

Experimental Investigation of Vinyl Chloride Polymerization at High Conversion— Temperature / Pressure / Conversion and Monomer Phase Distribution Relationships

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Synopsis

An equilibrium model relating temperature, pressure, monomer conversion, and monomer phase distribution for vinyl chloride polymerization has been developed. This model can be used to determine the monomer conversion beyond the pressure drop by measurement of reactor temperature and pressure. It can also be used to estimate monomer conversion at the pressure drop point and the distribution of monomer in all the phases over the entire extent of polymerization. A series of experiments to measure the solubility of VCM in water and PVC were carried out in the temperature range 40–70°C. Correlations of the solubility of VCM in water and the VCM–PVC interaction parameter with temperature, respectively, were obtained from the experimental data.

INTRODUCTION

An important feature of vinyl chloride polymerization (which includes suspension, emulsion, microsuspension, and bulk polymerization) is the low solubility of poly(vinyl chloride) (PVC) in its monomer so that the monomer phase is considered to be essentially pure monomer, while the PVC-rich phase is swollen with monomer (at about 30% weight monomer).^{1–9} As the reaction proceeds, the mass of the monomer phase decreases while that of the polymer phase grows, but the composition of each phase is considered constant (the diffusion of monomer into the PVC-rich phase is considered to be rapid). As long as vinyl chloride monomer (VCM) exists as a separate phase, it will exert its own vapor pressure and the pressure in the reactor will be a constant value during isothermal polymerization. Conversion increases to a critical value X_f at which point the monomer as a separate phase is consumed, then the pressure in the reactor begins to drop. This critical conversion is commonly considered to occur at about 70–80%.^{3–7,9–12} In commercial suspension polymerizations, the conversion continues past the critical value and the terminal conversion is controlled on the basis of the pressure drop in the range 85–95%.^{10,11} A comprehensive equilibrium model which relates conversion to reactor temperature and pressure and which would be useful to terminate commercial polymerizations has not been published.

Furthermore, the monomer concentrations in the water and in the vapor phases were neglected in previous kinetics calculations. Hence these kinetic

models may overestimate the polymerization rate at high conversion. Therefore, the objectives of this work are to develop an equilibrium model relating conversion to reactor temperature and pressure and one which can predict monomer phase distribution for vinyl chloride polymerization for use both in commercial production of PVC and in future kinetics studies.

MODEL DEVELOPMENT

The model is to relate conversion of VCM to polymer as a function of temperature and reactor pressure. Its development is based on the following assumptions:

1. The distributions of species among phases are in instantaneous equilibrium over the entire conversion range.
2. The solubility of PVC in its monomer is neglected (0.03% at ambient temperature,⁸ and < 0.1% at polymerization temperature 50°C).³
3. The PVT properties of the vapor phase obey the Ideal gas law.
4. The solubility of VCM in water follows Henry's law.
5. The solubility of VCM in PVC follows the Flory-Huggins equation.

Temperature, Pressure, and Conversion Relationship

For suspension or emulsion polymerization of vinyl chloride, at given conditions, the initial fractional fillage of the reactor W_i is given by

$$W_i = (W_w/D_w + (M_o - M_{go})/D_m)/V_r \quad (1)$$

where

$$M_{go} = (1.0 - W_i)V_r P_{mo} M_m / (RT) \quad (2)$$

Substituting Eq. (2) into Eq. (1), one has

$$W_i = (W_w/D_w + M_o/D_m - D_{go}V_r/D_m)/(V_r(1.0 - D_{go}/D_m)) \quad (3)$$

where

$$D_{go} = P_{mo} M_m / (RT)$$

When the monomer is converted into polymer, the total volume of liquid phase shrinks because of the lower density of the monomer relative to the polymer. Therefore, the total liquid volume in the reactor decreases and the vapor volume increases with conversion. When the vapor volume increases, liquid monomer vaporizes to maintain the reactor pressure constant as long as pure liquid monomer is available. Thus, the total change of vapor phase volume is the sum of the shrunken volume and the liquid monomer volume vaporized to fill the shrunken volume. It can be expressed as:

$$\Delta V_{g1} = XM_o(1/D_m - 1/D_p)/(1.0 - D_{go}/D_m) \quad (X \leq X_f) \quad (4)$$

Conversion X is defined by

$$X = (M_o - M)/M_o = W_p/M_o \quad (5)$$

Therefore, the volume of vapor phase is given by

$$V_{gx} = (1.0 - W_i)V_r + XM_o(1/D_m - 1/D_p)/(1.0 - D_{go}/D_m) \quad (6)$$

With $X = X_f$, Eq. (6) becomes:

$$V_{gxf} = (1.0 - W_i)V_r + X_f M_o(1/D_m - 1/D_p)/(1.0 - D_{go}/D_m) \quad (7)$$

When $X > X_f$, the monomer-rich phase no longer exists and using a monomer balance, one obtains:

$$M_o = M_{g2} + M_{w2} + M_{p2} + W_p \quad (X > X_f) \quad (8)$$

where

$$M_{g2} = M_m P_m V_{g2}/(RT) \quad (9)$$

and

$$V_{g2} = V_{gxf} + \Delta V_{g2} \quad (10)$$

In the absence of the monomer-rich phase, the shrinkage of the liquid volume causes the pressure to drop. Hence, the pressure drop is the result of the vapor volume increase and monomer vapor diffusing into the polymer phase. The increment of vapor volume can be expressed as:

$$\Delta V_{g2} = (X - X_f)M_o(1/D_m - 1/D_p) \quad (X > X_f) \quad (11)$$

Substituting Eqs. (7), (10), and (11) into Eq. (9), one obtains:

$$M_{g2} = \frac{M_m P_m}{RT} \left[(1.0 - W_i)V_r + \frac{X_f M_o(1/D_m - 1/D_p)}{1.0 - D_{go}/D_m} + (X - X_f)M_o(1/D_m - 1/D_p) \right] \quad (12)$$

The amount of monomer in water can be expressed by Henry's law:

$$P_m = HM_{w2}/W_w \quad (13)$$

where

$$P_m = P_t - P_w.$$

For convenience, Eq. (13) is rewritten as:

$$M_{w2} = KW_w P_m/P_{m0} \quad (14)$$

where $K = P_{m0}/H$, a dimensionless solubility constant.

The amount of monomer in the polymer phase can be expressed as a function of polymer volume fraction in the polymer phase.

$$M_p = M_o X D_m (1.0 - \phi_2) / (\phi_2 D_p) \quad (15)$$

The weight of polymer in the system can be calculated from the definition given in Eq. (5):

$$W_p = M_o X \quad (16)$$

Substituting Eqs. (12)–(16) into Eq. (8), one obtains:

$$X = \frac{M_o - [P_m M_m / (RT)] [(1.0 - W_i) V_r + X_f M_o (1/D_m - 1/D_p) D_{go} / (D_m - D_{go})] - K W_w P_m / P_{m_o}}{M_o + M_o D_m (1.0 - \phi_2) / (\phi_2 D_p) + P_m M_m M_o (1/D_m - 1/D_p) / (RT)} \quad (17)$$

Equation (17) correlates conversion, temperature, and the partial pressure relationship at given operating conditions. Polymer volume fraction can be found using the Flory-Huggins equation:¹⁴

$$\ln(P_m / P_{m_o}) = \ln(1.0 - \phi_2) + (1.0 - 1/n)\phi_2 + \chi\phi_2^2 \quad (18)$$

When the conversion is the critical conversion, $X = X_f$, the pressure is

$$P_m = P_{m_o} \quad (19)$$

Thus, conversion X_f , at which partial pressure starts to drop, can be derived from Eq. (17) by replacing X , P_m with X_f , P_{m_o} , respectively. That is

$$X_f = \frac{M_o - [D_{go}(1.0 - W_i)V_r + K W_w]}{M_o [(1.0 + D_{go}(1/D_m - 1/D_p)) / (1.0 - D_{go}/D_m) + D_m(1.0 - \phi_2) / (\phi_2 D_p)]} \quad (20)$$

and Eq. (18) then becomes at the critical conversion:

$$\ln(1.0 - \phi_2) + (1.0 - 1/n)\phi_2 + \chi\phi_2^2 = 0 \quad (21)$$

From Eqs. (17) and (20), it is seen that the relationship between conversion and partial pressure depends on initial operating conditions and physical properties of VCM and PVC, but it is independent of the polymerization mechanism. Therefore, Eqs. (17) and (20) may be used in suspension, micro-suspension, and bulk ($W_w = 0$) polymerization systems.

Furthermore, Eq. (20) may be used to estimate saturation solubility of VCM in PVC, while Eq. (17) is used for under unsaturation pressure. Equation (20) also has important kinetic significance because it relates the kinetics parameter X_f with the VCM-PVC interaction parameter.

Monomer Distribution During Polymerization of Vinyl Chloride

For suspension polymerization of VCM, with the above assumptions, the monomer mass balance is given by:

$$M_o = M_{g1} + M_{w1} + M_1 + M_{p1} + W_p \quad (X \leq X_f) \quad (22)$$

$$M_o = M_{g2} + M_{w2} + M_{p2} + W_p \quad (X > X_f) \quad (23)$$

The monomer weight fraction in the different phases is defined as:

$$F_i = M_i/M_o \quad (24)$$

Therefore, the task to find F_i is to calculate the amount of the monomer M_i in the different phases: vapor, water, polymer, and liquid monomer.

Monomer fraction in the vapor phase:

$$X \leq X_f$$

Using Eq. (6), one has:

$$M_{g1} = \frac{M_m P_{m_o}}{RT} \left[(1.0 - W_i) V_r + \frac{X M_o (1/D_m - 1/D_p)}{1.0 - P_{m_o} M_m / (RT D_m)} \right] \quad (25)$$

Therefore

$$F_{g1} = M_{g1}/M_o \quad (X \leq X_f) \quad (26)$$

$$X > X_f$$

Substituting Eq. (12) into Eq. (24), one obtains:

$$F_{g2} = \frac{M_m P_m}{M_o RT} \left[(1.0 - W_i) V_r + \frac{X_f M_o (1/D_m - 1/D_p)}{1.0 - D_{g_o}/D_m} + (X - X_f) M_o (1/D_m - 1/D_p) \right] \quad (X > X_f) \quad (27)$$

Monomer fraction in the water phase:

Substituting Eq. (14) into Eq. (24), one finds:

$$F_{w1} = M_{w1}/M_o = KW_w/M_o \quad (X \leq X_f) \quad (28)$$

$$F_{w2} = KW_w P_m / (P_{m_o} M_o) \quad (X > X_f) \quad (29)$$

Monomer fraction in the polymer phase:

Because the composition of the polymer phase remains constant up to conversion X_f , the ratio of monomer to polymer weight in the phase can be

written as:

$$\frac{M_o - M_{gxf} - M_{uxf} - M_o X_f}{M_o X_f} = \frac{M_{p1}}{M_o X} \quad (X \leq X_f) \quad (30)$$

Hence,

$$F_{p1} = X [M_o(1.0 - X_f) - M_{gxf} - M_{uxf}] / (X_f M_o) \quad (X \leq X_f) \quad (31)$$

where

$$M_{gxf} = \frac{M_m P_{mo}}{RT} \left[(1.0 - W_i) V_r + \frac{X_f M_o (1/D_m - 1/D_p)}{1.0 - P_{mo} M_m / (RTD_m)} \right]$$

and

$$M_{uxf} = KW_w$$

and

$$F_{p2} = [M_o(1.0 - X) - M_{g2} - M_{w2}] / M_o \quad (X > X_f) \quad (32)$$

Monomer fraction in the liquid monomer phase:

$$F_m = [M_o(1.0 - X) - M_{g1} - M_{w1} - M_{p1}] / M_o \quad (X \leq X_f) \quad (33)$$

Monomer fraction converted to polymer:

$$P_{pvc} = X \quad (0 \leq X \leq 1) \quad (34)$$

Using Eqs. (17), (18), (20), (21), and (23)–(32), one can calculate the monomer distribution as function of conversion.

EXPERIMENTAL

Solubility of VCM in water and in PVC in the temperature range 40–70°C was measured in order to find the parameters K and χ .

The equipment used in these experiments consisted of an agitated 5-L stainless steel reactor with a calibrated vacuum-pressure gauge. Temperature was controlled by a steam and water mixture that circulated in the jacket.

PVC used for the present measurements was made by the Rhone Poulenc Bulk Process (Diamond Shamrock/Alberta Gas Company, Fort Saskatchewan, Alberta).

VCM was provided by the B.F. Goodrich Company (Niagara Falls, Ontario, Canada).

The reactor was filled with a weighed amount of deionized, distilled water and a weighed amount of PVC powder. A weighed amount of monomer was injected into the reactor after the reactor was evacuated. The reactor temperature was then raised progressively to each of the four temperature levels used. The pressure reached a steady level after about 90 min for each temperature level.

Conversion was calculated using the relationship

$$X = \text{PVC}/(\text{PVC} + \text{VCM}) \quad (35)$$

Thus, conversion and partial pressure data were obtained by repeating this procedure.

The solubility of VCM in water was similarly determined within the same temperature range.

RESULTS AND DISCUSSIONS

Solubility of VCM in Water Phase

Solubility of VCM in water has been measured by a few authors,¹⁵⁻¹⁹ but few data in the normal polymerization temperature range were reported. Heretofore, a correlation between solubility and temperature has not been published.

The present results are shown in Figures 1 and 2, where the solubility is plotted against the relative pressure of VCM (P_m/P_{m0}), at the temperature of measurement. It can be seen that the data follow Henry's law over a wide pressure range. Therefore, the solubility constant K in Eq. (14) can be found on the basis of least-squares fit. The results are that the solubility constant has a value of 0.0106, 0.0114, 0.0129, and 0.0135 for 40, 50, 60, and 70°C, respectively.

The solubility constants, which seem to be a mild function of temperature, are shown in Figure 3 together with other reported data.^{15,17-19} At lower temperature levels the present results are in agreement with all the reported data. Above 60°C, our data are slightly higher than those reported by Hayduk and Laudie¹⁸ and Patel et al.,¹⁹ but lower than that reported by Benton et al.¹⁵ All the data except a few points which are far from the straight line were used for the least-squares calculation of solubility constant as a function

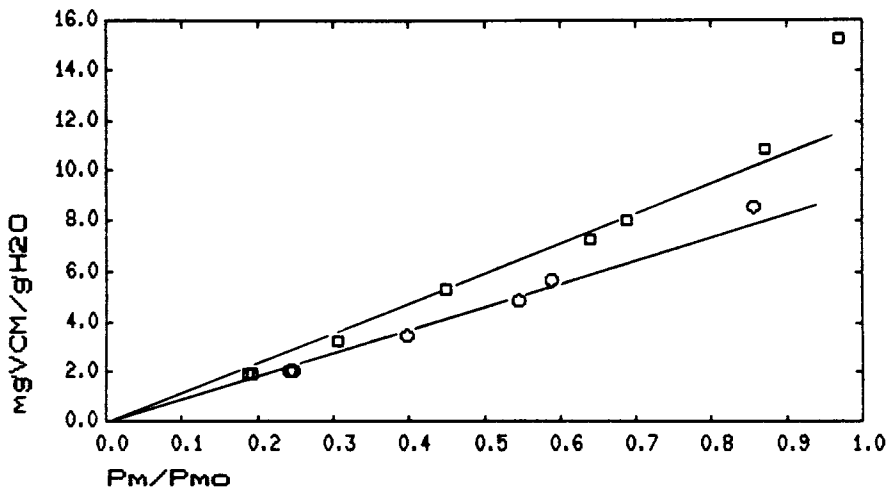


Fig. 1. Solubility of VCM in water. Temperature: 40°C (○); 60°C (□).

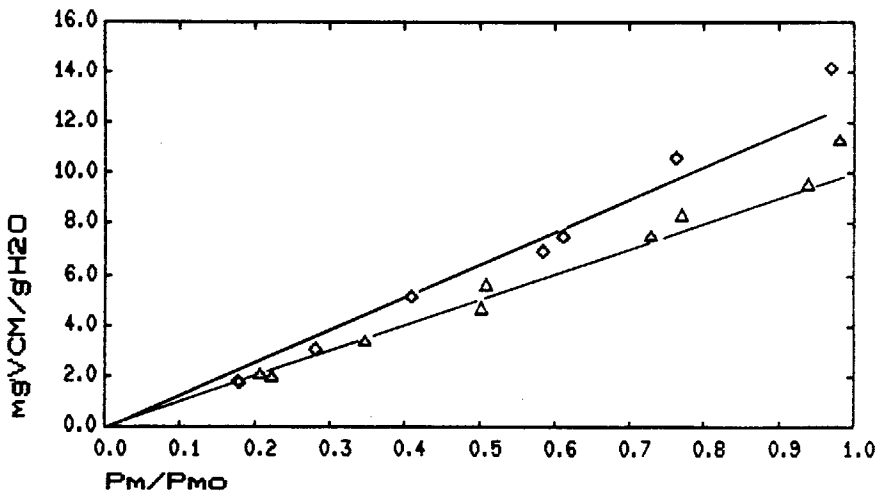


Fig. 2. Solubility of VCM in water. Temperature: 50°C (Δ); 70°C (\diamond).

of temperature. The following correlation was obtained:

$$K = 0.0472 - 11.6/T(^{\circ}\text{K}) \quad (36)$$

For suspension polymerization, the water phase is a surfactant solution. Hayduk and Laudie¹⁸ reported the effect of soap concentration on the solubility of VCM in water. When the soap concentration is more than 0.5%, the solubility of VCM in soap solution increases, but when the soap concentration is less than 0.1%, soap concentration appears to have no effect on solubility of VCM. Therefore, for the usual aqueous medium VCM polymerization system where the soap concentration is less than 0.1%, Eq. (36) can be used to estimate solubility of VCM in the water phase. Thus, within the usual polymerization temperature range, saturation solubility of VCM in water phase is around 1.0–1.3 wt%.

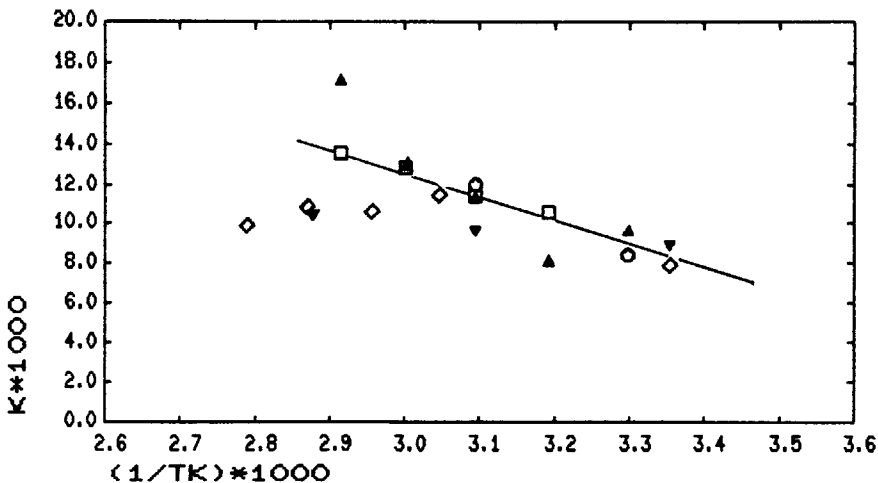


Fig. 3. Solubility constant vs. temperature: Present experimental data: (\square); Berens' Data: (\circ); Patel et al.'s data: (\diamond); Hayduk et al.'s data: (\blacktriangledown); *Encycl. Polym. Tech.*: (\blacktriangle).

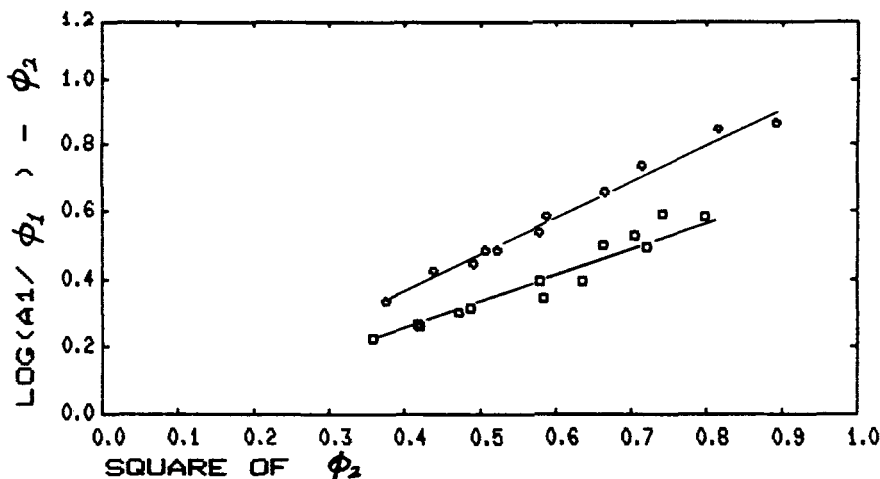


Fig. 4. VCM-PVC interaction parameter χ . Temperature: 40°C (○); 60°C (□).

VCM-PVC Interaction Parameter

Equation (18) can be rewritten as follows:

$$\ln[\alpha_1/(1.0 - \phi_2)] - \phi_2 = \chi\phi_2^2 \quad (37)$$

where $\alpha_1 = P_m/P_{mo}$, and the molecular weight effect is neglected. Hence, if the left-hand side of Eq. (37) is plotted against ϕ_2^2 , a straight line passing through the origin should result. The slope of the line is the interaction parameter χ . Our experimental results are shown in Figures 4 and 5. The interaction parameter was found by means of the least-squares method.

Gerrens et al.² first used the Flory-Huggins¹⁴ equation in the emulsion polymerization of vinyl chloride and found $\chi = 0.88$ at 50°C. Berens¹³ estimated $\chi = 0.98$ in VCM-PVC powder system from 30 to 60°C. Abdel-Alim¹¹

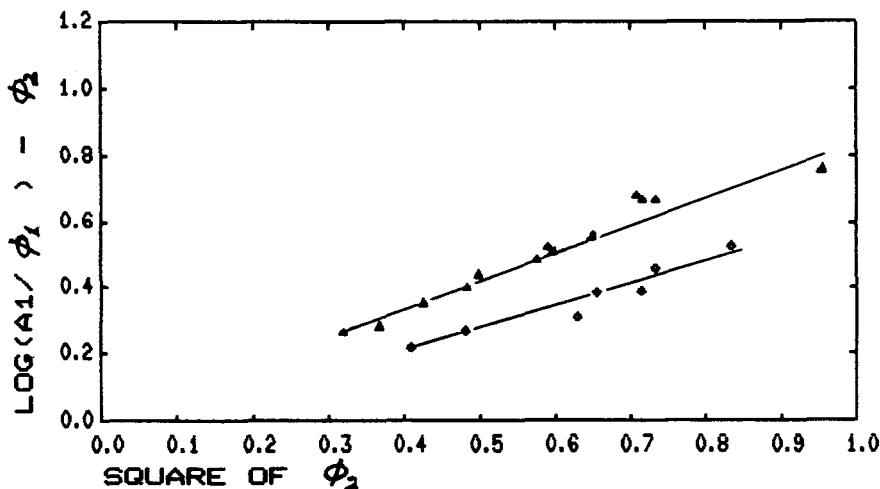


Fig. 5. VCM-PVC interaction parameter χ . Temperature: 50°C (▲); 70°C (△).

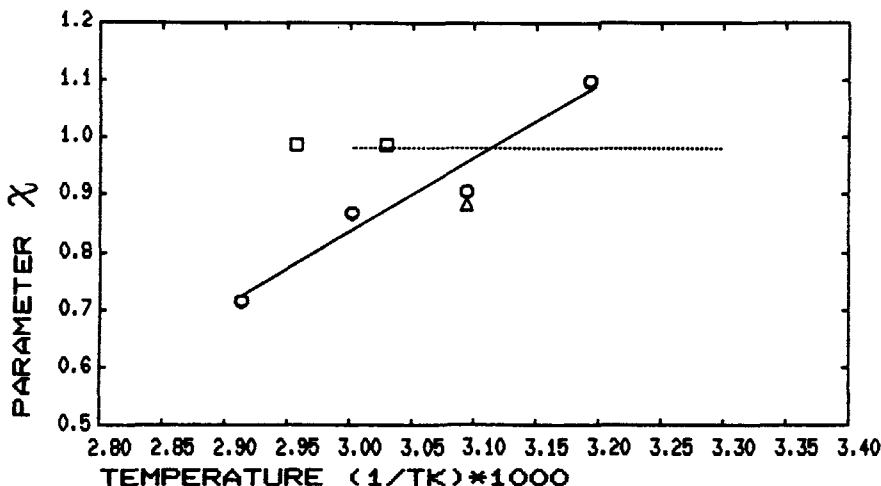


Fig. 6. Interaction parameter vs. temperature:
 Present experimental data: (○) $\chi = 1286.4/TK - 3.02$
 Berens' data: (---) $\chi = 0.98$ (30–60°C)
 Gerrens et al.'s data: (△) $\chi = 0.88$ (50°C)
 Abdel-Alim's data: (□) $\chi = 0.985$ (57°C, 65°C)

obtained $\chi = 0.985$ from plant data at 57 and 65°C. Our results are shown in Figure 6 together with those of these authors.

It can be seen from Figure 6 that our result (at 50°C) is in agreement with that of Gerrens et al.² The data show that the interaction parameter is a function of temperature. This is in disagreement with that of Berens.¹³ On the basis of our results, a correlation between the interaction parameter and temperature is as follows:

$$\chi = 1286.4/T(^{\circ}\text{K}) - 3.02 \quad (38)$$

Scamehorn and Yang²⁰ found that interaction parameter is a function of VCM volume fraction and their results are much lower than those shown in Figure 6. These authors believed that the solubility of VCM in PVC may be a function of resin type.

Model Evaluation

From Eqs. (36) and (38), the solubility constant and interaction parameter can be found at a given temperature. Some physical properties used in the model are given as follows:

$$D_m = 947.9 - 1.89t(^{\circ}\text{C}) \quad (\text{g/L})^{11} \quad (39)$$

$$D_p = 1403(\text{g/L}) \quad (40)$$

$$P_{mo} = 12722\text{EXP}(-2411.7/T^{\circ}\text{K}) \quad (\text{atm}) \quad (41)$$

Equation (41) was obtained from Johnston's data.²¹ In the present study careful measurements of the vapor pressure of VCM as a function of tempera-

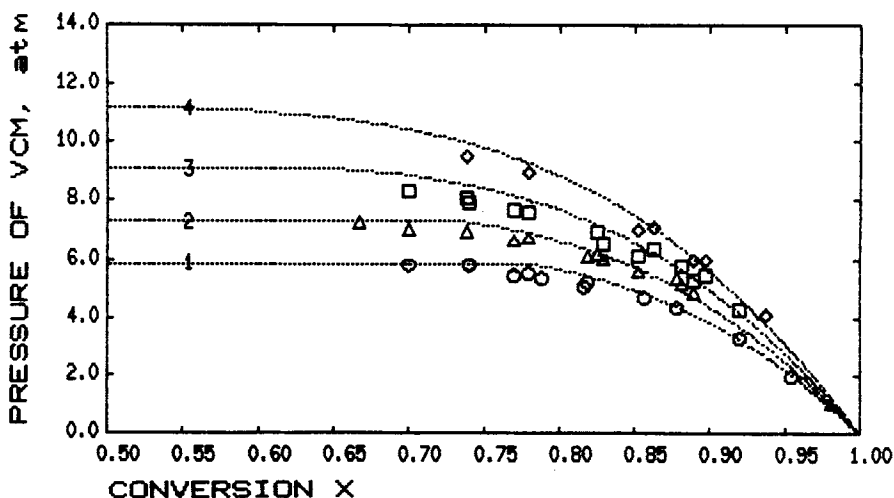


Fig. 7. Conversion vs. pressure of VCM: $M_o = 1200$ g, $W_w = 2500$ g, $V_r = 5.0$ L;
 Temperature °C: $\frac{1}{40}$ $\frac{2}{50}$ $\frac{3}{60}$ $\frac{4}{70}$
 Present experimental data: (○) (△) (□) (◇)
 Present model [Eq. (17)]: (---)(---)(---)(---)

ture were done at very low levels of inert gases. Our vapor pressure data were in excellent agreement with Eq. (41). In the evaluation of the data of Meeks⁴ and Abdel-Alim¹¹ (see Figs. 8, 9) the vapor pressure was calculated using Eq. (41). Water density can also be given as a function of temperature. Thus, all the equations can be solved by inputting initial conditions—temperature, monomer, and water weight charged and the reactor volume.

Our experimental conditions are as follows:

Reactor volume: 5.0 L

Temperature: 40, 50, 60, 70°C

Initial Monomer: 1200 g (PVC + VCM in this work)

Water: 2500 g

Relationship Between Conversion and Vapor Pressure. Comparison of experimental data with the modelling results is shown in Figures 7–9. Figure 7 shows that the model is in agreement with experimental results. In Figure 8, the data were read from continuous experimental curves reported by Meeks.⁴ Hence it is also proved that the model is consistent with experimental results for suspension polymerization. In Figure 9, the model is compared with plant data reported by Abdel-Alim.¹¹ In dotted line one, χ was calculated from Eq. (38). In dotted line 2, Abdel-Alim's $\chi = 0.985$ value was employed. The model appears sensitive to interaction parameter. The difference between the two dotted lines is because the χ value in this work is slightly lower than that of Abdel-Alim, as shown in Figure 6. From Figures 7–9, it is clear that the model satisfactorily describes the relationship between conversion and partial pressure after monomer as a separate phase is depleted. Figure 10 shows model predictions for the temperature range 30–70°C.

Critical Conversion X_c . Since Talamini [1] proposed a two-phase kinetic model on the basis of Gerrens' result about solubility of VCM in PVC,² a lot

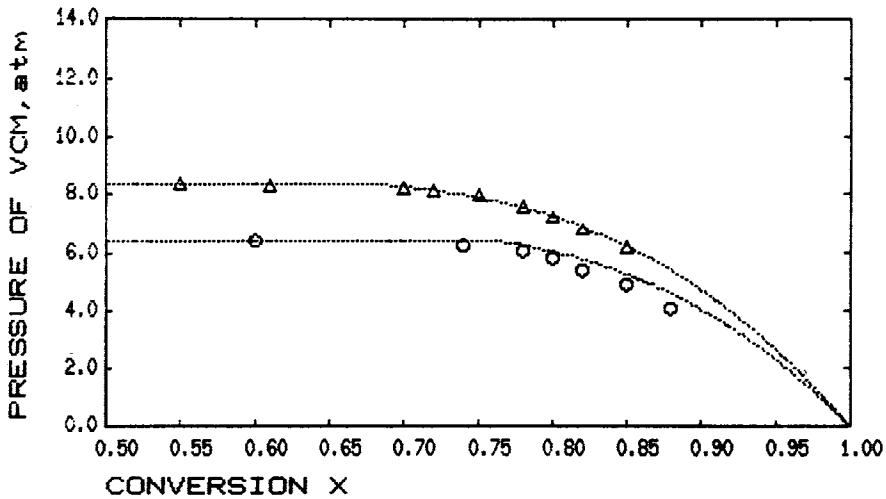


Fig. 8. Conversion vs. pressure of VCM:

Temperature °C:	44	56
Present Model (Eq. 17):	(---)	(---)
Meek's Data [4]:	(○)	(△)

of data on conversion at which reactor pressure begins to fall have been reported, as shown in Table I. But a correlation between X_f and operating conditions has not been reported to date.

Equation (20) indicates that X_f is a function not only of temperature but also other operating variables. According to the initial conditions in this work, X_f was obtained at a given temperature, as shown in Table II. For comparison, X_f for bulk polymerization conditions was also predicted using the present model with $W_w = 0$. Plotting temperature versus X_f , we obtained a

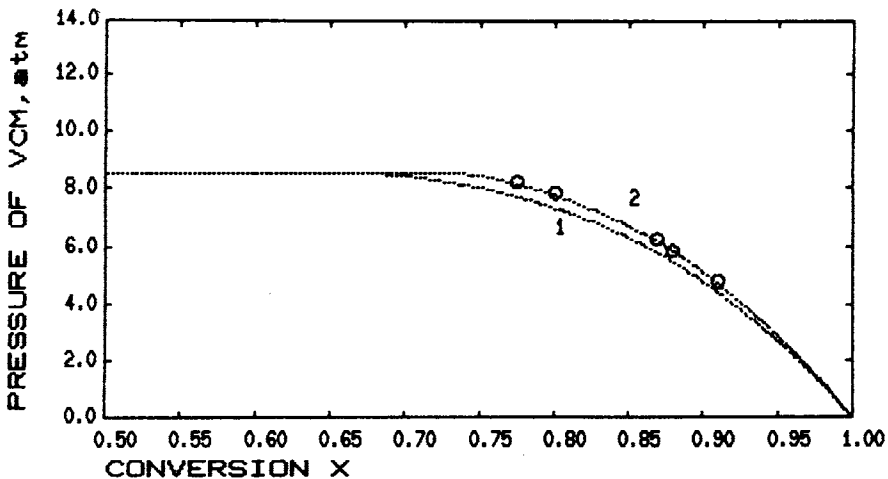


Fig. 9. Conversion vs. pressure of VCM:

Temperature °C:	57
Present model [Eq. (17)]:	(1: $\chi = 0.876$, eq. (38) 2: $\chi = 0.985$ [11])
Abdel-Alim's data ¹¹ :	(○)

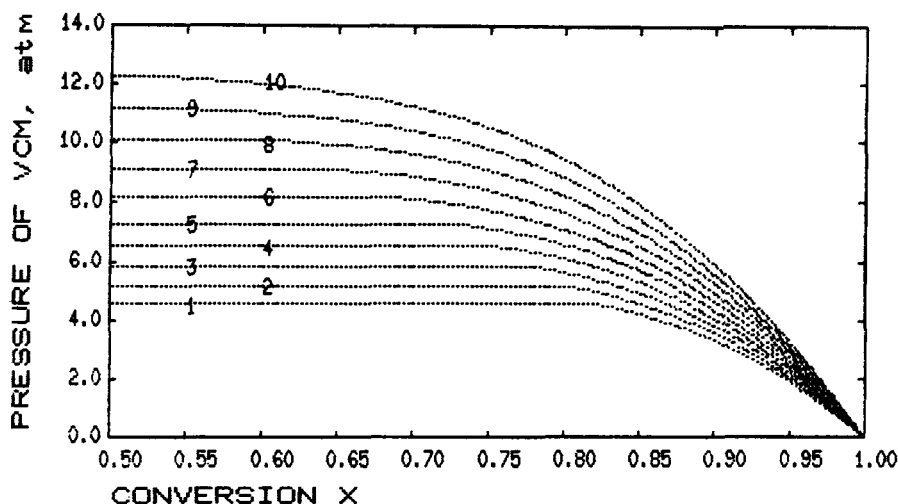


Fig. 10. Conversion vs. pressure of VCM:

$M_o = 1200$ g, $W_w = 2500$ g, $V_r = 5.0$ L, Temp. = 30–75°C

Present model: 1 2 3 4 5 6 7 8 9 10

Temperature °C: 30 35 40 45 50 55 60 65 70 75

curve similar to the equilibrium solubility curve, as shown in Figure 11, however, it is not a true solubility curve because it depends on nonequilibrium parameters such as reactor fillage. Dotted lines 1 and 2 are for suspension and bulk conditions, respectively. At a similar fillage of reactor, X_f in bulk polymerization is 2–2.5% greater than that in the aqueous medium polymerization. The circular points and the square points which are literature values shown in Table I were estimated from the solubility of VCM in PVC and from kinetic curves, respectively. Figure 11 shows that the modelling results are in satisfactory agreement with the literature values. Some data from the kinetic curves are somewhat higher than those predicted from the present model because the conversion at which polymerization rate begins to decrease may

TABLE I
A Relationship Between Conversion X_f and Temperature

Temperature, °C	X_f	Methods	References
50	0.71	solubility (emulsion)	[2]
55	0.70	kinetics (suspension)	[3]
44–56	0.70–0.75	solubility (suspension)	[4]
65	0.687	solubility (suspension)	[5]
30	0.80	kinetics (bulk)	[6]
50	0.77	kinetics (bulk)	[6]
70	0.72	kinetics (bulk)	[6]
50	0.677	solubility (bulk)	[7]
60	0.63–0.64	kinetics (suspension)	[8]
50–60	0.70–0.75	kinetics (suspension)	[9]
—	0.70	kinetics (suspension)	[10]
57–65	0.776	solubility (suspension)	[11]
—	0.77	kinetics (bulk)	[12]
30–60	0.77	solubility (bulk)	[13]

TABLE II
A Relationship Between Conversion X_f and Temperature—Model Prediction [Eq. (2)]

Temperature, °C	X_f (suspension)	X_f (bulk)
0	0.909	0.922
10	0.886	0.902
20	0.858	0.877
30	0.823	0.845
35	0.803	0.827
40	0.781	0.805
45	0.756	0.781
50	0.726	0.752
55	0.693	0.719
60	0.653	0.680
65	0.606	0.632
70	0.550	0.575
75	0.479	0.502
80	0.390	0.409

not be the same as the conversion at which the vapor pressure starts to drop or free monomer phase is depleted. In fact, the conversion at which polymerization rate begins to decrease strongly depends on the initiator system used.⁹ The polymerization rate begins to drop either before, at or after free monomer phase is depleted. At low temperatures (< 30°C) or high temperatures (> 70°C), X_f values have not been reported to date. It is not clear why the conversion at which the reactor pressure starts to drop is so low at high temperatures. Because X_f is very sensitive to the interaction parameter, over a wide temperature range, the effect of PVC molecular weight on interaction parameter must be considered. Therefore, the range of applicability of Eq. (38) needs to be proven with further polymerization experiments.

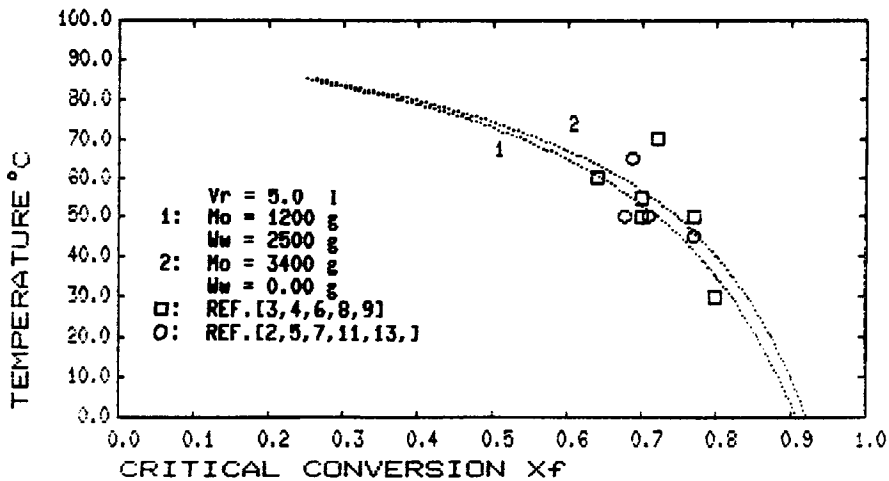


Fig. 11. Critical conversion vs. temperature.

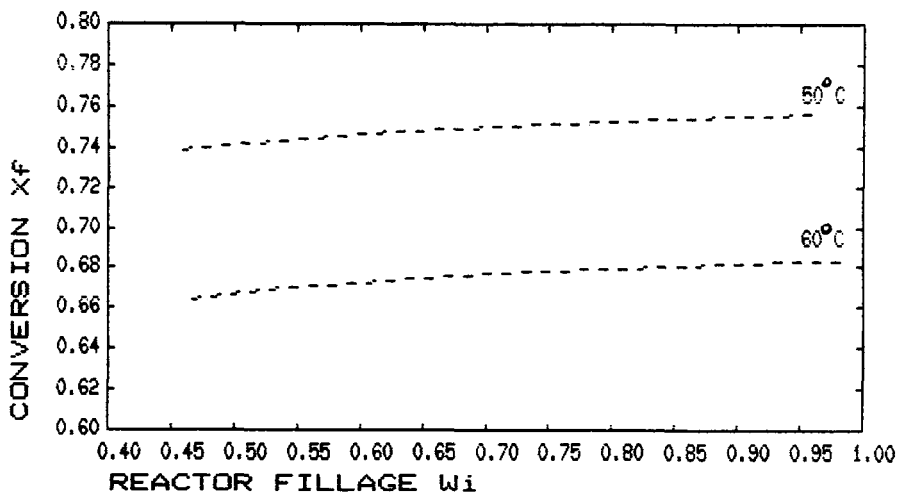


Fig. 12. Reactor fillage vs. conversion X_f .

The effect of reactor fillage on X_f is shown in Figure 12. At a given temperature, the critical conversion X_f slightly increases with reactor fillage. For example, X_f will increase about 2% at 50–60°C when the reactor fillage increases from 50 to 95%.

Monomer Distribution. Generally, monomer in the water phase or in the vapor phase has been neglected in previous kinetic studies. Chan et al.²² calculated the monomer distribution in vapor, water, and polymer phases, respectively, using partition coefficients. It was found that monomer in water and vapor phase is significant at the peak exotherm.

Once the relationship between conversion and reactor pressure is established, then the monomer distribution among phases can be found.

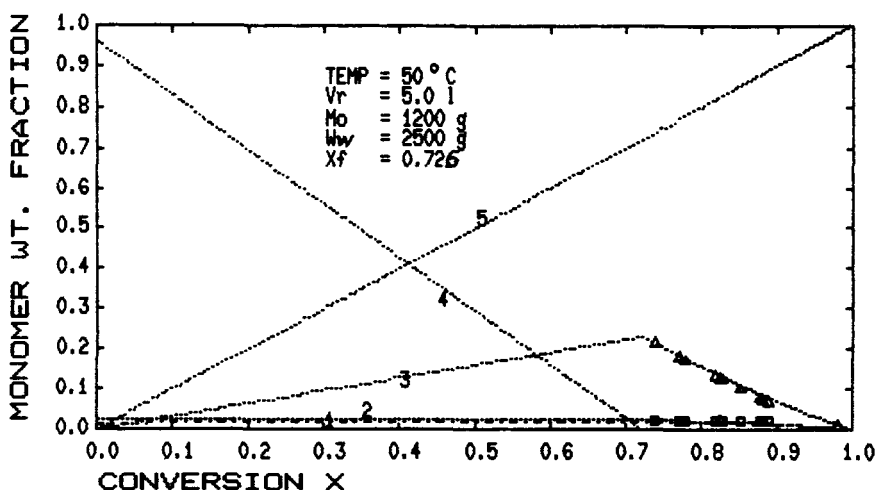


Fig. 13. Monomer distribution: (1) Monomer fraction in the vapor phase. (2) Monomer fraction in the water phase. (3) Monomer fraction in the polymer phase. (4) Monomer fraction in the liquid phase. (5) Monomer fraction converted to polymer in the system. (Δ , \square): Measured in present study.

From Eqs. (24)–(32), monomer weight fraction in the different phases as a function of conversion can be obtained at given operating conditions. The typical theoretical results are shown in Figure 13 together with our experimental data. Under the conditions shown in Figure 13, monomer in the water, vapor, and monomer phases is 2.4%, 1.6%, and 96.0%, respectively, at zero conversion. When conversion increases to X_f , monomer in the water, vapor, and polymer phases is 2.4, 2.2, and 23.2%, respectively. Monomer in the vapor and polymer phases reach maximum at X_f . The monomer in the water and vapor phases is 19.8% of that in the polymer phase at $X = X_f$. This is in agreement with that estimated by Chan et al.²² Therefore, neglecting the monomer dissolved in water and that in the head space of the reactor would cause a serious overestimation of the polymerization rate and result in an overdesign of the cooling system for the reactor.

CONCLUSIONS

A comparison of model predictions with the present and published experimental data confirms that the assumptions made in the model derivation are reasonable. Both the solubility constant of VCM in water and VCM-PVC interaction parameter depend on temperature. The model can satisfactorily describe the relationship between conversion and reactor pressure beyond the pressure drop and can be used to estimate terminal conversion with a pressure measurement. The model also permits one to calculate the conversion at the pressure drop (solubility of monomer in polymer) and monomer phase distribution. This kind of information should make polymerization kinetic models more reliable when used for PVC reactor calculations at high conversions. Of course, in large commercial PVC reactors equilibrium conditions may not be established sufficiently for the present model to be useful.

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NOMENCLATURE

- D_{g0} = vapor density at the vapor pressure, g/L
- D_m = density of monomer, g/L
- D_p = density of polymer, g/L
- ΔV_g = increment of volume in vapor phase, L
- D_w = density of water, g/L
- F_g = monomer weight fraction in the vapor phase
- F_i = monomer weight fraction in i phase
- F_m = monomer weight fraction in the free monomer phase
- F_p = monomer weight fraction in the polymer phase
- F_{pvc} = monomer weight fraction converted to polymer
- F_w = monomer weight fraction in the water phase
- H = Henry's law constant, atm
- K = solubility constant
- M = monomer at conversion X , g
- M_g = monomer in vapor phase, g

M_{go}	= initial monomer in vapor phase, g
M_{gxf}	= monomer in vapor phase at conversion X_f , g
M_i	= monomer in i phase, g
M_l	= liquid monomer
M_m	= monomer molecular weight
M_o	= initial monomer charged, g
M_p	= monomer in the polymer phase, g
M_w	= monomer in the water phase, g
M_{wxf}	= monomer in the water phase at X_f , g
n	= average number of monomer units in the polymer
P_w	= partial pressure of water, atm
P_m	= partial pressure of monomer, atm
P_{mo}	= vapor pressure of monomer, atm
P_t	= total pressure in the reactor, atm
R	= gas constant, atm. L/mol.°K
t	= temperature °C
T	= temperature °K
V_g	= volume of vapor phase, L
V_{go}	= initial volume of vapor phase, L
V_r	= reactor volume, L
V_{gx}	= volume of vapor phase at X , L
V_{gxf}	= volume of vapor phase at X_f , L
W_i	= initial reactor charge as liquid
W_p	= polymer in the system, g
W_w	= water charged, g
X	= conversion of monomer
X_f	= conversion at which monomer phase is consumed

Greek Letters

ϕ	= volume fraction of polymer in polymer phase
χ	= VCM-PVC interaction parameter (see Flory-Huggins equation)

Subscripts

1	= $X \leq X_f$
2	= $X > X_f$

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