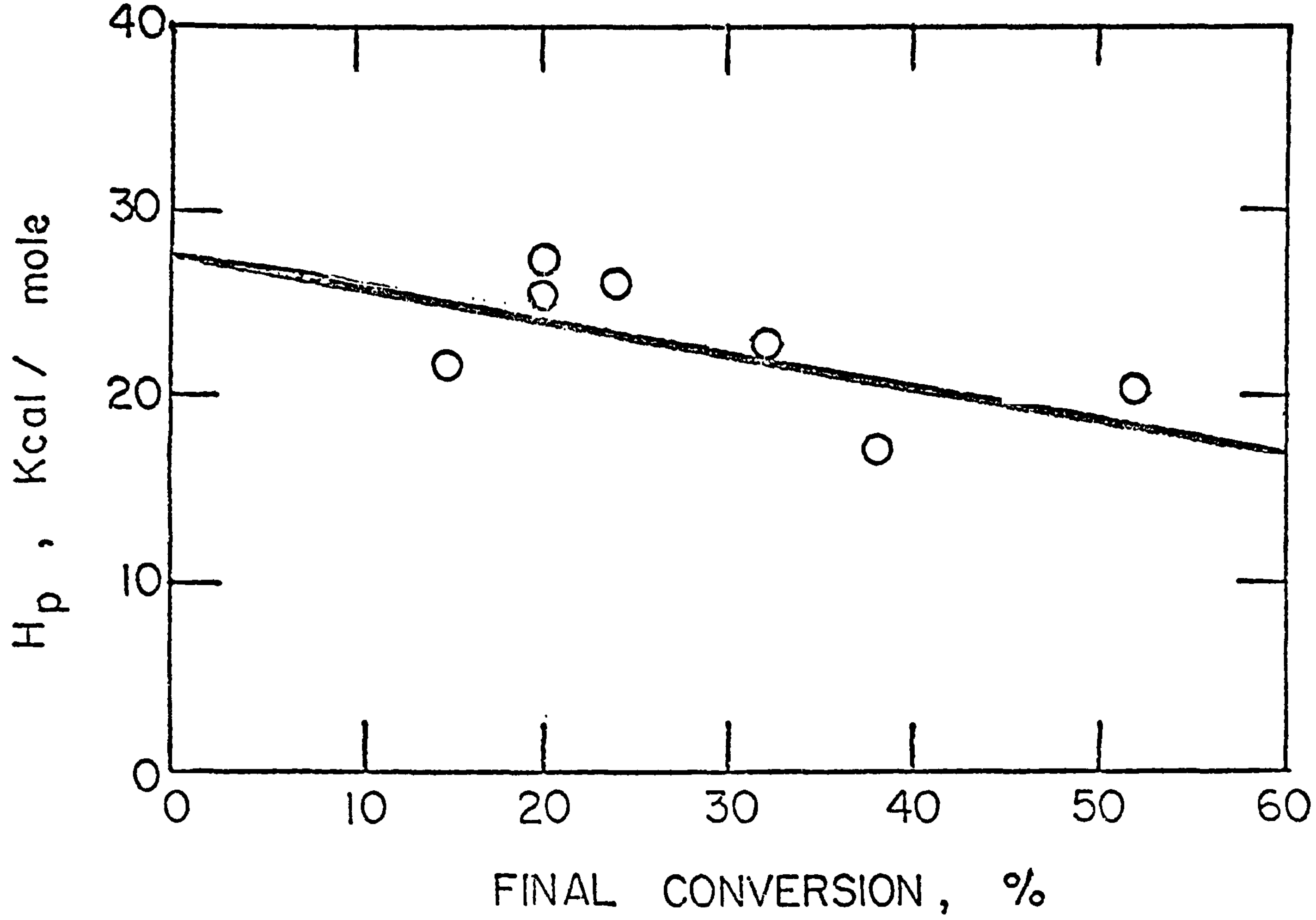


Figure 24 - Heat of polymerization versus final conversion.

Reaction rate data were obtained by substituting the ΔH_p values into Equation 11 and calculating the PVC production rate for successive 10 minute periods as applied to the reaction as it proceeded. The PVC production rate at a conversion corresponding to 100 g PVC/l water is compared in Figures 20 and 23 with those values obtained by taking the slope of the conversion-time curves. Thus substantial agreement between the two methods for obtaining reaction rate data was obtained.

The conversion is shown in Figure 25 with the values obtained by sampling for comparison. Agreement between the two methods is good at low conversions but deviations increase as the conversion increases. There are two possible reasons for the discrepancies. First, the calorimetric data may be in error since only a linear correction for heat transfer characteristics, depending on associated viscosity increases, density increases, etc., was used in the calculations. Secondly, the sampling data may be in error. Because each sample withdrawn could represent up to 5-6% of the emulsion volume, withdrawing of three or four samples during the course of the reaction probably reduced the water/VCM ratio since the sample was taken near the bottom of the reactor, thus modifying the kinetics for the remaining emulsion. This would give the effect of a higher conversion than it would if no sampling had taken place. The latter explanation appears more likely.

Initial reaction rate data were also obtained by means of the calorimetric measurements. The rate data obtained from the calorimetric measurements were extrapolated to zero time or zero

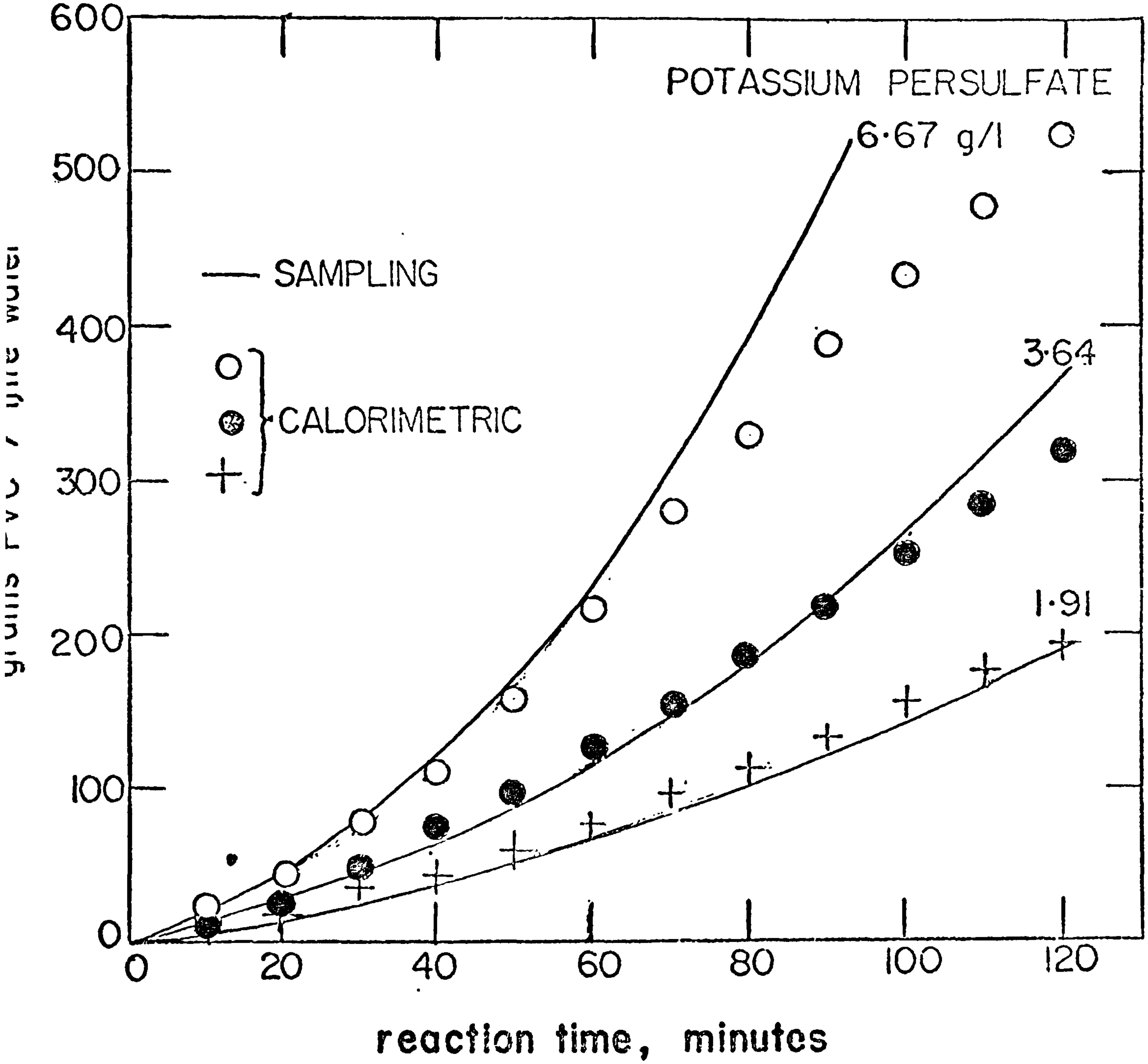


Figure 25 - Cumulative mass product of PVC is determined by calorimetry and by sampling.

conversion to obtain initial rates of polymerization, r_{po}. The initial rates, also plotted in Figures 20 and 23, exhibit a larger scatter in their values, which are indicative of the difficulties in accurate extrapolation.

For the purpose of interpretation of the calorimetric rate data, taken at varying initiator and emulsifier concentrations and reaction times, the rates were normalized at the particular conversion with respect to the initial rates. The plot of r_p/r_{po} versus X is shown in Figure 26. The dimensionless rate increases with increasing conversion up to about 30-40% conversion, indicating autoacceleration of the reaction rate. Having reached a peak, the rate then decreases and it would be expected that at 100% conversion the rate would be zero and the data were extrapolated accordingly. This peak in the rate-conversion curve has been noticed by other researchers but usually at higher conversions. Also shown in Figure 26 are plots of r_p/r_{po} obtained by graphical differentiation of conversion-time data found in the literature. A fairly definite trend can be noticed with the number of particles, N, being the correlating parameter. The value for N for the present work was estimated as will be explained later. It would be expected that the more particles, the greater the number of polymerization sites and the fewer radical-radical terminations so that a slowly increasing concentration of active sites would result. The data which span a four-fold initiator concentration range, can be reasonably correlated by a single curve indicating that the number of particles may be independent of initiator concentration. This dependence has been experimentally verified by several authors (Ugelstad et al, 1969; Ugelstad et al, 1973 b).

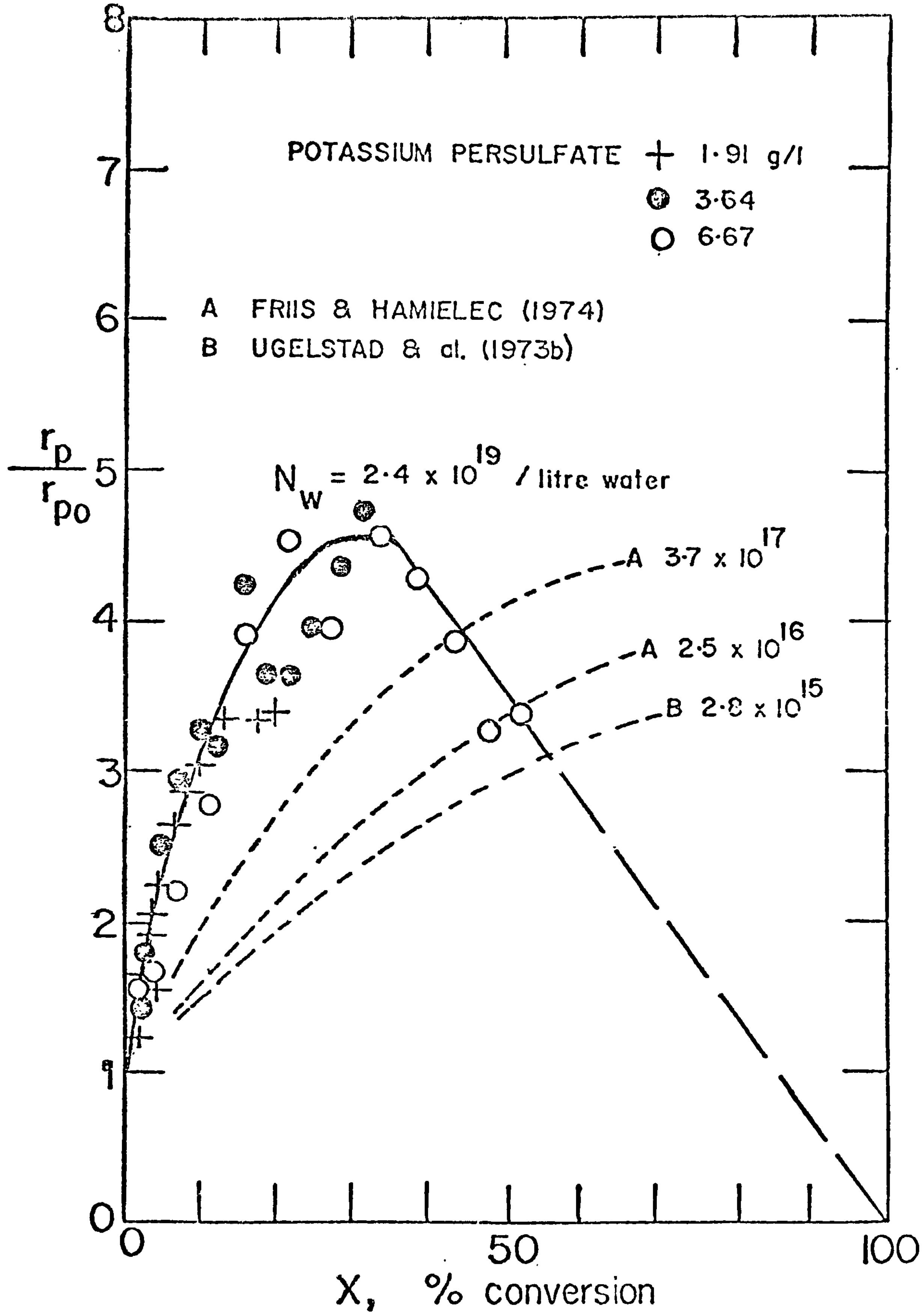


Figure 26 - Normalized rate of polymerization versus conversion.

In the present study, it was supposed that the peak in the r_p/r_{po} versus X curve is indicative of a slowing in the reaction rate brought about by the increasing latex viscosity. Horie et al (1968) have indicated that the propagation rate constant, k_p, is likely to be proportional to the monomer diffusivity. As monomer diffusivity decreases, k_p and hence the rate is likewise reduced. At low conversions, the availability of free radicals limits the reaction rate while at higher conversions, the availability of monomer or monomer diffusion effect predominates so that the reaction becomes essentially diffusion controlled. Even though this change in rate controlling step occurs at low conversion, apparently radical chain activity continues for a sufficient time period so that PVC molecular weights are little affected. At higher conversions (>60%), when the free monomer phase has disappeared entirely and latex viscosity is high, cross-linking and gel formation begins.

Utilizing the plot of r_p/r_{po} versus X, and that for r_{po} versus emulsifier concentration, it was possible to predict the conversion history for any emulsifier concentrations. Predicted conversions are shown in Figure 27 for two emulsifier concentrations and compared with experimentally determined values. The predicted conversions compare most favourably with the measured conversions, especially for the lower emulsifier concentration.

Since the number of polymer particles, N, was not measured in this study, the method used for estimating this number will now be described. It has been noted by several authors that the number of particles is independent of the initiator concentration. However, it is certainly a function of emulsifier concentration. Ugelstad et al (1971) have

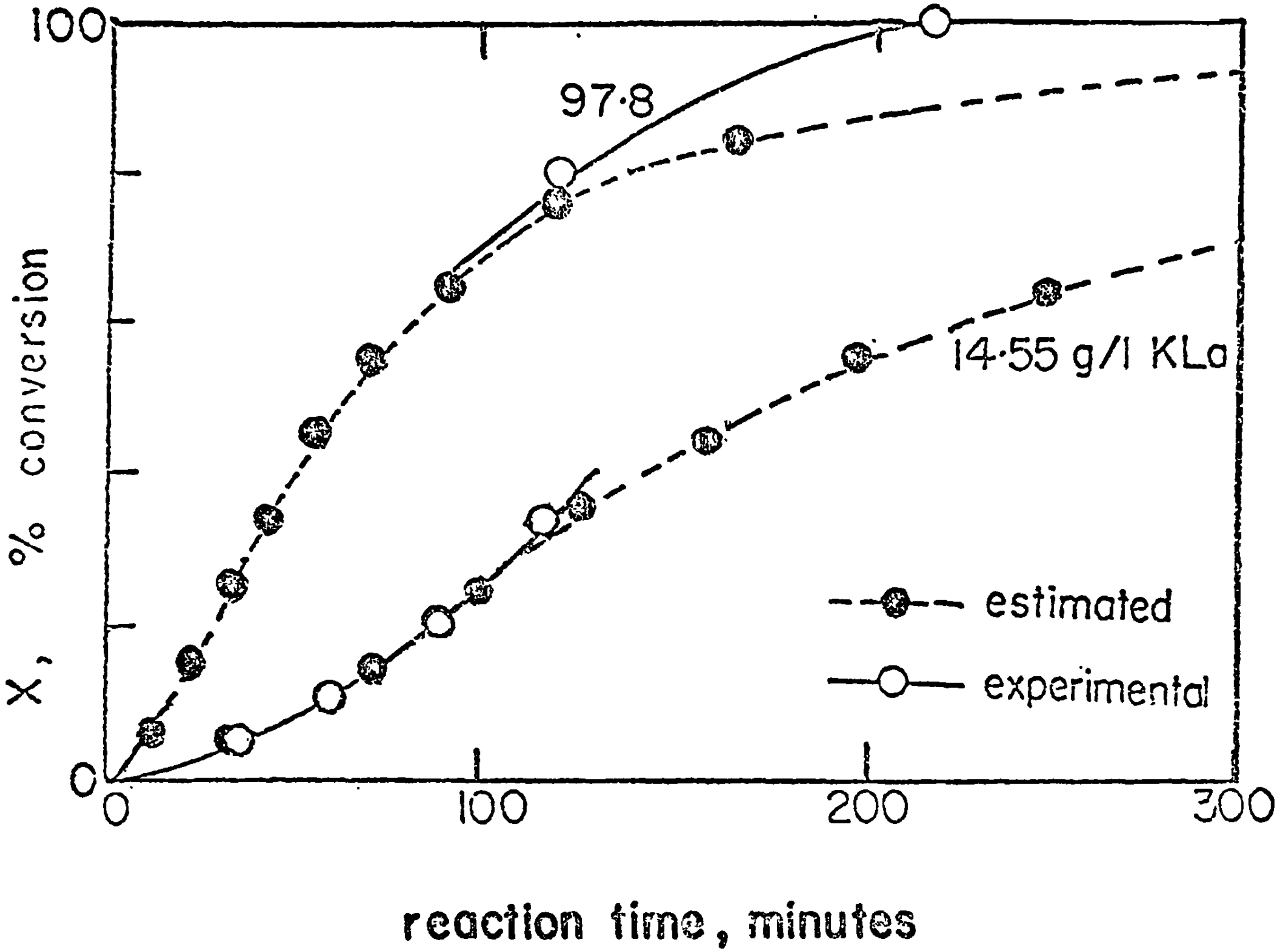


Figure 27 - Conversion history of a VCM emulsion polymerization.

published a correlation for the reaction rate versus the number of polymer particles for a large number of various soaps. Using this graphic correlation, N was determined for the corresponding emulsifier concentrations. The actual values are given in Appendix G. From this data, it was determined that the number of particles was approximately proportional to the 3rd power of the emulsifier concentration. Combining this relationship with the emulsifier-rate relationship, it can be determined that the reaction rate varies with the 1/6 power of N, which, to a first approximation, is that obtained from Equation 10. By combining the present data with the data from the literature, the following relationships were obtained:

$$N \alpha [E]^3 \ [I]^0 \tag{19}$$

$$\bar{r}_p \alpha \ N^{1/6} \ [E]^{\frac{1}{2}} \ [I]^{\frac{1}{2}} \tag{20}$$

With the exception of the 1/6 exponent for N, Equation 20 describes the emulsion polymerization system of Medvedev and Sheinker as described by Odian (1970). They proposed an exponent for N of 1/5. In their system the reaction was considered to occur on the particle surface because, the radicals had difficulty in penetrating the interior of the particles due to the high viscosity inside the particles. For conversions exceeding approximately 30%, the latex viscosity was found to increase by a factor of 4, which resulted in a decrease in the diffusion rate of radicals and free monomer. The viscosity inside the particles was estimated from data given by Omi et al (1973). At an approximate conversion of 30%, the viscosity inside the polymer particles was estimated to increase by a factor of 20. Although based on styrene emulsion polymerization, a comparable order of magnitude increase would be reasonably expected for VCM emulsion polymerization, giving the polymer particle a very high internal viscosity. For the reaction occurring on the surface of the polymer particles, the reaction rate was considered to be linearly dependent on the total particle surface area.

According to Odian (1970), polymerizations in which the polymer is insoluble in its own monomer and where the monomer has an appreciable water solubility - both are descriptive of VCM - are usually best described by the Medvedev-Sheinker theory. In this theory it was suggested that N was large, that is, greater than 3×10^{17} particles per liter. In the present work N was estimated to be in the range from 10^{18} up to 2×10^{20} particles per liter. This certainly was larger than the aforementioned minimum and generally about 100 times larger than the number of particles obtained in the recent studies of Ugelstad et al (1973 b) and of Friis and Hamielec (1974) for which N varied from 10^{17} to 10^{18} particles per liter. The present work is considered to encompass an experimental region of large particle numbers not usually reported in the literature. The apparent large number of particles generated is judged to be a result of the small volume of reactant emulsion combined with the thorough agitation produced by the unique plunger method of mixing.

To estimate the size of the polymer particles, the data of Giskehaug (1966) were linearly extrapolated to larger particle numbers. Based on this extrapolation the size of the polymer particles was estimated to be 4 to 25 mμ. The large number of particles and their small size would indicate the possibility of a reaction on the surface of the particles as proposed by the Medvedev-Sheinker theory. The small particle size may also result in a rapid desorption and re-absorption of radicals, as proposed by Ugelstad and Mork (1970). This mechanism implies that a very small fraction of the particles actually contain a radical on the surface or in the interior, at any given time. This fraction of the particles, $\bar{n}$, may be estimated from Equation 21.

$$r_p = \frac{k_p \, C_M}{N_A} \cdot \bar{n} \cdot N \tag{21}$$

From the literature, C_M and k_p are taken as 6 moles/liter and 3.6 x 10^7 1/mole-hr respectively (Ugelstad et al, 1969). The value of N was taken from a correlation of Ugelstad et al (1971). Utilizing the reaction rates measured in this work, the value of $\bar{n}$ was estimated to be between 4.6 x 10^{-5} to 5.2 x 10^{-2} (Appendix G).

To estimate the extent of chain transfer to monomer, an equation developed by Friis and Hamielec (1974) was applied:

$$\bar{M}_N = \frac{m_o\left(1 + \frac{k_p^*}{k_p} * X_c\right)}{(1-X_c)\left[\frac{k_{fm}}{k_p}\right]} \tag{22}$$

Assuming that k_p^* was essentially zero for low conversions, the literature value for k_p was 3.6 x 10^7 1/mole-hr, and utilizing a typical value for $\bar{M}_N$ of 35000 found in the present study, and X_c as 0.7, the value of the rate constant for monomer transfer, k_{fm}, was found to be about 3500 l-mole/hr. This value for k_{fm} is about 5 times the literature value of 660 l-mole/hr (Friis and Hamielec, 1974). Therefore, in the present study, it was estimated that transfer to monomer occurred to a much greater degree than usual, resulting in a low molecular weight PVC product.

For the present work, a general overview of the reaction can be summarized as follows. The emulsion polymerization system consists of a dispersion of soap micelles and monomer droplets in an aqueous medium containing an emulsifier and a buffer, potassium laurate and potassium bicarbonate respectively. An initiator, potassium persulfate is added. The initiator thermally decomposes at 50^{o} C to form free radicals. A free radical diffuses to a micelle where it reacts with a VCM molecule to start the polymerization process and to form a growing polymer particle. These growing polymer particles are smaller than those usually described in the literature, possibly because of the method of mixing, and at any given moment only a small fraction of the particles will contain a radical. Hence, it is suggested that the radicals are absorbed, desorbed and then re-absorbed by the polymer particles very quickly. In fact, some of the reaction may take place on the surface of the particles. As the reaction procedes, VCM diffuses from the monomer droplets, which act as VCM reservoirs, to the growing polymer particles. There is substantial transfer to monomer so that the PVC produced has low molecular weight and also has low polydispersity ($\sigma<2$) at low conversions of less than 30%. The reaction is autocatalytic up to about 30-40%. At higher conversions, little free monomer is available and the reaction is probably controlled by the diffusion of VCM to the polymer particles, especially as the emulsion thickens. As a result, the reaction rate decreases and at higher conversions, branching and cross-linking of the PVC molecules occur. At very high conversions, gel formation takes place and the emulsion solidifies.

CONCLUSIONS

Solubilities of VCM in water and aqueous potassium laurate solutions have been determined at and above atmospheric pressure from 0 to 50^{o} C. These data were interpreted to determine VCM concentrations in potassium laurate emulsions at saturation. Diffusivities of VCM in water and aqueous potassium laurate solutions were also determined. An empirical relationship between VCM solubility and diffusivity in potassium laurate solutions was determined and micelle molecular weight was estimated from experimental measurements of aqueous potassium laurate solution properties.

A moderate pressure polymerization reactor was developed which would appear to be useful for emulsion polymerization studies. The effect of the process variables of reaction time, temperature, VCM concentration, emulsifier concentration and initiator concentration upon molecular weights, $\overline{M}_N$ and $\overline{M}_W$ and upon polymerization reaction rates have been determined. At conversions of less than 50%, PVC molecular weights are essentially independent of initiator and emulsifier concentrations.

Polymerization rates were obtained by both calorimetric and gravimetric methods. It was determined that the kinetics were similar to those proposed by Medvedev and Sheinker and polymerization probably takes place by a rapid desorption and re-absorption of radicals by the polymer particles as proposed by Ugelstad and Mork (1970). Their kinetic scheme was considered applicable because its requirements were observed in the present experimental work, such as: VCM is fairly soluble in water. PVC is insoluble in its own monomer, VCM. The number of particles is large, greater than 10^{18}. The particle size is small, less than 12 mμ, so that some of the reaction may occur on the particle surface. The number of radicals per particle is much less than unity, less than 10^{-2}. The reaction is autocatalytic. The reaction rate is proportional to the emulsifier and initiator concentrations to the ½ power. In conclusion, it was determined that the reaction rate dependence upon the process variables can be best summarized by the following equation:

$$\overline{r}_p \alpha N^{1/6} [E]^{\frac{1}{2}} [I]^{\frac{1}{2}} [M]^3$$

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APPENDIX A

Compressibility of VCM

Compressibility of VCM

The compressibility apparatus consisted essentially of a calibrated 100-ml volumetric pump (Rusha Instrument Corp.) equipped with a vernier readable to 0.01 ml, connected to an absolute pressure transducer (Statham Model PA 822). Equipment details and operation have appeared in the literature (Hayduk and Laudie, 1974 b). The compressibility of VCM is given in Table 3.

TABLE 3

VINYL CHLORIDE GAS COMPRESSIBILITY

Pressure, atm At 0° C	Z	Pressure, atm At 50° C	Z	Pressure, atm At 75° C	Z
0.52	0.988		0.990	0.68	0.992
1.00	0.974	0.68	0.985	1.00	0.988
1.18	0.969	1.00	0.983	1.59	0.981
1.41	0.956	1.22	0.969	2.26	0.972
1.65	0.933	1.88	0.958	2.71	0.965
1.71	0.905	2.57	0.948	3.41	0.954
		3.26	0.938	3.90	0.946
At 25° C		3.80	0.932	4.42	0.939
		4.14	0.916	5.40	0.922
1.00	0.981	5.06	0.900	6.07	0.911
1.43	0.975	5.67	0.879	6.91	0.892
1.67	0.969	6.43	0.850	8.02	0.869
2.27	0.961	7.22	0.820	9.49	0.830
2.95	0.945	7.55	0.700	10.20	0.808
3.41	0.916	7.97			
3.65	0.888				
3.90	0.846				

APPENDIX B

Solubility of VCM in Water and in Aqueous Potassium Laurate Solutions

Solubilities of VCM

Solubilities of VCM, expressed as Ostwald coefficients, were calculated from the measured volume of vapor-free gas required to saturate the corresponding solvent volume by means of:

$$L = \frac{V'_G \; P_t}{V'_L \; (P_t - P_1 \; (1-x))}$$

where: L Ostwald coefficient, volume gas, cm^3/volume solution, cm^3

V'_G volume of vapor-free gas, cm^3

P_t total pressure, atm

V'_L volume of liquid, cm^3

P_1 solvent vapor pressure, atm

x gas solubility, mole fraction

The mole fraction solubility was determined by:

$$x = \frac{L/V_G}{\frac{L}{V_G} + \frac{1}{V_L}}$$

where: V_G molar volume of gas

V_L molar volume of liquid

An iterative calculation process for L and x was used until the difference in successive calculated values of x were small (10^{-7}). Gas molar volumes were calculated from compressibility measurements.

The solubilities of VCM in water and aqueous potassium laurate solutions are given in Tables 4 and 5. The description of the equipment used and its method of operation may be found in the literature (Hayduk and Laudie, 1974 b). For the tables:

L	Ostwald coefficient, volume gas cm^3/volume solution cm^3
x	mole fraction solubility at a gas partial pressure equal to the total pressure
( )	percent increase of solubility in soap solutions as compared to solubility in water $((x_s - x_w)/x_w) \times 100$

TABLE 4

Solubility of VCM in Water

Temp 0° C		Total Pressure, atm			
		1.00	1.36	3.06	6.12
0.2° C	L	2.645	2.15	-	-
	$(10^4)x$	21.74	23.67	-	-
25° C	L	1.067	-	0.868	-
	$(10^4)x$	7.98	-	20.50	-
50° C	L	0.0603	-	0.543	0.473
	$(10^4)x$	4.11	-	11.97	22.42
75° C	L	0.361	-	0.340	0.349
	$(10^4)x$	2.25	-	6.97	15.20

TABLE 5

Solubility of VCM in Aqueous Potassium Laurate Solutions

	Potassium laurate		Temp, °C		
Press	Concn, g/l.		25	50	75
Atmospheric	0.1	l	1.09	0.612	0.363
		$(10^4)\ x$	7.92 (1.7)[a]	3.77 (2.4)	1.47 (0.4)
	0.5	l	1.12	0.637	0.376
		$(10^4)\ x$	8.15 (4.6)	3.94 (5.8)	1.52 (4.0)
	1.0	l	1.14	0.667	0.387
		$(10^4)\ x$	8.30 (6.5)	4.08 (11.0)	1.56 (6.9)
	5.0	l	...	0.811	0.515
		$(10^4)\ x$	...	4.99 (35.3)	2.09 (43.2)
	10.0	l	...	0.935	0.698
		$(10^4)\ x$	...	5.78 (57.0)	2.80 (91.8)
	15.0	l	...	0.989	0.792
		$(10^4)\ x$	...	6.15 (67.1)	3.29 (125)
3.06 atm	1.0	l	...	0.610	...
		$(10^4)\ x$	...	12.9 (11.2)	...
	10.0	l	...	0.859	...
		$(10^4)\ x$	...	18.3 (59.1)	...
6.12 atm	1.0	l	...	0.530	...
		$(10^4)\ x$	...	24.6 (11.3)	...
	10.0	l	...	0.732	...
		$(10^4)\ x$		34.3 (55.2)	...

[a] Values in brackets indicate percentage increase in solubility compared with that in water.

APPENDIX C

Diffusivity of VCM in Water and in Aqueous Potassium Laurate Solutions

Diffusivity of VCM

The diffusivities were determined by means of the steady-state diffusion cell developed by Malik and Hayduk (1968) in conjunction with the following equation:

$$D = \frac{A_1}{A_2} \times \frac{h}{60.0} \times \frac{P_2M_2}{V_2} \times L/\rho \ln \left[\frac{1+w_2^0}{1+w_2^L}\right]$$

where

D	diffusion coefficient, cm^2/sec
A_1	cross sectional area of small capillary, cm^2
A_2	cross sectional area of large capillary, cm^2
h	rate of travel of bead down the capillary, cm/min
L	diffusion path length, cm
M_2	molecular weight of VCM
P_2	partial pressure of VCM
V_2	molal volume of VCM
ρ	total mass concentration of solution, gm/cm^3
w_2^0	mass fraction of VCM at gas-liquid interface
w_2^L	mass fraction of VCM in bulk of solution

The diffusivity of VCM in water and in aqueous potassium laurate solutions is given in Table 6. The diffusivity of VCM in water Table 6 and the correlations of Othmer-Thakar (1953) and Hayduk-Laudie (1974 a) are shown in Figure 23. Experimental details are available in the literature (Hayduk and Laudie, 1974 a).

TABLE 6

Diffusivity of VCM in water and aqueous potassium laurate solutions.

In water

Temp °C	Diffusivity cm^2/sec x 10^5
0	0.70
25	1.33
50	2.43
75	3.67

In aqueous potassium laurate solutions at 50° C

Potassium laurate g/l	Diffusivity cm^2/sec x 10^5	$\frac{D_s}{D_w}$	$\frac{x_w}{x_s}$
water	2.43	1.0	1.0
0.1	2.38	0.98	0.98
0.5	2.26	0.93	0.95
1.0	1.98	0.81	0.90
5.0	1.32	0.54	0.74
10.0	0.78	0.32	0.64
15.0	0.55	0.23	0.60

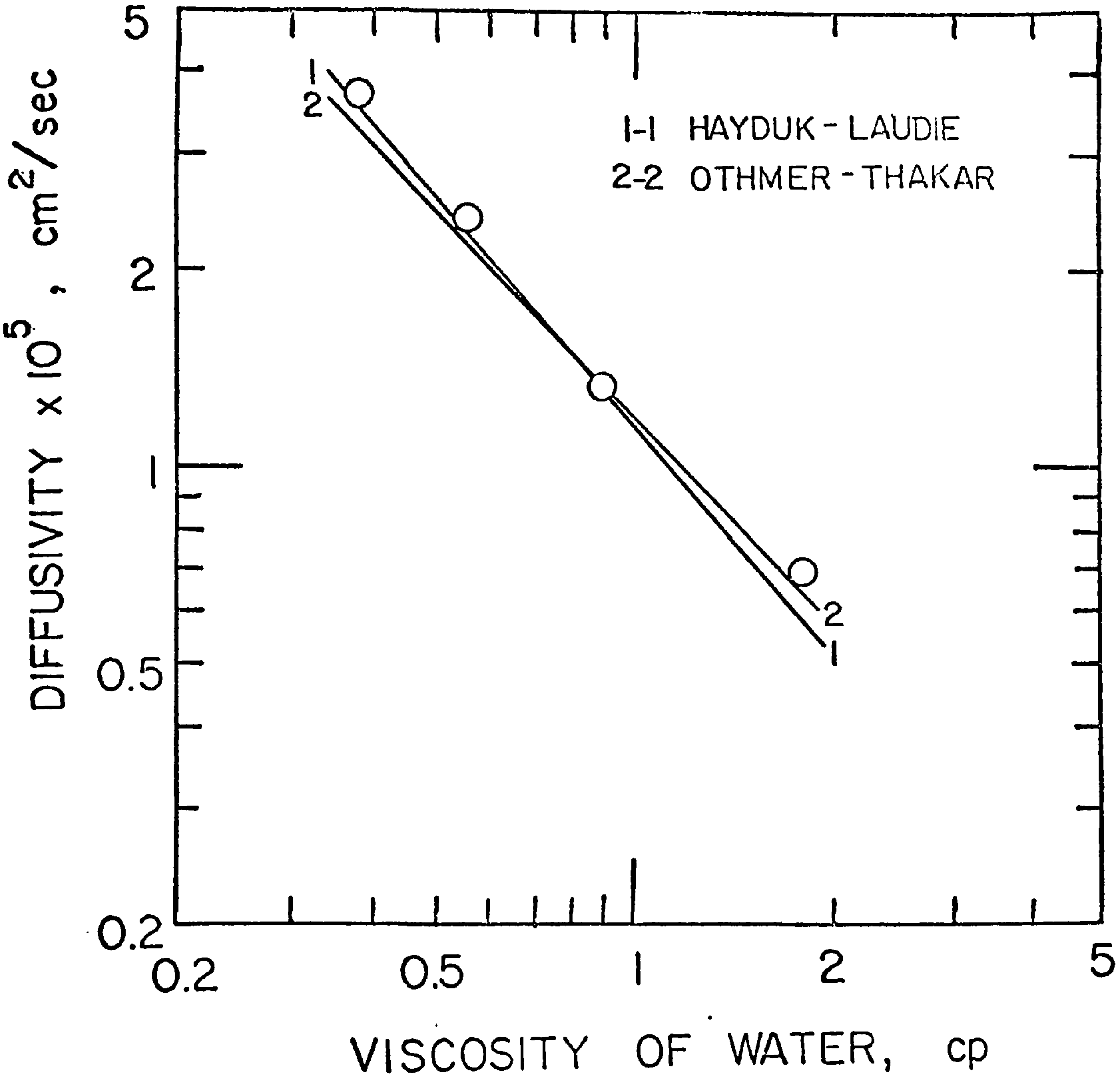

Figure 28 - Diffusivity of VCM in water as correlated with the viscosity of water.

APPENDIX D

Physical Properties of Aqueous Potassium Laurate Solutions

TABLE 7

Physical Properties of Aqueous Potassium Laurate Solutions at 50°C

C	σ	π	π/c	$\kappa \times 10^6$	$\frac{\kappa}{C} \times 10^6$	Λ	$\Delta n \times 10^6$	$\frac{\Delta n \times 10^6}{C}$	pH	$\tau \times 10^5$	$H \times 10^{12}$	$\frac{Hc \times 10^5}{\tau_{excess}}$
0	68.11	-	-	10.6	-	-	0	-	-	9.063	-	-
0.1	36.27	4.09	40.9	54.5	545	131.45	12	120	7.968	9.717	1.571	0.024
0.5	26.90	6.82	13.64	185	380	89.21	31	62	7.662	10.861	0.4195	0.012
1.0	25.49	7.17	7.17	348	348	83.-0	70	70	7.895	12.363	0.5347	0.016
5.0	24.96	7.41	1.48	1350	270	65.08	496	99.2	9.473	27.291	1.074	2.941
10.0	24.96	7.62	0.76	2400	240	57.84	1038	103.8	9.850	46.648	1.176	3.128
15.0	24.96	8.08	0.54	3050	204	48.99	1564	104.3	10.201	65.845	1.186	3.134

TABLE 7 (continued)

Physical Properties of Potassium Laurate Solutions at 50° C

C g/l	ρ g/ml	η cp	$\frac{\eta_{sp}}{C}$ cp l/g	η/η_w
0	0.988070	0.5494	-	1.0
0.1	0.988085	0.5498	0.00728	1.0007
0.2	0.988129	-	-	-
0.25	0.988184	-	-	-
0.50	0.988284	0.5534	0.1451	1.0073
0.75	0.988317	-	-	-
1.0	0.988327	0.5559	0.01182	1.0118
2.5	0.988400	-	-	-
2.867	-	0.5587	0.00590	1.0169
4.818	-	0.5612	0.00446	1.0215
5.0	0.988504	0.5612	0.00430	1.0215
7.5	0.988635	0.5649	0.00376	1.0282
9.636	-	0.5695	0.00379	1.0366
10.0	0.988737	0.5701	0.00377	1.0377
15.0	0.988968	0.5825	0.00402	1.0603
21.372	-	0.6119	0.00532	1.1138

APPENDIX E

Molecular Weights of PVC

TABLE 8

Variation of PVC molecular weight during the reaction

Temperature	50^{o}C
Initiator	3.64 g/l
Emulsifier	14.55 g/l
VCM	0.0048 mole fraction

Time, hours	X	$\overline{M}_N$x10^3	$\overline{M}_W$x10^3	$\overline{M}_W/\overline{M}_N$
0.25	2	33.7	62.6	1.8
0.5	5	35.9	66.1	1.8
1.0	11	35.5	65.4	1.9
1.5	22	35.1	62.3	1.7
2.0	35	37.2	64.9	1.7
3.0	50	41.4	66.7	1.6
4.0	63	36.5	74.1	2.0
5.0	72	47.6	98.1	2.1
6.0	87	55.8	158.9	2.7
10.0	100	73.4	210.0	2.9

TABLE 9

Effect of a variation of VCM concentration upon PVC molecular weight.

Temperature	50^{o} C
Initiator	3.64 g/l
Emulsifier	14.55 g/l
Conversion	30%

Pressure atm	X_s mole fraction	$\overline{M}_N x10^3$	$\overline{M}_W x10^3$	$\overline{M}_W/\overline{M}_N$
1.0	0.000685	3.1	3.2	1.0
3.06	0.002000	12.0	12.3	1.0
6.12	0.003744	20.1	31.6	1.5
7.83	0.004858	29.0	60.9	2.1

TABLE 10

Effect of a variation in emulsifier concentration upon PVC molecular weight.

Temperature	50° C
Initiator	3.64 g/l
VCM	Saturated
Conversion	approximately 30%

Emulsifier, g/l	$\overline{M}_N \times 10^3$	$\overline{M}_W \times 10^3$	$\overline{M}_W/\overline{M}_N$
0.36	12.9	16.3	1.2
1.82	18.4	30.9	1.6
3.64	29.7	48.6	1.6
6.75	27.9	54.0	1.9
6.75	32.6	-	-
9.91	30.5	62.4	2.0
11.88	31.8	58.3	1.8
13.86	28.5	-	-
14.55	38.4	60.2	1.5
15.39	29.5	56.1	1.9
18.42	35.8	71.7	2.0
24.62	38.7	68.3	1.7

TABLE 11

Effect of a variation of initiator concentration upon PVC molecular weight.

Temperature	50^{o} C
Emulsifier	14.55 g/l
VCM	Saturated
Conversion	30% approximately

Initiator, g/l	$\overline{M}_N x10^3$	$\overline{M}_W x10^3$	$\overline{M}_W/\overline{M}_N$
0.72	39.7	71.1	1.7
1.67	36.3	65.8	1.8
3.33	28.5	74.5	2.6
3.64	38.4	60.2	1.5
5.33	30.4	-	-
5.80	31.8	73.9	2.3
6.67	30.5	-	-
6.67	36.7	88.1	2.4
11.43	35.2	81.7	2.3

TABLE 12

Effect of a variation in temperature upon PVC molecular weight

Initiator	3.64 g/l
Emulsifier	5.78 g/l
VCM	Saturated
Conversion	approximately 30%

Temperature, °C	$\overline{M}_N \times 10^3$	$\overline{M}_W \times 10^3$	$\overline{M}_W/\overline{M}_N$
25	53.9	156.0	2.8
30	44.3	111.6	2.5
40	39.2	78.1	1.9
50	29.5	61.0	2.0

APPENDIX F

Rate of Polymerization of PVC

TABLE 13

Cumulative Mass Product of PVC

Initiator	3.64 g/l
Temperature	50^{o} C

Emulsifier 14.55 g/l

Time Minutes	$\frac{\text{g PVC}}{\text{Liter Water}}$
15	21
30	44
60	126
120	382

30	39
60	122
90	235
120	369

0	1
30	37
60	137
90	204
120	378

Emulsifier 7.28 g/l

Time Minutes	$\frac{\text{g PVC}}{\text{Liter Water}}$
30	19
60	71
90	123
120	209
180	447

Emulsifier 3.64 g/l

60	30
120	125
180	255

Emulsifier 29.09 g/l

Time Minutes	$\frac{\text{g PVC}}{\text{Liter Water}}$
30	74
70	194
90	549

TABLE 14

Cumulative Mass Product of PVC

Emulsifier	14.55 g/l
Temperature	50° C

Initiator 3.64 g/l

Time Minutes	$\frac{\text{g PVC}}{\text{Liter Water}}$
15	21
30	44
60	126
120	382
30	39
60	122
90	235
120	369
0	1
30	37
60	137
90	204
120	378

Initiator 1.91 g/l

Time Minutes	$\frac{\text{g PVC}}{\text{Liter Water}}$
30	27
60	76
90	144
120	202
60	81
120	195
150	284
180	414

Initiator 0.78 g/l

60	35
120	92
180	185
140	332

Initiator 6.67 g/l

Time Minutes	$\frac{\text{g PVC}}{\text{Liter Water}}$
30	81
60	249
90	484

TABLE 15

Rates of PVC production obtained by graphical differention of cumulative mass of PVC curve.

Production of PVC 100 g PVC/l water

Emulsifier 14.55 g/l

Initiator g/l	0.78	1.91	3.64	6.67
Rate g PVC/l water-minute	1.34	1.89	2.72	4.00

Initiator 3.64 g/l

Emulsifier g/l	3.64	7.23	14.55	24.09
Rate g PVC/l water-minute	1.96	2.08	2.72	3.45

TABLE 16

Rates of Polymerization by Calorimetry

Initiator g/l	Emulsifier g/l	Final Conversion %	Heat of Polymerization kcal/g mole	Initial Rate gPVC/l water-minutes	Rate at Production of 100 gPVC/l water
1.91	14.55	20	27.3	0.6	1.8
3.64	14.55	32	22.8	0.8	2.6
3.64	14.55	24	26.1	0.7	2.9
3.64	29.09	20	25.6	1.7	3.5
6.67	14.55	15	21.2	1.4	3.4
6.67	14.55	38	17.2	1.3	4.3
6.67	14.55	52	20.2	0.9	3.6

TABLE 17

Rate of PVC Production versus Monomer Concentration

Temperature	50° C
Initiator Concentration	3.67 g/l $K_2S_2O_8$
Emulsifier Concentrations	14.55 g/l KLa

Pressure, atm	$x_s \times 10^4$	$\bar{r}_p$, g PVC/ $1H_2O$ - Min
1.0	6.85	.00775
	6.85	.0176
	6.85	.00854
	6.85	.0118
	6.85	.0252
3.06	20.00	.288
	20.00	.288
	20.00	.146
	20.00	.0885
	20.00	.199
6.12	37.44	1.19
	37.44	1.32
	37.44	0.719
	37.44	1.56
7.83	36.65	1.96
	41.60	2.08
	48.28	2.74
	51.70	3.45

APPENDIX G

Properties of the Emulsion Polymerization Latex

TABLE 18

Particle Density and Diameters

C gKla/l water	3.64	7.23	14.55	29.09
r_p gPVC/l water min	1.96	2.08	2.74	3.45
N # particles/l water	10^{18}	2.5×10^{18}	2.4×10^{19}	2×10^{20}
particle diameter mμ	1.2	.8	.4	.2
$\bar{n}$ # radicals per polymer particle	5.2×10^{-2}	2.3×10^{-3}	3.1×10^{-4}	4.6×10^{-5}

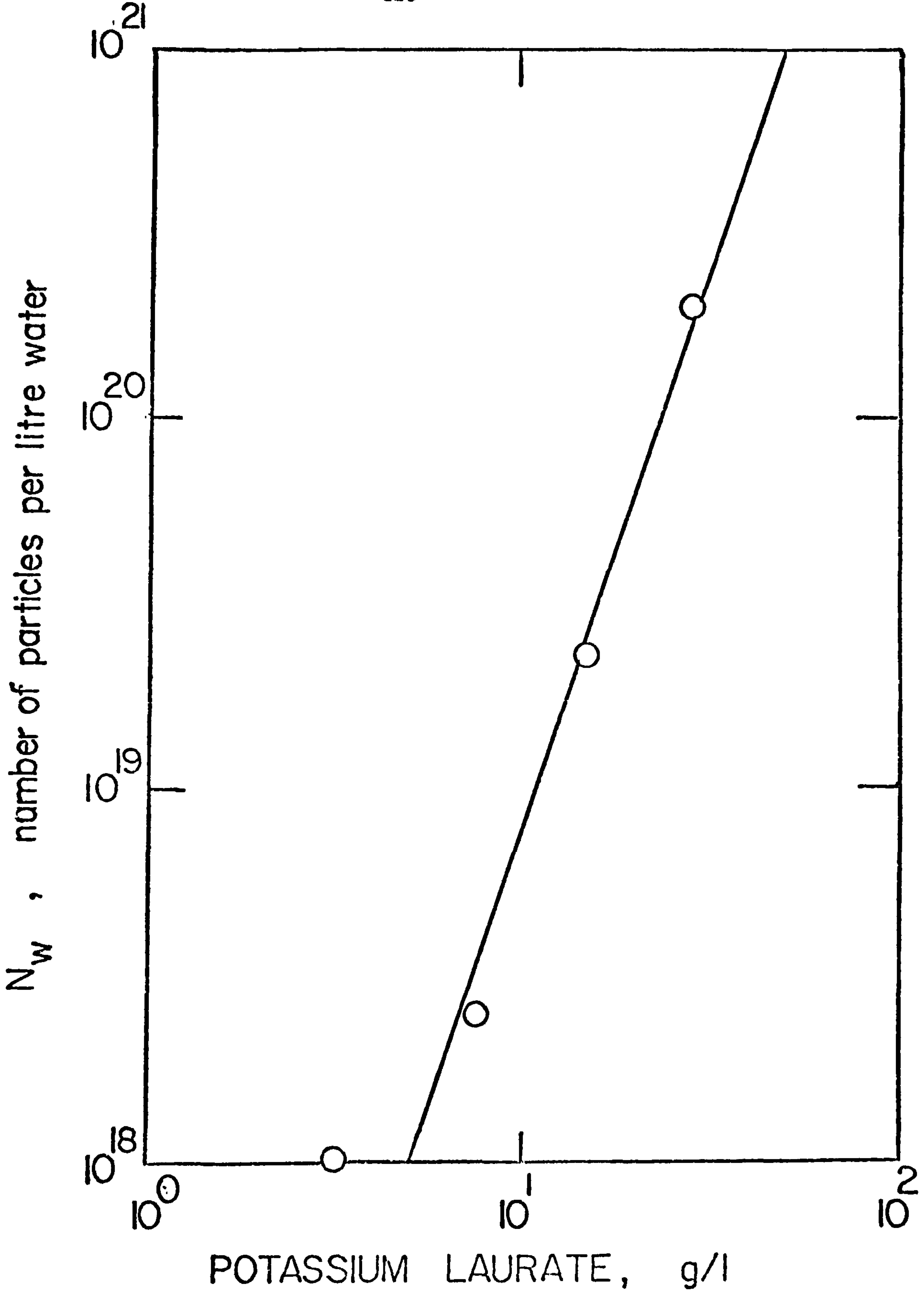

Figure 29 - Number of polymer particles versus the emulsifier concentration.

TABLE 19

Viscosity and Densities of Latexes

TIME Minutes	DENSITY g/ml	INCREASE %	VISCOSITY cp	INCREASE %
0	1.02307	0	0.6396	0
45	1.07339	4.9	0.9643	50.8
120	1.17964	15.3	2.3851	272.9
0	1.02854	0	0.6798	0
60	1.09612	6.6	1.2916	90.0
120	1.17305	14.1	2.6526	290.2

APPENDIX H

Molecular Weight of Micelles

Molecular Weights of Micelles

Micelles are polydispersed, similar to PVC, and hence are assigned molecular weight weighted averages as opposed to the potassium laurate soap which has a singular molecular weight of 238.4. The number average molecular weight is defined as

$$\overline{M}_N = \frac{\Sigma n_i M_i}{\Sigma n_i}$$

This $\overline{M}_N$ is calculated from osmotic pressure measurements obtained with an osmometer. The osmotic pressure of a solution depends only upon the number of molecules in solution. Applying van't Hoff's equation at infinite dilution, the number average molecular weight is

$$\overline{M}_N = R\ T\ /\ \lim_{c \to 0} (\pi/c)$$

where R is the gas constant

T is the absolute temperature

π is the measured osmotic pressure

c is the solution concentration

The approximate number of molecules of potassium laurate per micelle is obtained by dividing $\overline{M}_N$ by the molecular weight of a single potassium laurate molecule (238.4).

The weight average molecular weight is defined as

$$\overline{M}_W = \frac{\Sigma n_i M_i^2}{\Sigma n_i M_i}$$

The $\overline{M}_W$ was calculated from light scattering measurements. When the soap was dissolved in water, the light scattered by the micelles is greater than the light scattered by the pure water. It has been shown by Debye that the solution turbidity is proportional to the intensity of the scattered light and that turbidity is proportional to the weight average molecular weight of the substance dissolved in the solvent. The absolute turbidity is calculated from light scattering measurements made with a Brice-Phoenix light scattering photometer. The excess turbidity, τ, is also calculated. A function of the refractive index difference between solution and pure solvent, H, is also determined. The two functions are machine dependent and are related to the combination of light filters and of the color of the light used. The weight average molecular weight, $\overline{M}_W$, is determined from a linear plot of Hc/τ versus c by the equation

$$\frac{H_c}{\tau} = Ac + \frac{1}{\overline{M}_W}$$

where c is the soap concentration in the water. The polydispersity of the micelles is defined as

$$\sigma = \overline{M}_N/\overline{M}_W$$

APPENDIX I

Molecular Weights of Polymers

Molecular Weights of Polymers

Polymers are not of a single molecular weight and hence average molecular weights are used to describe PVC molecular weights. The number average molecular weight is defined as

$$\overline{M}_N = \frac{\Sigma n_i M_i}{\Sigma n_i}$$

This $\overline{M}_N$ is calculated from osmotic pressure measurements obtained with an osmometer. The osmotic pressure of a solution depends only on the number of molecules in solution. Applying van't Hoff's equation at infinite dilution, the number average molecular weight is

$$\overline{M}_N = R\ T\ /\ \lim_{c \to 0} (\pi/c)$$

where R is the gas constant

T is the absolute temperature

π is the measured osmotic pressure

c is the solution concentration

The approximate number of monomer molecules per polymer molecule is obtained by dividing $\overline{M}_N$ by the molecular weight of VCM (62.5).

The weight average molecular weight is defined as

$$\overline{M}_W = \frac{\Sigma n_i M_i^2}{\Sigma n_i M_i}$$

The $\overline{M}_W$ was calculated from viscosity measurements and the Freeman-Manning correlation. The viscosity of PVC in THF solution was experimentally measured using standard Cannon-Fenske viscometers. Viscosity versus PVC concentration data were extrapolated to zero concentration to get the intrinsic viscosity from the equation

$$\frac{\eta - \eta_o}{\eta_o c} = k\ c + [\eta]$$

where c is the PVC concentration in THF

η is the PVC solution viscosity

η_o is the pure THF solvent viscosity

Then $\overline{M}_W$ is obtained from the Freeman-Manning correlation (1964).

$$[\eta] = 1.63\text{x}10^{-5}\ (\overline{M}_W)^{0.766}$$

Further details may be found in the thesis of Bromfield (1973).