



PREDICTION OF RADICALS OF CRITICAL LENGTH IN EMULSION POLYMERIZATION PROCESSES

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Abstract: There is the need of a reliable process model of the emulsion polymerization so that process control and optimization may be adequately performed. Although process models for the emulsion polymerization have been proposed for over three decades, several discrepancies still exist. Here we discuss discrepancies that appear in the way the radicals of critical length are modeled in the literature. We show that the discrepancies cause significant deviations in the prediction of the behavior of the polymerization reactor. *Copyright © 2006 IFAC*

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1. INTRODUCTION

Many important polymers are commercially produced in batch or semi-batch reactors since they provide an efficient way to produce either high value-added products or products with specified properties. So, it is of interest to optimally operate these reactors, which is, however, not a simple task, since optimal operating policies rely on model predictions. Although models for polymerization reactors have been proposed for many years, still many unsolved issues remain, particularly when it comes to the emulsion polymerization process, where dozens of different models exist, all being claimed to marvelously represent the polymerization process (Araújo and Giudici, 2003, Casella et al., 2003, Zubitur et al., 2003, Gao & Penlidis, 2002, Saldivar et al., 1998, Liotta et al., 1998, Dubé et al., 1997, Gilbert, 1995, Ray, 1972), which is accomplished by properly adjusting selected model parameters to particular reacting conditions. This is why models have been published where, e.g., the critical length for methyl methacrylate has been taken as 65 and nowadays it is known that the accepted value is about 10 (Forcada and Asua, 1990, Gilbert, 1995). Several discrepancies in modeling emulsion polymerization reactors are well known. Others are not explicitly discussed in the literature, like the ones related to the

modeling of the mass balance for the radicals of critical length, i.e., radicals that become so large that get insoluble in the aqueous phase. So, in this paper we aim to discuss the several unsolved issues regarding the modeling of the radicals of critical length. We state that instead of ignoring the several discrepancies that exist among the different proposed models in the literature, effort should be made in unifying the phenomenological description of what happens with radicals of critical length, as is being performed for the establishment of propagating, chain transfer and termination rates (Van Berkel et al., 2005, Beuermann et al., 1997).

In section 2, a discussion on the current different available models for the mass balance for the radicals of critical length is provided and a unified general model is presented that is able to represent the main modeling tendencies in the literature, as well as some variations to them. In section 3, we discuss the different modeling possibilities. It seems clear for us that it is not acceptable that different assumptions be made to represent the same process, by just adjusting some parameters. In section 4, the paper is concluded and in appendix A, the remaining equations of the model with their parameters used for the simulations presented in this paper are given.

2. MATHEMATICAL MODELING OF EMULSION POLYMERIZATION REACTORS

As stated before, there is no definite model of the emulsion polymerization process. Different authors postulate different hypotheses and simply adjust some parameters so that experimental results are reproduced. It is known that some parameters should not depend on a particular system and universal values should be used like values for the propagation reactions (Gilbert, 1995), which are being established by a IUPAC party for several polymerization systems by the PLP technique (Van Berkel et al., 2005, Beuermann et al., 1997, Gilbert, 1995). Termination rates' coefficients should also not be adjusted to meet particular results, but still no definite values have been postulated for termination coefficients in spite of the several recent works (Van Berkel et al., 2005, Buback et al., 2003) on estimating them together with chain transfer rate coefficients. When it comes to modeling the capture of free-radicals in micelles and polymer particles, several discrepancies in the way of modeling emulsion polymerization reactors are well known and discussed in the literature (Herrera-Ordóñez et al., 2004, Fitch, 2003, Gao and Penlidis, 2002) and no conclusion exists on how to proceed. The same is true when models are written for the prediction of particle nucleation. Other discrepancies in the existing models are more subtle and less commented, like the different approaches in modeling the mass balance for the free-radical of critical length in the aqueous phase, which will be considered in the next paragraphs.

In the literature, the mass balances for the oligomeric radicals in the aqueous phase are generally written assuming a pseudo-stationary condition. Some exceptions can be found, though (Casella et al., 2003). Here, non-stationary mass balances are considered for the radicals in the aqueous phase. The advantages of using dynamic equations instead of stationary ones to evaluate the concentrations of the radicals in the aqueous phase is the easiness of incorporating different hypotheses in the description of the equations making them more general. Moreover, the dynamic representation makes it easier to numerically solve a model constructed by the specifications of hypotheses made by the user. Because of the lack of space and in order to make the discussion clearer, we will restrict our attention in this section to reactors operated in batch mode. Moreover, the presentation here is restricted to the homopolymerization case, so that the equations become not too much visually polluted.

Homogeneous nucleation occurs when radicals become insoluble in the aqueous phase, which occurs when radicals achieve the critical length j_{cr} . Three distinct rates for predicting homogenous nucleation are most used in the literature, which are given in equations (1) to (3). One popular approach is to consider that the nucleation rate is proportional to the propagation rate of radical $j_{cr}-1$ in case a partial solubility is assumed or equal to the propagation rate when radical j_{cr} is assumed to be totally insoluble in

the aqueous phase (Gao & Penlidis, 2002, Araújo and Giudici, 2003). In the former case $f_{ef,hom}$ in equation (1) may be adjusted (between 0 and 1) and in the latter case $f_{ef,hom}=1$. Equation (2) is also commonly used (Gilbert, 1995, Forcada and Asua, 1990, Abad et al., 1994). It is somewhat awkward, since it suggests that radicals of critical length are actually soluble in the aqueous phase and precipitate when they encounter a monomer. Again the parameter $f_{ef,hom}$ may be adjusted. Equation (3) may be used in two different contexts. In the first, it is a way to model the precipitated radicals and the constant k_h is set to 1 and $f_{ef,hom}$ is properly adjusted to experimental data or calculated from solubility considerations. The second interpretation for equation (3) is due to Fitch and Tsai (1971), who state that radicals of length j_{cr} are not captured by either micelles and particles and the constant k_h is thus modeled accordingly to (4) (Dubé et al., 1997, Casella et al., 2003).

$$R_{hom} = f_{ef,hom} k_p [M]_w [R'_{j_{cr}-1}]_w V_w \quad (1)$$

where, R_{hom} is the rate of nucleation, k_p is the propagation rate constant, $[M]_w$ is the concentration of monomer in the aqueous phase, $[R'_{j_{cr}-1}]_w$ is the concentration of radical of length $j_{cr}-1$, V_w is the volume of the aqueous phase and $f_{ef,hom}$ is a parameter as described above.

$$R_{hom} = f_{ef,hom} k_p [M]_w [R'_{j_{cr}}]_w V_w \quad (2)$$

where, $[R'_{j_{cr}}]_w$ is the concentration of radical of length j_{cr}

$$R_{hom} = f_{ef,hom} k_h [R'_{j_{cr}}]_w V_w \quad (3)$$

where, k_h is equal to 1 or obtained from equation (4).

$$k_h = k_{ho} e^{-E_{R,h}/T} \left(1 - \frac{A_p}{4V_w} \sqrt{\frac{2j_{cr}\mathcal{A}'}{k_p [M]_w^{sat}}} \right) \quad (4)$$

where, k_{ho} , $E_{R,h}$ are constants, T is the temperature of the reacting medium, A_p is the surface area of polymer particles, $[M]_w^{sat}$ is the saturation concentration of monomer in the aqueous phase and \mathcal{A}' is the diffusivity of the radical.

Equation (5) describes the amount of radicals of critical length dissolved in the aqueous phase. No distinction is made between initiator originated radicals and monomeric radicals, i.e., radicals formed from the monomeric radical desorbed from the particles. This is generally the adopted strategy. Zubitur et al. (2003) are a noteworthy exception, except for the fact that the way they model the radicals not originated from the initiator is not presented. In the presentation of equation (5) four flags e_2 to e_5 are used in order to take into account variations in the models from the literature. If the radical of critical length is assumed to be totally insoluble in the aqueous phase, $e_3=e_4=0$, $e_5=1$ and $f_{ef,hom}=1$ (Gao and Penlidis, 2002, Araújo and Giudici, 2003). If absorption of the radical of length j_{cr} is not possible, then e_2 must be set to zero. Some authors consider that the radical of length j_{cr} may propagate

(Dubé et al., 1997, Gilbert, 1995) and even participate in termination reactions. The fate of the larger radicals and oligomers is however not discussed. Some authors claim that the radical of length jcr may participate in termination reactions but may not propagate. Each of these considerations may be taken into account by adequately selecting 0 or 1 values for the flags e_3 and e_4 . Curiously, some authors do not include the precipitation term given by the homogeneous nucleation rate, as if it were possible that no radicals of length jcr were needed to generate polymer particles. That is why the flag e_5 appears in equation (5). One must just note that equation (2) corresponds to the propagation rate, so e_3 must be set to zero or e_5 to zero when equation (2) is used. So, equation (5) encompasses all the actual modeling approaches for describing the amount of radicals of length jcr in the reactor.

$$\begin{aligned} \frac{dR_{jcr,w}^*}{dt} = & k_p \left([R_{jcr-1}^*]_w [M]_w - e_3 [R_{jcr}^*]_w [M]_w \right) V_w - \\ & - e_2 \left(k_{a,m} [R_{jcr}^*]_w N_{mic} + k_{a,p} [R_{jcr}^*]_w N_p \right) - \\ & - e_4 \left(k_t^w [R_{jcr}^*]_w [R^*]_w^{tot} + k_t^w [R_{jcr}^*]_w^2 \right) V_w - \\ & - e_5 R_{hom} \end{aligned} \quad (5)$$

where, $k_{a,m}$ and $k_{a,p}$ are the absorption constants by micelles and polymer particles, respectively, N_{mic} and N_p , are respectively the number of micelles and polymer particles, k_t^w is the termination rate constant and $[R^*]_w^{tot}$ is the total concentration of radicals in the aqueous phase.

As for the mechanism for capture of radicals, three major approaches are considered, presented in equations (6) to (8), which correspond to the propagation, diffusion and collision models. The latter equations are written for radical capture by micelles. For radical capture by particles, one just has to substitute the radius of micelles by the radius of the particles and $f_{abs,m}$ is substituted by $f_{abs,p}$. Further discussions regarding $f_{abs,m}$ and $f_{abs,p}$ are postponed to section 3.

$$k_{a,m} = f_{abs,m} \quad (6)$$

sendo, $f_{abs,m}$ is a constant.

$$k_{a,m} = f_{abs,m} \mathfrak{A}_{M,w} N_{av} 4\pi r_{mic} \quad (7)$$

where, $\mathfrak{A}_{M,w}$ is the diffusivity of monomer in the aqueous phase, N_{av} is the Avogadro number, r_{mic} is the micelle radius.

$$k_{a,m} = f_{abs,m} N_{av} 4\pi r_{mic}^2 \quad (8)$$

3. COMPARISON OF DIFFERENT MODEL PREDICTIONS

Table 1 summarizes the simulations performed in order to analyze the effect of different model formulations for the description of the radical of

critical length. The simulations are referred to the homopolymerization of vinyl acetate with potassium persulfate used as initiator and sodium lauryl sulfate as emulsifier. The initial number of moles fed to the reactor of water, monomer, initiator and emulsifier are, respectively, 55.51, 3.44, 0.003124 and 0.0417. The simulations were carried for a temperature of 60°C.

Several situations were considered. For example, simulations were performed in order to analyze the effect of different modeling possibilities for capture of the radicals of critical length on the response of the reactor (cases a, b to e). Also some simulations were performed in order to analyze differences in the modeling of the homogeneous nucleation (cases a, b, f, g, h). Case b is considered as the base case for comparison purposes.

Table 1 Different model formulations for the radical of critical length

case	e_2	e_3 $/e_4$	e_5	R_{hom}	$f_{ef,hom}$ (%)	$k_{a,m/p}$	$f_{abs,m}$ (SI)	$f_{abs,p}$ (SI)
a	0	0	1	eq. 1	100	eq. 6	25	4000
b	1	1	1	eq. 1	80	eq. 6	25	4000
c	0	0	1	eq. 1	100	eq. 7	1.3e-5	1.3e-3
d	0	0	1	eq. 1	100	eq. 7	1.0e-4	1.0e-2
e	0	0	1	eq. 1	100	eq. 8	5.3e-7	1.3e-5
f	1	1	0	eq. 2	-/-	eq. 6	25	4000
g(*)	1	1	0	eq. 3	-/-	eq. 6	25	4000
h	1	1	0	eq. 3	-/-	eq. 6	25	4000

(*) for this case all radicals were assumed to be surface active in accordance to Casella's et al. (2003) model

In figures 1 to 4, the homogenous nucleation model was altered. The propagation micelar nucleation model was considered in these figures with the parameters presented in Casella et al. (2003). It is noteworthy to say that Casella's et al. (2003) model considers equation (3) for the homogeneous nucleation and assumes $e_2=e_3=e_4=1$, $e_5=0$ and k_h modeled as in (4), but they assume that all radicals are surface active. The response to their model is presented in case g. One can see that cases a and b behave in a similar way, which may signify that as long as the radical of critical length exhibits only a slight solubility in the aqueous phase, its propagation, termination with any radical and capture by particles or micelles is not very relevant. Case f shows a very slight deviation in respect to case a. This is because the numerical difference between the models of equations (1) and (2) is very little. Differences in the latter equations should therefore be regarded in terms of the physical meaning of the equations. Case h is the same as case g except that only the radicals that become surface active can be absorbed. As expected significant deviations are observed. So now attention must be turned towards the huge discrepancies in the responses between cases a and h. It becomes evident that completely different behaviors are observed and that the dynamic response of the reactor provides insights into what happens, i.e. by monitoring not only conversion, but the diameter of polymer particles as well as taking some measurements of the concentration of radicals, one might better devise what mechanism should be taking place.

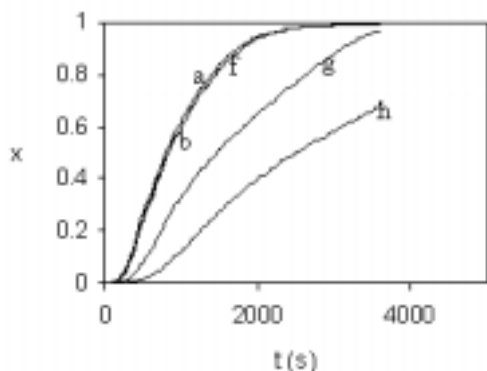


Fig. 1. Effect of the homogeneous nucleation model on the conversion.

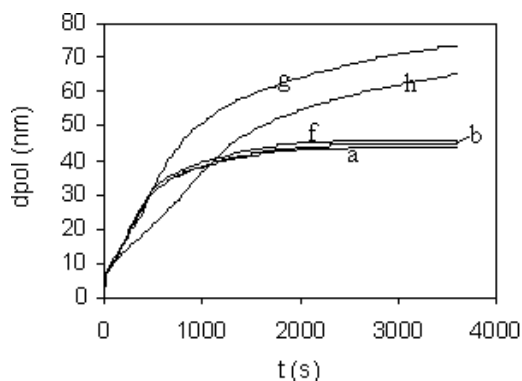


Fig. 2. Effect of the homogeneous nucleation model on the polymer diameter.

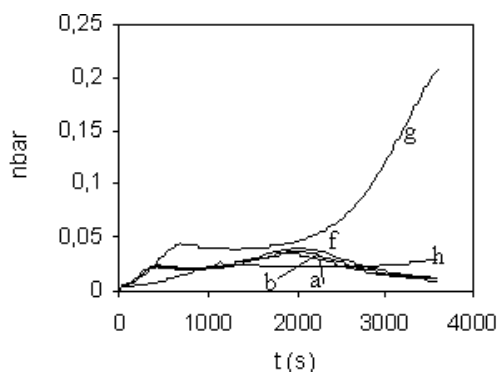


Fig. 3. Effect of the homogeneous nucleation model on means number of radicals in the particles.

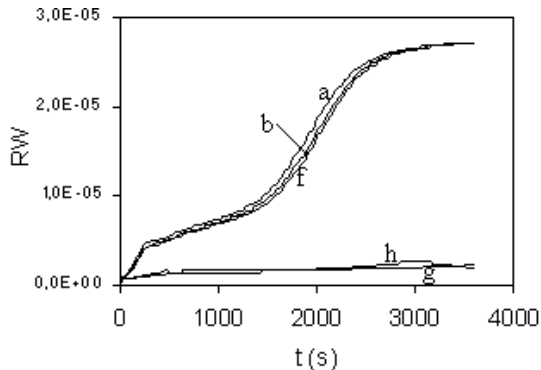


Fig. 4. Effect of the homogeneous nucleation model on the total concentration of radicals in the aqueous phase.

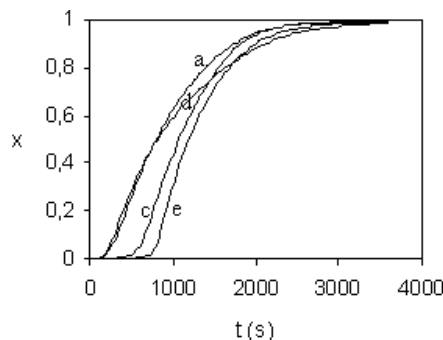


Fig. 5. Effect of the absorption model on the conversion.

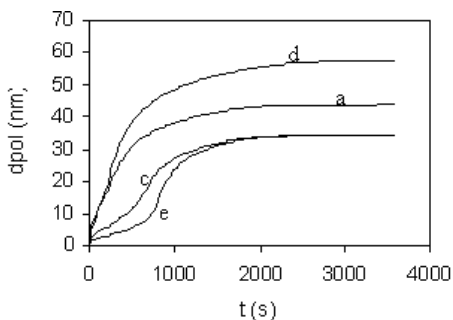


Fig. 6. Effect of the absorption model on the polymer diameter.

In figures 5 to 8 simulation responses are presented for different absorption models. As expected, great differences in the responses can be observed and one can clearly see how the process is dependent on the adjustment of the parameters $f_{abs,m}$ and $f_{abs,p}$. As already commented, the values in case b were simply taken from Casella et al. (2003). The parameters in cases c and e were calculated from the values presented in case a considering a particle diameter of about 10 nm and a micellar radius of 2.5 nm. The values in case d were taken arbitrary from several simulations performed in order to better adjust the parameters. One can see that it is not easy to adjust all curves. Moreover, the deviations to the base case, are very significant. So, it is clear that it is relevant that the real absorption model should be known. Figures 5 to 8 clearly show that the dynamic response is strongly affected by the choice of the model and that different models produce different dynamic responses for all four variables shown in figures 5 to 8. Lara (2005) has shown that reliable on-line monitoring of the diameter of polymer particles may be made by Raman and NIR spectrometry. Recently, the ESR technique has been routinely used to obtain information regarding the concentration of radicals. In spite of the fact that the latter technique is strongly dependent on the interpretation of the measured signals and relies on expensive equipment, not usually available in all research centers, one can see that measurements of the concentration of radicals will help to elucidate what absorption mechanism occurs. Moreover, measurements of the concentration of radicals and on-line monitoring of the polymer particle's diameter also help to clarify how homogenous nucleation may be modeled. We think that efforts towards the clarification of the absorption mechanism should be made as is being already

performed for the propagation and termination rate constants.

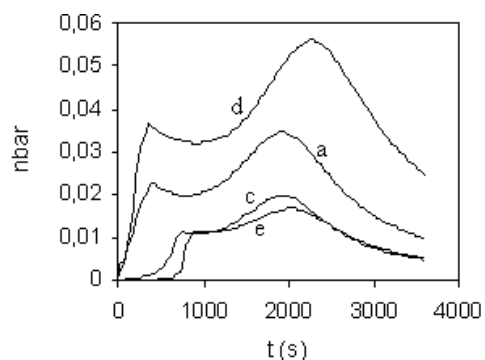


Fig. 7. Effect of the absorption model on means number of radicals in the particles.

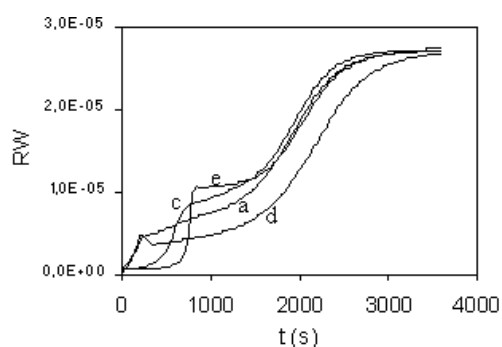


Fig. 8. Effect of the absorption model on the total concentration of radicals in the aqueous phase.

4. CONCLUDING REMARKS

In this paper we have shown that different modeling hypotheses regarding the fate of the radicals of critical length affect the dynamic behavior of the polymerization reactor. Moreover, we have stressed that is important to better understand the absorption mechanism, since the dynamic response of the reactor is strongly dependent on the adjustment of the absorption parameters. We have also shown that different models used to predict the homogenous nucleation rate also present large discrepancies. Hence, NIR, Raman and ESR measurements should be conducted in order to better clarify the really occurring mechanism.

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APPENDIX A

Here we present the other equations used to generate the simulation results presented in section 3. They are based on the following assumptions: (i) thermodynamic equilibrium is assumed to govern the partition of monomer between the aqueous and polymer phases and the term corresponding to the surface tension was neglected; (ii) the reactor is considered to be ideally mixed; (iii) the reacting medium is assumed to be monodisperse; (iv) additivity of volumes is assumed; (v) only radicals that become surface-active can be captured, i.e., only radicals with chains longer than Z-mer can be captured by either micelles or particles; (vi) emulsifier is added above the CMC; (vii) chemical initiation is used; (viii) particles may be formed by either micellar and homogeneous nucleation; (ix) monomeric radicals may be desorbed; (x) the model of Li and Brooks (1993) was considered for predicting the average number of radicals inside the polymer particles.

$$\frac{dN_p}{dt} = k_{a,m} N_{mic} [R^*]_w^{nu} + R_{hom} \quad (9)$$

where, $[R^*]_w^{nu}$ is the concentration of all radicals that become surface active.

$$N_{mic} = \frac{([E]_w - CMC) a_s V_w - A_p - A_d \frac{a_s}{a_{ms}}}{N_{av} 4\pi r_{mic}^2} \quad (10)$$

where, $CMC=2.43 \text{ mol/m}^3$, $a_s=3 \times 10^5 \text{ m}^2/\text{mol}$, $A_d=0$.

$$\frac{dN_M}{dt} = -N_p k_p [M]_p \bar{n} - k_p [M]_w [R^*]_w^{tot} V_w \quad (11)$$

where, $k_p = 5.87 \times 10^4 e^{-3358.29/T}$.

$$\begin{aligned} \frac{dR_{1,w}^*}{dt} = & 2 f_{ef,1r} k_t [I]_w V_w + k_{des} \bar{n} N_p - k_p [M]_w [R_1^*]_w V_w - \\ & - k_t^w V_w \left([R_1^*]_w [R^*]_w^{tot} + [R_1^*]_w^2 \right) \end{aligned} \quad (12)$$

where, $k_t = 1.8 \times 10^{17} e^{-17161.55/T}$ in SI units, $f_{ef,1r}=0.5$,

$k_t^w = 4.303 \times 10^6 e^{-1652.12/T}$ in SI units.

$$\begin{aligned} \frac{dR_{j,w}^*}{dt} = & k_p [R_{j-1}^*]_w [M]_w V_w - k_p [R_j^*]_w [M]_w V_w - \\ & - k_t^w [R_j^*]_w [R^*]_w^{tot} V_w - k_t^w [R_j^*]_w^2 V_w - \\ & - e_2 \left(k_{a,m} N_{mic} [R_j^*]_w + k_{a,p} N_p [R_j^*]_w \right) \end{aligned} \quad (13)$$

where, $e_2=0$ if $j < Z_{mer}$ and $e_2=1$ if $j \geq Z_{mer}$. For vynil acetate $Z_{mer} = 8$ and $j_{cr} = 16$.

$$k_{des} = k_{tsf} [M]_p \frac{k_o}{\beta k_o + k_p [M]_p} \quad (14)$$

where, $k_{tsf} = 693e^{-4654.56/T}$, k_o is given in (17) and β in (18).

$$\frac{d\bar{n}}{dt} = k_{a,p} [R^*]_w^{nu} - k_{des} \bar{n} - \gamma \frac{k_t^P}{N_{av} V_{1P}} \bar{n}^2 \quad (15)$$

$$\gamma = \frac{2 \left(2k_{a,p} [R^*]_w^{nu} + k_{des} \right)}{\left(2k_{a,p} [R^*]_w^{nu} + k_{des} \right) + \frac{k_t^P}{N_{av} V_{1P}}} \quad (16)$$

$$k_o = \frac{\frac{12 \mathfrak{A}_{M,w}}{K_M^P d_p^2}}{1 + \frac{2 \mathfrak{A}_{M,w}}{K_M^P \mathfrak{A}_{M,p}}} \quad (17)$$

where, $\mathfrak{A}_{M,w} = \mathfrak{A}_{M,p} = 10^{-10} \text{ m}^2/\text{s}$.

$$\beta = \frac{k_p [M]_w + k_t^w [R^*]_w^{totM}}{k_p [M]_w + k_t^w [R^*]_w^{totM} + k_{a,p} [N_p]} \quad (18)$$

$$0 = 1 - \phi_M^P + \ln \phi_M^P + \psi_M \left(1 - \phi_M^P \right)^2 - \ln \frac{[M]_w}{[M]_w^{sat}} \quad (19)$$

where, $\psi_M = 0.556$.

$$[M]_w = \frac{N_M - \phi_M^P V_p \tilde{\rho}_M}{V_w} \quad (20)$$

$$V_p = \frac{(N_{M,o} - N_M) M M_M}{\phi_p^P \rho_{pol}} \quad (18)$$

$$V_{1p} = \frac{V_p}{N_p N_{av}} \quad (19)$$

$$d_p = \sqrt[3]{\frac{6 V_{1p}}{\pi}} \quad (20)$$

$$A_p = \pi d_p^2 N_p N_{av} \quad (21)$$