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# Calculations of the Average Number of Radicals per Particle in Emulsion Polymerization

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**Abstract:** In emulsion polymerization, the free radicals enter the particles intermittently from the aqueous phase. The number of radicals per particle is given by the Smith-Ewart recursion relation which balances the rate of radical entry into, the rate of radical exit from and the rate of radical termination inside the particle. Models for emulsion polymerisation are based on the 0-1 kinetics or the pseudo-bulk kinetics. Small particles, low initiator concentrations and large number of particles favour the 0-1 kinetics, whereas the large particles, high initiator concentrations and small number of particles will favour pseudo-bulk kinetics. A given polymerization system may exhibit both these kinetic behaviours, initially following the 0-1 kinetics and during the later stages of polymerization following the pseudo-bulk kinetics. The aim of this work is to calculate the time dependent values of the average number of radicals per particle in emulsion polymerization for the pseudo-bulk kinetics.

**Keywords:** average number of radicals per particle; emulsion polymerization; 0-1 kinetics; pseudo-bulk kinetics; time dependent solutions

## I. INTRODUCTION

In emulsion polymerization, radicals are segregated from one another i.e. they are physically separated from one another due to compartmentalized nature. Due to this segregation, the radicals present in the different particles cannot terminate with one another and the total number of growing radicals is higher than other modes of free radical polymerization and this leads to increase reaction rates. Also, the life time of these growing radicals, segregated from one another, is higher, giving rise to higher molecular weights. Emulsion polymerization kinetics can be conveniently divided into two types: the 0-1 kinetics and the pseudo-bulk kinetics. In pseudo-bulk kinetics approach, the need to consider bivariate particle size distribution is avoided with both the particle size and the number of radicals in the particles as the internal coordinates. It assumes that the particles with the same size have same number of radicals. The pseudo-bulk approach neglects the stochastic broadening of the particle size distribution but it can account for particles with more than 1 radical in them which is true for larger particles. In pseudo-bulk kinetics all particles larger than the cross over diameter makes system equivalent to bulk polymerization. It does not assume compartmentalization in any given latex particle so more than one radical can reside in swollen latex particle.

## II. NUMBER OF RADICALS PER PARTICLE

Smith and Ewart (Smith and Ewart, 1948) gave the following recursion differential equation for number of particles which contain  $i$  radicals in them:

$$\frac{dN_i}{dt} = (N_{i-1} - N_i)\sigma + [(i+1)N_{i+1} - iN_i]k + [(i+2)(i+1)N_{i+2} - i(i-1)N_i]C \quad (1)$$

Where  $i = 0, 1, 2, \dots$

$N_i$  = Number of particle which contain  $i$  radical

$\sigma$  = Average rate at which radical capture the particle

$k$  = Rate coefficient for radical desorption particles

$C$  = Rate coefficient for radical termination

Li and Brooks (Li and Brooks, 1993) have written this equation in terms of particle fraction;

$$\frac{dv_i}{dt} = (v_{i-1} - v_i)\sigma + [(i+1)v_{i+1} - iv_i]k + [(i+2)(i+1)v_{i+2} - i(i-1)v_i]C \quad (2)$$

$v_i$  = Number-Fraction of particle containing  $i$  radical

Solving further by summing from  $i=1$  to  $i \rightarrow \infty$  and multiplying by  $i$ , give

$$\frac{d\bar{n}}{dt} = \sigma - k\bar{n} - 2C(\sum_{i=1}^{\infty} i^2 v_i - \bar{n}) \quad (3)$$

On writing the equation in terms of variance of the distribution;

$$\frac{d\bar{n}}{dt} = \sigma - k\bar{n} - 2C(D + \bar{n}^2 - \bar{n}) \tag{4}$$

Where D is the variance of distribution, is given by  $D = \sum_{i=1}^{\infty} i^2 v_i - \bar{n}^2$

Assuming, the radical number in the particles follow Poisson distribution whose  $D = \bar{n}$ , equation (4) reduces to:

$$\frac{d\bar{n}}{dt} = \sigma - k\bar{n} - 2C\bar{n}^2 \tag{5}$$

Birtwistle and Blackely (Birtwistle and Blackley, 1981) gave following time dependent equation for modelling of  $\bar{n}$  ;

$$\frac{d\bar{n}}{dt} = \sigma - k\bar{n} - fC\bar{n}^2 \tag{6}$$

Here,  $f$  is a coefficient which varies between zero and two and  $f$  is given by  $f = \frac{2(2\sigma+k)}{2\sigma+k+C}$ .

This expression results by simplifying the Smith and Ewart recursion equation.

In this work our aim is to find explicit analytic solutions to the completely general non-steady state equation for the calculation of average number of radical per particle. The derivation is given in Appendix A and the results are tabulated in Table 1. The general solution of equation (6) is as follows:

$$\bar{n} = \frac{2\sigma f \left(1 - e^{-\frac{qt}{C}}\right)}{(k+q) - \{(k-q)e^{-\frac{qt}{C}}\}} \tag{7}$$

It can also be expressed as:

$$\bar{n} = \frac{[2\sigma f \tanh \frac{qt}{2C}]}{[q+k \tanh (qt/2C)]} \tag{8}$$

### III. CONCLUSIONS

The prediction of average number of radicals per particle is important in emulsion polymerization. Generally, the Smith-Ewart recursion equation is solved by assuming a pseudo-steady state for the number of radicals per particle. In this work, the time dependent equations for the average number of radicals per particle are solved.

Table 1: The solution of  $\bar{n}$  as a function of time for different values of  $f$ .

$\frac{d\bar{n}}{dt}$ Equation	$f$	$\bar{n}$
$\frac{d\bar{n}}{dt} = \sigma - k\bar{n} - fC\bar{n}^2$	$f = \frac{2(2\sigma + k)}{2\sigma + k + C}$	$\bar{n} = \frac{[2\sigma f \tanh \frac{qt}{2C}]}{[q + k \tanh (qt/2C)]}$ $q = \sqrt{k^2 + 4\sigma f C}$
$\frac{d\bar{n}}{dt} = \sigma - k\bar{n} - 2C\bar{n}^2$	$f = 2$	$\bar{n} = \frac{[4\sigma \tanh \frac{qt}{2C}]}{[q + k \tanh (qt/2C)]}$ $q = \sqrt{k^2 + 8\sigma C}$
$\frac{d\bar{n}}{dt} = \sigma - k\bar{n} - C\bar{n}^2$	$f = 1$	$\bar{n} = \frac{[2\sigma \tanh \frac{qt}{2C}]}{[q + k \tanh (qt/2C)]}$ $q = \sqrt{k^2 + 4\sigma C}$
$\frac{d\bar{n}}{dt} = \sigma - k\bar{n}$	$f = 0$	$\bar{n} = \frac{[\sigma(1 - e^{-kt})]}{k}$

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### APPENDIX A

#### A. Calculation for the explicit value of $\bar{n}$

Derivation of equation (5)

$$\frac{d\bar{n}}{dt} \text{Equation } \frac{d\bar{n}}{dt} = -k\bar{n} - fC\bar{n}^2$$

$$\text{Solution: } \frac{d\bar{n}}{\sigma - k\bar{n} - fC\bar{n}^2} = dt \tag{A.1}$$

$$\text{Where } \sigma = \sqrt{k^2 + 4\sigma fC} \tag{A.2}$$

$$\frac{d\bar{n}}{\left[\bar{n} - \frac{-k+q}{2C}\right] \left[\bar{n} - \frac{-k-q}{2C}\right]} = -dt$$

From partial fraction

$$\frac{d\bar{n}}{\left[\bar{n} - \frac{-k+q}{2fC}\right]} + \frac{(-)d\bar{n}}{\left[\bar{n} - \frac{-k-q}{2fC}\right]} = (q/fC)(-dt) \tag{A.3}$$

On integrating (A.3)

$$\ln\left[\bar{n} - \frac{-k+q}{2fC}\right] - \ln\left[\bar{n} - \frac{-k-q}{2fC}\right] = \frac{-qt}{fC} + c' \tag{A.4}$$

Applying boundary condition:  $\bar{n}(0) = 0$ , we have:

$$\ln\left[\bar{n} - \frac{-k+q}{2fC}\right] - \ln\left[\bar{n} - \frac{-k-q}{2fC}\right] = \frac{-qt}{fC} + \ln\frac{-k+q}{-k-q} \tag{A.5}$$

Rearranging the equation (A.5)

$$\frac{\left\{\frac{\bar{n} - \frac{-k+q}{2fC}}{\frac{-k+q}{2fC}}\right\}}{\left\{\frac{\bar{n} - \frac{-k-q}{2fC}}{\frac{-k-q}{2fC}}\right\}} = e^{-qt/fC} \tag{A.6}$$

Solving the equation (A.6) for value of  $\bar{n}$ , we get

$$\bar{n} = \frac{\left[\frac{-k+q}{2C} \left(1 - e^{-\frac{qt}{C}}\right)\right]}{1 - \left[\frac{\left\{\frac{-k+q}{2C}\right\} e^{-\frac{qt}{C}}}{\frac{-k-q}{2C}}\right]}$$

Substituting the values of  $\sigma$  from equation (A.2), we have:

$$\bar{n} = \frac{2\sigma f \left(1 - e^{-\frac{qt}{c}}\right)}{(k+q) - \{(k-q)e^{-\frac{qt}{c}}\}} \quad (\text{A.7})$$

On further simplifying equation (A.7) and converting that equation in form of tan hyperbolic, we have:

$$\bar{n} = \frac{[2\sigma f \tanh \frac{qt}{2c}]}{[q+k \tanh (qt/2c)]} \quad (\text{A.8})$$

#### B. Author Contributions

Ms. Aishwarya Tiwari, II M. Tech. (Chemical Engineering) has carried out this work under the supervision of Dr. Ashwini Sood, Associate Professor, Department of Chemical Engineering, School of Chemical Technology, Harcourt Butler Technical University, Kanpur, India.

#### C. Conflict of Interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.



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