Calculation and Applications of VCM Distribution in Vapor/Water/Solid Phases during VCM Polymerization

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ABSTRACT

The distribution of vinyl chloride monomer (VCM) in vapor, water, swollen polymer, and free monomer phases as a function of conversion of VCM can be calculated from the related partition coefficients. It was found that the amount of monomer in the vapor and water phases is particularly significant, being 20% (at 60°C) of that in the polymer phase at the peak exotherm. Neglecting the VCM dissolved in water and that in the head space of the reactor would seriously overestimate the polymerization rate and overdesign the required cooling capacity of the reactor. From the distribution the relation between conversion (x) vs pressure (P) after the pressure starts to drop can be developed and used to determine conversion at termination by pressure measurement. The results of x vs P from our partition coefficient approach are consistent with those derived from Flory-Huggin's equation. Also the knowledge of VCM distribution at termination of the polymerization will assist VCM accountability and stripper design.

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INTRODUCTION

In previous kinetics calculations [1-3] the VCM concentrations in vapor and water phases were neglected. The objectives of this work are to evaluate such concentrations in terms of conversion (x) reactor size (V_r) and charging conditions (initial % fillage of reactor W_i and water-to-monomer weight ratio, γ), and to explore the application of same.

DERIVATIONS

VCM Concentrations in Three Phases during Polymerization

The following two expressions (derived in the Appendix) will be useful for later derivations:

$$M_0 = V_r F_1(T, \gamma, W_i) \tag{1}$$

$$W = W_i + \left\{ \frac{x(v_m - v_p)[RTW_i + (1 - W_i) P_m^0 M_w v_m]}{(RT - P_m^0 M_m v_m)(v_m + v_w)} \right\} \tag{2}$$

where

$$F_1(T, \gamma, W_i) = \frac{RTW_i + P_m^0 M_m v_m (1 - W_i)}{RT(v_m + \gamma v_w)} \tag{3}$$

Equation (1) means that M_0 and V_r are interchangeable. Equation (2) signifies that the % fillage of reactor (W) is a function of conversion x, polymerization temperature T, and changing conditions W_i and γ.

VCM in Vapor Phase Before, At, and After the Pressure Starts to Drop, N_v

Before the pressure starts to drop,

$$N_v = \frac{(1 - W)V_r P_m^0}{RT} \tag{4}$$

Because of viscosity effect on termination in the solid phase, the peak exotherm (or hot spot) occurs at a pressure drop (usually about 8 psi) which varies with polymerization conditions. Let the pressure at the "hot spot" be denoted by P^{hs},

$$N_v^{hs} = \frac{(1 - W)V_r P^{hs}}{RT}$$

$$= \frac{V_r P^{hs}}{RT} \left[1 - W_i + x^{hs} \frac{(v_m - v_p)}{\left(1 - \frac{P_m^{\,0} M_m V_m}{RT}\right)} F_1(T, \gamma, W_i) \right] \quad (5)$$

After the pressure begins to drop,

$$N_v' = \frac{V_r P_m}{RT}(1 - W) = \frac{M_0(P - P_w)}{RTF_1(T, \gamma, W_i)}(1 - W) \quad (6)$$

It will be later derived that the total pressure (P) is a function of x.

VCM in Water Phase Before, At, and After the Hot Spot, N_w

Before the hot spot,

$$N_w = \frac{C_w^{max} \gamma M_0}{M_m} \quad (7)$$

when and after the pressure starts to drop,

$$N_w' = \frac{C_w \gamma M_0}{M_m} = \frac{P_m \gamma M_0}{P_m^{\,0} H_{\ell v} M_m} = \frac{(P - P_w)\gamma M_0}{P_m^{\,0} H_{\ell v} M_m} \quad (8)$$

VCM in Solid Phase

Before the pressure starts to drop,

$$N_s = \frac{mx M_0}{M_m} \quad (9)$$

After the pressure starts to drop,

$$N_s' = C_s \chi M_0 / M_m = \frac{P_m x M_0}{P_m^{~0} H_{sv} M_m}$$

$$= \frac{(P - P_w) x M_0}{P_m^{~0} H_{sv} M_m} \tag{10}$$

The total pressure P in Eqs. (9) and (11) will be expressed as a function of X.

Derivation of an Expression for Total Pressure, P, as a Function of Conversion x after Pressure Drop Starts

$$M_0 / M_m = N_v' + N_w' + N_s' + N_p \tag{11}$$

Substitute Eqs. (1), (6), (8), and (10) into Eq. (11):

$$\frac{M_0}{M_m} = \frac{M_0 (P - P_w)}{RTF_1 (T, \gamma, W_i)} (1 - W) + \frac{(P - P_w) \gamma M_0}{P_m^{~0} H_{\ell v} M_m}$$

$$+ \frac{(P - P_w) x M_0}{P_m^{~0} H_{sv} M_m} + \frac{x M_0}{M_m}$$

since $P_w \cong P_w^{~0}$, upon rearrangement,

$$(P - P_w)/P_m^{~0} = F_2(x, ~T, ~\gamma, ~W_i) \tag{12}$$

where

$$F_2(x, ~T, ~\gamma, ~W_i) = (1 - x) \left[\frac{M_m P_m^{~0} (1 - W)}{F_1(T, \gamma, W_i) RT} + \frac{\gamma}{H_{\ell v}} + \frac{x}{H_{sv}} \right]^{-1} \tag{13}$$

Equation (12) dictates the conversion x at different pressures (or pressure drop, $\Delta P = P_m^{~0} - P$) after pressure starts to drop. Abdel-Alim derived a similar relationship based on Flory-Huggins equation [4]. Substitution of Eq. (12) into Eqs. (6), (8), and (10) would give the

moles of VCM in vapor, water, and solid phases as a function of conversion after the pressure starts to drop:

$$N_v' = \frac{M_0 P_m^{\ 0} F_2(X, T, \gamma, W_i)}{RTF_1(T, \gamma, W_i)} (1 - W) \tag{14}$$

$$N_w' = \frac{M_0 \gamma F_2(X, T, \gamma, W_i)}{H_{\ell v} M_m} \tag{15}$$

$$N_s' = \frac{M_0 x \ F_2(x, T, \gamma, W_i)}{H_{sv} M_m} \tag{16}$$

Equations (4), (7), and (9) define VCM distribution before the pressure drop and Eqs. (14), (15), and (16) after the pressure starts to drop in VCM polymerization.

Calculation of VCM Mole Fractions in Different Phases during VCM Polymerization

Let VCM mole fraction with respect to total monomer charge, M_0/M_m be defined as

$$F_v = N_v M_m/M_0, \qquad F_w = N_w M_m/M_0, \qquad F_s = N_s M_m/M_0$$

$$F_v' = N_v' M_m/M_0 \qquad F_w' = N_w' M_m/M_0 \qquad F_s = N_s' M_m/M_0 \tag{17}$$

Substituting Eqs. (4), (6), (7), (8), (9), (10) into (19):

$$F_v = \frac{M_m P_m^{\ 0} (1 - W)}{RTF_1(T, \gamma, W_i)} \tag{18}$$

$$F_w = C_w^{\ max} \gamma \tag{19}$$

$$F_s = Mx \tag{20}$$

$$F_v' = \frac{(P - P_w^{\ 0})M_m(1 - W)}{RTF_1(T, \gamma, W_i)} \qquad (21)$$

$$F_w' = \frac{\gamma(P - P_w^{\ 0})}{H_{\ell v}P_m^{\ 0}} \qquad (22)$$

$$F_s' = \frac{x(P - P_w^{\ 0})}{H_{sv}P_m^{\ 0}} \qquad (23)$$

The mole fraction of free monomer is

$$F_{fm} = 1 - x - F_v - F_w - F_s \qquad (24)$$

When either x or P is known, the VCM mole fractions can be calculated through Eqs. (18) to (24). Table 1 shows the fixed parameters at different temperatures used for calculation.

The calculated results of total pressure and mole fractions of VCM in different phases vs conversion are tabulated in Tables 2, 3A, and 3B and plotted in Figs. 1 and 2. The partition coefficients $H_{\ell v}$ and H_{sv} for calculation were taken from our previous work [5] and Berens' work [6].

TABLE 1. Fixed Parameters for Calculation at Different Polymerization Temperatures[a]

Temperature (°C)	Temperature (°K)	$P_m^{\ 0}$ in		$\dfrac{(v_m + \gamma v_w)P_m^{\ 0}M_m}{RT}$	$P_w^{\ 0}$
		PSI	dyn/cm^2		(psi)
30°C	303	66.9	0.461×10^7	0.000283	0.615
40°C	313	88.2	0.608×10^7	0.000362	1.07
50°C	323	114.7	0.791×10^7	0.000456	1.79
60°C	333	145.4	1.00×10^7	0.000559	2.890

[a] $W_i = 0.8$, $\gamma = 1.3$, $(v_m + \gamma v_w) = 2.4766$ (cc/g); $v_w = 1$ (cc/g),

$R = 8.3144 \times 10^7 \ \dfrac{dyn \cdot cm}{g \cdot mol \cdot K^0}$, $M_m = 62.5$, $\dfrac{(vm + \gamma vw) M_m}{R} = 0.1862$

$\times 10^{-7} \ \dfrac{cm^2 \ K}{dyn}$, $v_p = 0.7143$ (cc/g), $(v_m - v_p) = 0.4622$ (cc/g).

TABLE 2. Mole Fraction of VCM in Different Phases at Different Conversions at 50°C[a]

P (psi)	x	P_m (psi)	P_m/P_m^0 [$= F_z(x, T, \gamma, W_i)$]	$H_{\ell v}$	H_{sv}	F_{FM}	F_v	F_w	F_s	$(F_v + F_w)/F_s$
116.5	0	114.7	1	83.3	3.45	0.973	0.0113	0.0156	0	
116.5	0.10	114.7	1	83.3	3.45	0.843	0.0122	0.0156	0.029	0.951
116.5	0.2	114.7	1	83.3	3.45	0.713	0.0130	0.0156	0.058	0.493
116.5	0.3	114.7	1	83.3	3.45	0.584	0.0139	0.0156	0.087	0.369
116.5	0.4	114.7	1	83.3	3.45	0.454	0.0147	0.0156	0.116	0.292
116.5	0.5	114.7	1	83.3	3.45	0.324	0.0156	0.0156	0.145	0.246
116.5	0.6	114.7	1	83.3	3.45	0.194	0.0164	0.0156	0.174	0.216
116.5	0.749	114.7	1	83.3	3.45	0.0011	0.0173	0.0156	0.217	0.185
108.5*	0.781	106.7	0.924	84.0	3.85	0	0.0166*	0.0143*	0.187	0.173
106.5	0.822	104.7	0.913	89.5	5.07	0	0.0167	0.0133	0.148	0.203
96.5	0.850	94.7	0.826	90.8	5.70	0	0.0154	0.0118	0.123	0.248
86.5	0.871	84.7	0.738	93.4	6.15	0	0.0138	0.0103	0.105	0.254
76.5	0.890	74.7	0.651	103.3	6.51	0	0.0123	0.0082	0.089	0.251
66.5	0.930	64.7	0.564	102.5	10.25	0	0.0109	0.00715	0.051	0.372
46.5	0.946	44.7	0.39	108.3	8.67	0	0.0076	0.00461	0.042	0.291

[a] P_w^0 = 1.79 psi, P_m^0 = 114.7 psi, F_1 = 0.3248 (g/cc), W_i = 0.8; γ = 1.3, * means "at the maximum reaction rate."
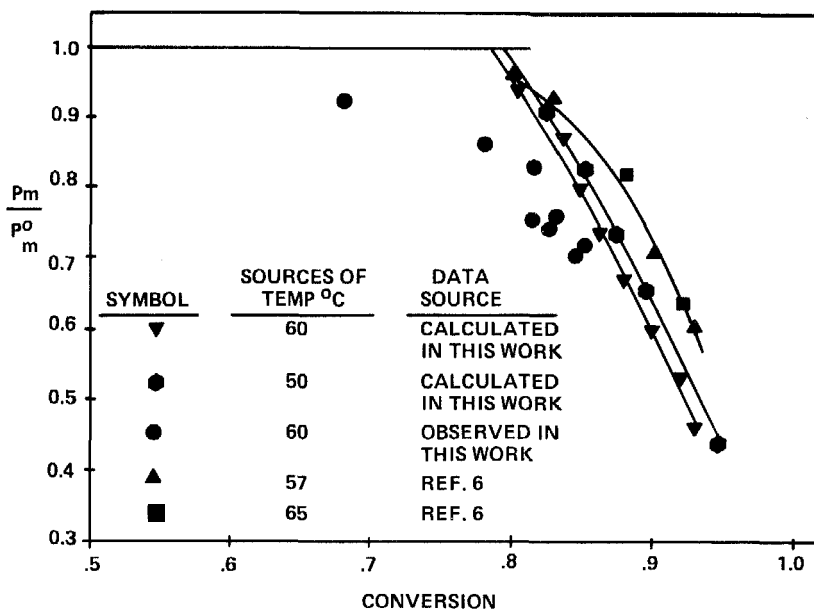
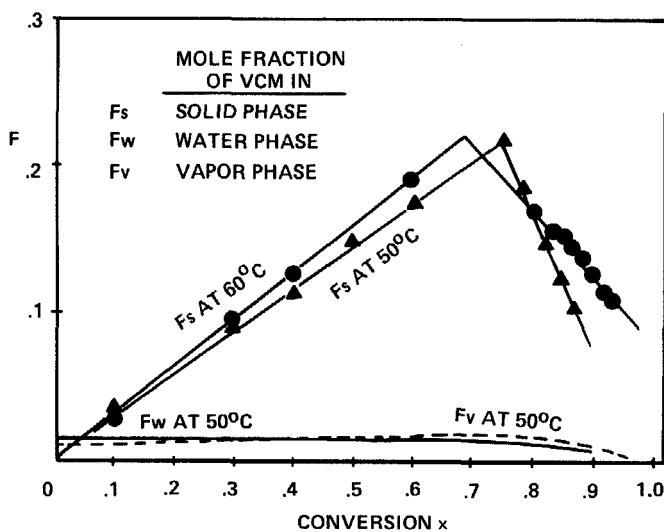FIG. 1. Monomer activity $P_m/P_m^{\,o}$ vs conversion.

FIG. 2. Mole fraction of vinyl chloride F in different phases vs conversion x in VCM polymerization.

TABLE 3A. Mole Fraction of VCM in Different Phases at Different Conversions at 50°C[a]

x	P (psi)	P_m (dyn/cm²)	$P_m/P_m^{\,\circ}$ [= $f_2(x, T, \gamma, W_i)$]	$H_{\ell v}$	H_{sv}	F_{fm}	F_v	F_w	F_s	$(F_v + F_w)/F_s$
0	116.5	0.791×10^7	1	83.3	3.45	0.973	0.0113	0.0156	0	
0.10	116.5	0.791×10^7	1	83.3	3.45	0.843	0.0122	0.0156	0.029	0.951
0.2	116.5	0.791×10^7	1	83.3	3.45	0.713	0.0130	0.0156	0.058	0.493
0.3	116.5	0.791×10^7	1	83.3	3.45	0.584	0.0139	0.0156	0.087	0.369
0.4	116.5	0.791×10^7	1	83.3	3.45	0.454	0.0147	0.0156	0.116	0.292
0.5	116.5	0.791×10^7	1	83.3	3.45	0.324	0.0156	0.0156	0.145	0.246
0.6	116.5	0.791×10^7	1	83.3	3.45	0.194	0.0164	0.0156	0.174	0.216
0.749	116.5	0.791×10^7	1	83.3	3.45	0.0011	0.0173	0.0156	0.217	0.185
0.781	108.5*	0.736×10^7	0.924	84.0	3.45	0	0.0166*	0.0143*	0.187	0.173
0.822	106.5	0.722×10^7	0.913	89.5	5.07	0	0.0167	0.0133	0.148	0.203
0.850	96.5	0.653×10^7	0.826	90.8	5.70	0	0.0154	0.0118	0.123	0.248
0.871	86.5	0.584×10^7	0.738	93.4	6.15	0	0.0138	0.0103	0.105	0.254
0.890	76.5	0.515×10^7	0.651	103.3	6.51	0	0.0123	0.0082	0.089	0.251
0.930	66.5	0.446×10^7	0.564	102.5	10.25	0	0.0109	0.00715	0.051	0.372
0.946	46.5	0.308×10^7	0.39	108.3	8.67	0	0.0076	0.00461	0.042	0.291

[a]$P_w^{\,\circ}$ = 1.79 psi, $P_m^{\,\circ}$ = 114.7 psi, W_i = 0.8; γ = 1.3, * means "at the maximum reaction rate."

TABLE 3B. Mole Fraction of VCM in Different Phases at Different Conversions at $60°C$

x	P (psi)	P_m (dyn/cm²)	P_m/P_m^0	$H_{\ell v}$	H_{sv}	F_{fm}	F_v	F_w	F_s	$(F_v + F_w)/F_s$
0	145	1.0×10^7	1	87.0	3.13	0.916	0.0694	0.0149	0	0
0.1	145	1.0×10^7	1	87.0	3.13	0.838	0.0149	0.0149	0.032	0.931
0.2	145	1.0×10^7	1	87.0	3.13	0.705	0.0160	0.0149	0.064	0.483
0.3	145	1.0×10^7	1	87.0	3.13	0.572	0.0171	0.0149	0.096	0.333
0.4	145	1.0×0^7	1	87.0	3.13	0.439	0.0182	0.0149	0.128	0.259
0.5	145	1.0×10^7	1	87.0	3.13	0.306	0.0192	0.0149	0.160	0.213
0.6	145	1.0×10^7	1	87.0	3.13	0.713	0.0203	0.0149	0.192	0.183
0.7	145	1.0×10^7	1	87.0	3.13	0.040	0.0214	0.0149	0.224	0.162
0.804	137	0.945×10^7	0.945	87.1	4.73	0	0.0225	0.0149	0.170	0.220
0.835	127	0.8759×10^7	0.8759	87.6	5.54	0	0.0228	0.0148	0.151	0.249
0.851	117	0.8069×10^7	0.8069	88.7	5.76	0	0.0230	0.0147	0.148	0.255
0.864	107	0.7380×10^7	0.7380	86.8	5.90	0	0.0231	0.0150	0.146	0.261
0.882	97	0.6690×10^7	0.6690	86.9	6.37	0	0.0233	0.0150	0.138	0.278
0.900	87	0.6000×10^7	0.6000	87.6	7.06	0	0.0235	0.0148	0.127	0.302
0.920	77	0.5310×10^7	0.5310	87.0	8.17	0	0.0237	0.0149	0.113	0.342
0.931	67	0.4621×10^7	0.4621	88.0	8.40	0	0.0239	0.0148	0.111	0.349

COMPARISON OF THEORETICAL AND EXPERIMENTAL RESULTS

Conversion vs pressure data at termination after the pressure drop have been collected in our laboratory through gravimetric method (see Fig. 1). It appears that the calculated results closely approximate the observed data from both our laboratory and Abdel-Alim's work [4].

CONCLUSIONS

From Fig. 2 it is apparent that the VCM concentrations in vapor and water phases are not negligible. At the hot spot the amount of VCM in vapor and water phases is about 20% of that in the solid phase. The reaction rate at the hot spot would be overestimated if FCM in the vapor and water phases is not accounted for, as previously done. The relation of conversion vs pressure after the pressure starts to drop, calculated from the VCM concentrations in three phases, appears to be a close approximation of the practice. Also, knowledge of VCM distribution at termination of the polymerization will assist VCM accountability and stripper design.

APPENDIX 1: DERIVATION OF EQS. (1) AND (2)

The initial liquid phase volume is

$$W_i V_r = M_0 \gamma v_w + v_m \left[M_0 - \frac{(1 - W_i) V_r P_m^{\,0} M_m}{RT} \right]$$

or

$$M_0 = V_r \left[\left\{ W_i + \frac{(1 - W_i) P_m^{\,0} M_m v_m}{RT} \right\} \Big/ (v_m + \gamma v_w) \right]$$

$$= V_r F_1(T, \gamma, W_i) \tag{1}$$

where

$$F_1(T, \gamma, W_i) = \frac{RTW_i + (1 - W_i) P_m^{\,0} M_m v_m}{RT(v_m + \gamma v_w)} \tag{A1}$$

During VCM polymerization the vapor phase volume, V_v increases by

$$\Delta V_v = x M_0 (v_m - v_p)/(1 - \frac{v_m M_m P_m^{\,0}}{RT}) \tag{A2}$$

The denominator represents free monomer vaporization to fill up the shrinked volume:

$$V_v = (1 - W)V_r = (1 - W_i)V_r + \Delta V_v$$

$$= (1 - W_i)V_r + x(v_m - v_p)V_r F_1(T, \gamma, W_i)/(1 - \frac{v_m M_m P_m^{\,0}}{RT})$$

$$= \left\{ (1 - W_i) - \frac{x(v_m - v_p)}{\left(1 - \frac{P_m^{\,0} M_m v_m}{RT} \right)} F_1(T, \gamma, W_i) \right\} V_r \tag{A3}$$

Also, from combining Eqs. (A1) and (A3),

$$W = W_i + \left\{ \frac{X(v_m - v_p)[RTW_i + (1 - W_i)P_m^{\,0} M_w v_m]}{(RT - P_m^{\,0} M_m v_m)(v_m + \gamma v_w)} \right\} \tag{2}$$

SYMBOLS

x	conversion
M_0	weight of monomer charged
V_r	reactor volume
γ	water to monomer weight ratio
v_m, v_w, and v_p	specific volumes of monomer, water, and polymer
M_m, M_w	molecular weight of monomer and water
R	gas constant
T	absolute temperature
$P_m^{\,0}$	vapor pressure of VCM (all pressures are in absolute pressure, not gauge pressure)

P_m	partial pressure of VCM
P_w, $P_w^{\,0}$	partial pressure and vapor pressure of water
C_s	VCM concentration in PVC (g/g PVC)
C_w	VCM concentration in water (g/g H_2O)
m	maximum VCM concentration in PVC (g VCM/ g PVC)
$H_{s\ell}$, $H_{\ell v}$, H_{sv}	partition coefficient of VCM in solid/water, water/vapor, and solid/vapor phases, respectively
t^{hs}	the reaction time where reaction rate is maximum. It usually takes place at pressure drop equal to 8 psi
W	% fillage of reactor at time, t
W_i	% fillage of reactor at t = 0
V_v	vapor-phase volume
N_v, N_w, and N_s	moles of VCM in vapor, water, and PVC phases
N_p, N_{fm}	moles of VCM in polymer form and in free monomer phase
$N_v{}'$, $N_w{}'$, and $N_s{}'$	N_v, N_w, and N_s after pressure starts to drop
F_v, F_w, F_s, $F_v{}'$, $F_w{}'$ and $F_s{}'$	mole fraction of N's with respect to moles charged

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