Parametric Sensitivity Study of a Butyl Acrylate Emulsion Polymerization Model

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Abstract:- **In the present work, parametric sensitivity study of a previously developed model for butyl acrylate emulsion polymerization is conducted. The values of few important parameters of the model are changed and the effects on conversion versus time behaviour and total number of particles formed for a fixed recipe are reported. It is found that the effects of the change in the values of these parameters on the conversion versus time behaviour and hence, polymerization kinetics is not significant whereas the effects of the change in the values of these parameters on the total number of particles formed and hence, the nucleation kinetics is quite significant.**

Keywords:- butyl acrylate; emulsion polymerization; parametric sensitivity; polymerization kinetics; nucleation kinetics.

I. INTRODUCTION

A model for butyl acrylate emulsion polymerization was developed, solved and validated in our previous work [1]. The model contained number of parameters. These parameters relate to the physio-chemical and kinetic properties of reaction ingredients which are monomer (butyl acrylate), polymer (poly butyl acrylate), emulsifier (sodium dodecyl sulfate) and initiator (potassium persulfate). The aim of the present work is to conduct a parametric sensitivity study of the model. The values of few selected parameters are varied and their effects on the total number of particles formed and the conversion-time curve for one chosen amount of recipe components are studied systematically. Thus, the influences of the variations in the values of parameters on nucleation dynamics and polymerization kinetics were determined. Majority of the models are validated against conversion versus time data whereas only a few models are validated against variables like total number of particles formed. The readers are referred to our previously published work for the details of the model [1]. Here, parametric sensitivity studies are presented.

II. PARAMETRIC SENSITIVITY STUDIES

The base values of all the parameters used in the model are given in Table 1[1,2]

Butyl Acrylate
MW_M = 128.17 g/gmol
ρ_M = 0.869 g/cm^3
ρ_p = 1.026 g/cm^3
Φ_{sat} = 0.737
$[M]_{p.sat}$ = 5 gmol/l
$[M]_{W,sat}$ = 6.4×10^{-3}gmol/l
k_p = 24000000 cm^3/gmols (at 50ºC)
k_{trm} = 1.55×10^3 cm^3/gmols (at 50ºC)
k_{tp} = 10$^{11.92}$ cm^3/gmols (at 50ºC)
k_{mm} = k_{mp} = 28
D_W = 7.1×10^{11} cm^2/s
γ = 0
χ =0.61
Sodium Dodecyl Sulfate
MW_E = 288.3 g/gmol
E_{CMC} = 0.0005g/cm^3 (at 50ºC)
r_m = 2.5×10^{-7} cm
a_{em}= a_{ep} = 79×10^{-16} cm^2/molecule
Potassium Persulfate
MW_I = 270.33 g/gmol
k_d = 0.0000015 s^{-1} (at 50ºC)
f = 0.5

Table 1: Base values of various parameters

The recipe used in the simulation is given in Table 2.

Recipe Ingredient	Amount
Monomer (Butyl Acrylate)	111.11 g
Water	1000 cm^3 = 1 Litre
Initiator (Potassium Persulfate)	0.01 M or 2.7033 g/l
Emulsifier (Sodium Dodecyl Sulfate)	0.01 M or 2.8833 g/l

Table 2: Recipe used in the Simulation

The reaction temperature was 50 ºC and the reaction occurred in an isothermal, well-stirred batch reactor.

In Table 3, the effect of the variation in the value of initiator efficiency factor, f on the total number of particles formed (N_P) is given.

[E]	[I]	f	N_P
2.8833	2.7033	0.5	3.1876×10^{17}
2.8833	2.7033	0.4	2.9123×10^{17}
2.8833	2.7033	0.3	2.5929×10^{17}

Table 3: Effect of variation in the value of initiator efficiency factor, f on the total number of particles formed (N_P)

As can be seen, at the base value of f = 0.5, the total number of particles formed is close to the experimental value of 3.0×10^{17}. As the value of f is decreased, the value of the total number of particles formed also decreases considerably.

In Figure 1, the effect of the variation in the value of initiator efficiency factor, f on the conversion versus time curve is given.
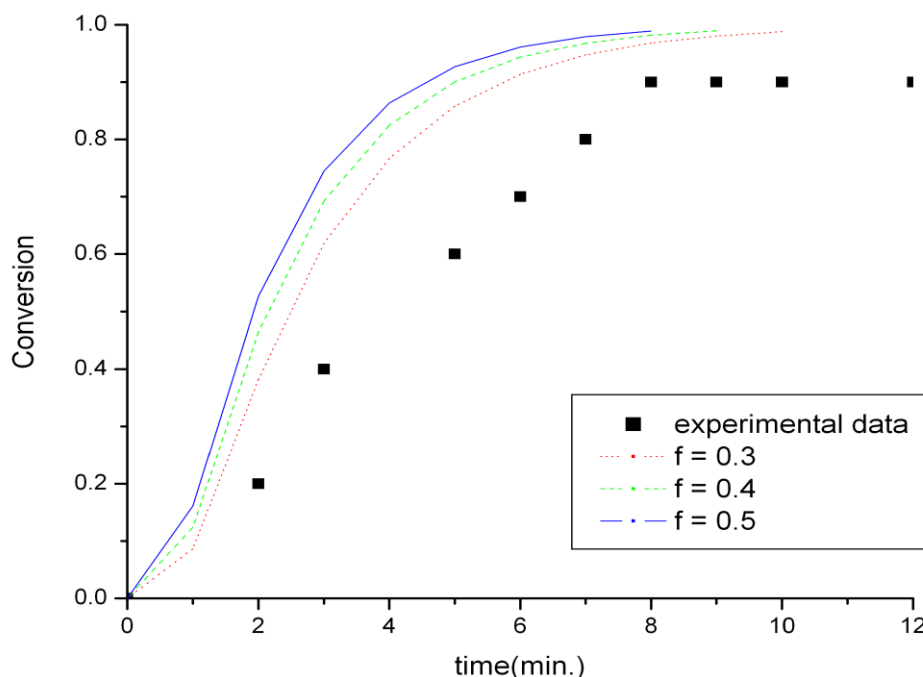

Fig. 1: Effect of the variation in the value of initiator efficiency factor, f on the conversion versus time curve

As can be seen, the variation in the initiator efficiency factor has a small effect on the conversion time curve. With the decrease in the value of f, the conversion-time curve tends to approach the experimentally measured conversion versus time curve.

In Table 4, the effect of the variation in the value of emulsifier coverage area on micelle, a_{em} on the total number of particles formed (N_P) is given.

[E]	[I]	a_{em}	N_P
2.8833	2.7033	79×10^{-16}	3.1876×10^{17}
2.8833	2.7033	65×10^{-16}	2.8387×10^{17}
2.8833	2.7033	50×10^{-16}	2.4294×10^{17}

Table 4: Effect of variation in the value of emulsifier coverage area on micelle, a_{em} on the total number of particles formed (N_P)

As can be seen, at the base value of $a_{em} = 79 \times 10^{-16}$, the total number of particles formed is close to the experimental value of 3.0×10^{17}. As the value of a_{em} is decreased, the value of the total number of particles formed also decreases considerably.

In Figure 2, the effect of the variation in the value of emulsifier coverage area on micelle, a_{em} on the conversion versus time curve is given
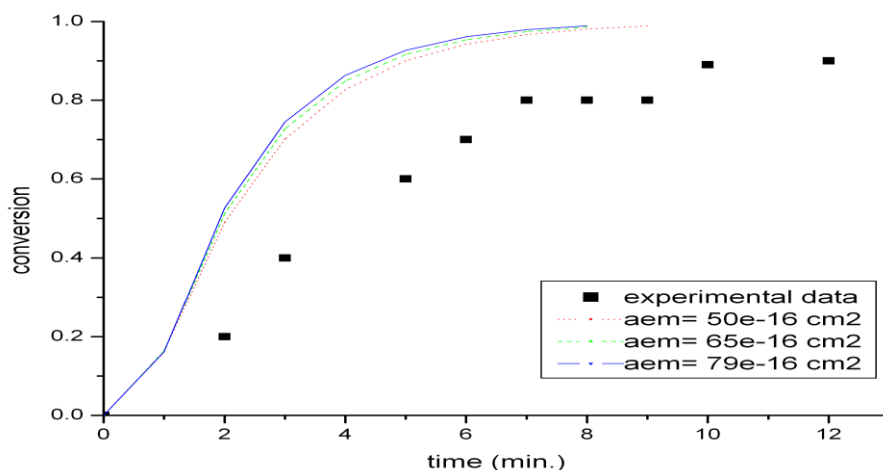
Fig. 2: Effect of the variation in the value of emulsifier coverage area on micelle, a_{em} on the conversion versus time curve

As can be seen, the variation in the emulsifier coverage area on micelle has a small effect on the conversion time curve. With the decrease in the value of a_{em}, the conversion-time curve tends to approach the experimentally measured conversion versus time curve.

In Table 5, the effect of the variation in the value of propagation rate constant, k_p on the total number of particles formed (N_P) is given.

[E]	[I]	k_p	N_P
2.8833	2.7033	18000000.0	3.7100×10^{17}
2.8833	2.7033	20000000.0	3.5095×10^{17}
2.8833	2.7033	24000000.0	3.1876×10^{17}

Table 5: Effect of variation in the value of propagation rate constant, k_p on the total number of particles formed (N_P)

As can be seen, at the base value of k_p = 24000000.0, the total number of particles formed is close to the experimental value of 3.0×10^{17}. As the value of k_p is decrease, the value of the total number of particles formed increases considerably.

In Figure 3, the effect of the variation in the value of propagation rate constant, k_p on the conversion versus time curve is given
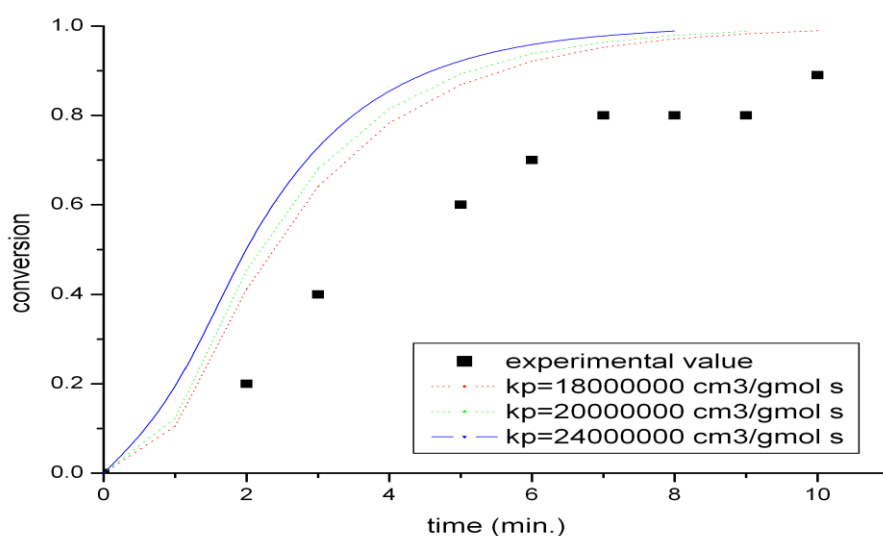

Fig. 3: Effect of the variation in the value of propagation rate constant, k_p on the conversion versus time curve

As can be seen, the variation in the propagation rate constant, k_p has a small effect on the conversion time curve. With the decrease in the value of k_p, the conversion-time curve approaches the experimentally measured conversion versus time curve.

In Table 6, the effect of the variation in the value of initiator decomposition rate constant, k_d on the total number of particles formed (N_P) is given.

[E]	[I]	k_d	N_P
2.8833	2.7033	0.00000075	2.4087×10^{17}
2.8833	2.7033	0.000001	2.7053×10^{17}
2.8833	2.7033	0.0000015	3.1876×10^{17}

Table 6: Effect of variation in the value of initiator decomposition rate constant, k_d on the total number of particles formed (N_P)

As can be seen, at the base value of $k_d = 0.0000015$, the total number of particles formed is close to the experimental value of 3.0×10^{17}. As the value of k_d is decrease, the value of the total number of particles formed decreases considerably.

In Figure 4, the effect of the variation in the value of initiator decomposition rate constant, k_d on the conversion versus time curve is given
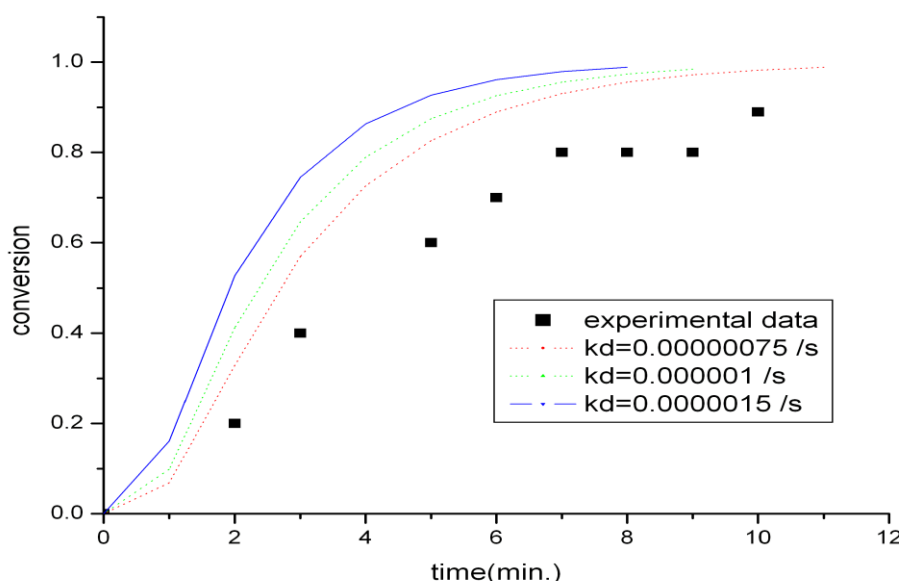

Fig. 4: Effect of the variation in the value of initiator decomposition rate constant, k_d on the conversion versus time curve

As can be seen, the variation in the initiator decomposition rate constant, k_d has a small effect on the conversion time curve. With the decrease in the value of k_d, the conversion-time curve approaches the experimentally measured conversion versus time curve.

In Table 7, the effect of the variation in the value of termination rate constant in particle, k_t on the total number of particles formed (N_P) is given.

[E]	[I]	k_t	N_P
2.8833	2.7033	1000*10**7.92	3.1876×10^{17}
2.8833	2.7033	2500*10**7.92	1.4614×10^{17}
2.8833	2.7033	5000*10**7.92	1.5973×10^{17}

Table 7: Effect of variation in the value of termination rate constant in particle, k_t on the total number of particles formed (N_P)

As can be seen, at the base value of $k_t = 1000*10**8.5$, the total number of particles formed is close to the experimental value of 3.0×10^{17}. As the value of k_t is increase, the value of the total number of particles formed decreases considerably.

In Figure 5, the effect of the variation in the value of termination rate constant in particle, k_t on the conversion versus time curve is given
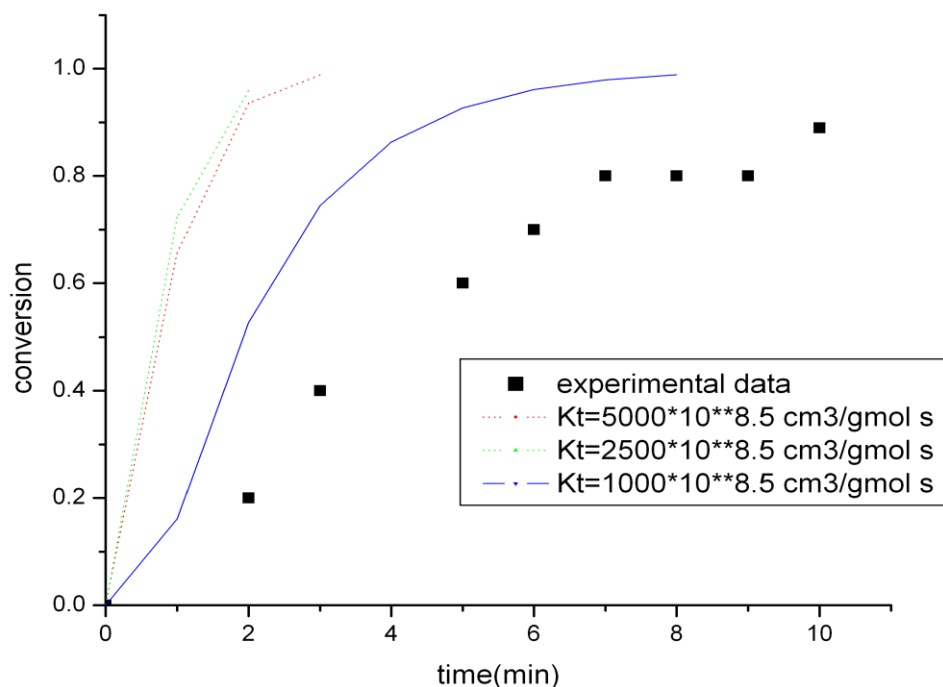
Fig. 5: Effect of the variation in the value of termination rate constant in particle, k_t on the conversion versus time curve

As can be seen, the variation in the termination rate constant in particle, k_t has a small effect on the conversion time curve. With the increases in the value of k_t, the conversion-time curve approaches the experimentally measured conversion versus time curve.

III. CONCLUSION

It is found that the effects of the change in the values of the selected parameters on the conversion versus time behaviour and hence, polymerization kinetics is not significant whereas the effects of the change in the values of these parameters on the total number of particles formed , and hence the nucleation kinetics is quite significant. The model validation should not only be done against the conversion versus time behaviour but also against the variables like the total number of particles formed which will provide a more rigorous test of the validation of any model.

- **Nomenclature**
  - ➤ English letters

a_{em} Emulsifier coverage area on a micelle, cm^2/molecule

a_{ep} Emulsifier coverage area on a particle, cm^2/molecule

D_W Effective diffusivity of the monomeric radical in the aqueous phase , cm^2/s

$[E]$ Emulsifier concenration in the reactor, gmol/l

f Initiator decomposition efficiency

$[I]$ Initiator concentration in the reactor, gmol/l

k_d Initiator decomposition rate constant, s^{-1}

k_{mm} Mass transfer coefficient for radical capture by micelles, $cm^{-2} s^{-1}$

k_{mp} Mass transfer coefficient for radical capture by particles, $cm^{-2} s^{-1}$

k_p Propagation rate constant, cm^3/gmol/s

k_{tp} Termination rate constant in the particle, cm^3/gmol/s

MW_E Molecular weight of emulsifier

MW_I Molecular weight of initiator

MW_M Molecular weight of monomer

$[M]_p$ Monomer concentration in the particle

$[M]_w$ Monomer concentration in the aqueous phase

N_P Number of particles

r_m radius of a micelle

- ➤ Greek letters

γ Interfacial tension, dyne/cm

ρ_M Density of monomer, g/cm^3

ρ_p Density of polymer, g/cm^3

Φ Monomer volume fraction inside the particle

χ Flory-Huggin's interaction parameter

➢ Subscripts
CMC　　　　　　　Critical micelle concentration
sat　　　　　　　　Saturation

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