Analysis of Mass Transfer Effects in Ethyl Cellulose Manufacture*

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Synopsis

A theoretical analysis of mass transfer effects in ethyl cellulose manufacture has been reported. This is the first model to describe a complex fluid–solid reaction in the presence of two immiscible liquids. The model derived here can be used to evaluate the dependency of the overall rate on different parameters incorporating the multiphase mass transfer effects.

INTRODUCTION

Ethyl cellulose has several important applications as a thermoplastic material including its use as an inhibitor in rocket propellant.[1,2] The manufacturing process for ethyl cellulose involves a reaction between ethyl chloride and alkali cellulose with benzene as diluent.[1] This is a typical case of multiphase reaction in which gas (ethyl chloride), liquid (benzene + water), and solid (alkali cellulose) phases are involved. Under typical conditions used in industry, the various mass transfer steps and the rate of surface reaction would decide the overall performance of the process. The literature on this process is mostly patented, and no attempts to investigate the reaction engineering aspects of this process have been made before. The objective of this article is to present a theoretical analysis of the mass transfer effects for ethyl cellulose synthesis.

It is important to note that in this process the solid (alkali cellulose) will be dispersed in the liquid consisting of two immiscible phases benzene and water. The reaction can occur in both the phases. As ethyl chloride is highly soluble in benzene, most of it will be present in benzene phase. Thus this process involves a series of steps such as gas–liquid, liquid–liquid, and liquid–solid mass transfer and a complex surface reaction. While extensive work on analysis of gas–liquid–solid reactions has been published,[3] no attempts to model the effect of two immiscible liquids have been made before. In this paper, a theoretical model has been proposed which allows us to account for the effect of these steps on the overall rate of reaction.

THEORY

Let us consider a problem where the reaction of a dissolved gas phase reactant *A* and a solid reactant takes place on solid surface in the presence of two immiscible liquid phases. The solid reactant is dispersed in two

immiscible liquid phases and hence reaction occurs in both the phases. The objective is to develop a theoretical model for the rate of reaction incorporating the various mass transfer steps. The following assumptions have been made:

1. Solid reactant is uniformly distributed in both the liquid phases.
2. The system is isothermal.
3. Pore diffusion effects are negligible
4. The two liquid interfaces with the gas phase are in equilibrium with gas phase concentration of A.
5. The reaction is first order with respect to A.

Being a multiphase system, the following steps will be necessary for the overall reaction to take place:

1. Mass transfer of A (ethyl chloride) from gas phase to the two immiscible phases (B and W).
2. Mass transfer of A from benzene phase (B) to the surface of solid reactant.
3. Reaction on solid surface in benzene medium.
4. Mass transfer of A from benzene phase (B) to aqueous phase (W).
5. Mass transfer of A from bulk aqueous phase to the solid surface.
6. Reaction at the solid surface in aqueous phase.

The overall rate of reaction of A is given by

$$R_A = R_{AB} + R_{AW} \tag{1}$$

The rates of various steps given above and interrelations are given by the following set of equations:

Benzene Phase Reaction.

$$R_{AB} = k_{gl}a_B (A_B^* - A_{Bl}) - k_{ll}a_{ll}(A_{Bl} - A_{Wl}) \tag{2}$$

$$R_{AB} = \frac{6\epsilon_B w k_s}{\rho_p d_p} (A_{Bl} - A_{Bs}) \tag{3}$$

$$= \epsilon_B w k A_{Bs} \tag{4}$$

Aqueous Phase Reaction.

$$R_{AW} = k_{gl}a_W(A_W^* - A_{Wl}) + k_{ll}a_{ll}(A_{Bl} - A_{Wl}) \tag{5}$$

$$= \frac{6\epsilon_W w k_s}{\rho_p d_p} (A_{Wl} - A_s) \tag{6}$$

$$= \epsilon_W w k A_{Ws} \tag{7}$$

In above equations A_{Bs}, A_{Ws}, A_{Bl}, and A_{Wl} are the unknown terms and can be eliminated to obtain the overall rate of reaction as

$$\begin{aligned}
R_A &= R_{AB} + R_{AW} \\
&= \frac{\epsilon_B w k}{1 + f} \left[\frac{k_{gl}a_B A_B^* + k_{ll}a_{ll}A_{Wl}}{\epsilon_B w k/(1 + f) + k_{gl}a_B + k_{ll}a_{ll}} \right] + \frac{\epsilon_W w k A_{Wl}}{1 + f}
\end{aligned} \tag{8}$$

where the factor f is defined as

$$f = \frac{k \rho_p d_p}{6 k_s} \tag{9}$$

and

$$A_{Wl} = \frac{f_1[(1 + f_1 + f_5)A_W^* + f_2 A_B^*]}{f_2[(1 + f_1 + f_5)(1 + f_1/f_2 + f_5/f_4) - 1]} \tag{10}$$

where

$$f_1 = k_{gl} a_B / k_{ll} a_{ll} \tag{11}$$

$$f_2 = a_B / a_W \tag{12}$$

$$f_3 = A_W^* / A_B^* \tag{13}$$

$$f_4 = \epsilon_B / \epsilon_W \tag{14}$$

$$f_5 = \frac{\epsilon_B w k}{(1 + f) k_{ll} a_{ll}} \tag{15}$$

and substituting for A_{Wl} in eq. (8), we obtain the final rate equation as

$$R_A = \left[\frac{k_{gl} a_B A_B^* f_5}{(1 + f_1 + f_5)} \right] \tag{16}$$

$$+ \left[\frac{\{k_{ll} a_{ll} A_B^* f_l + (f_1/f_2) k_{ll} a_{ll} A_W^* (1 + f_1 + f_5)\} \{f_5/f_4 + f_5/(1 + f_1 + f_5)\}}{[(1 + f_1 + f_5)(1 + f_1/f_2 + f_5/f_4) - 1]} \right]$$

Equation (16) can be also represented in terms of a dimensionless reaction factor ϕ defined as

$$\phi = R_A / k_{gl} a_B A_B^* \tag{17}$$

Equation (17) then becomes

$$\phi = \frac{f_5}{(1 + f_1 + f_5)} + \left[\frac{f_3(1 + f_1 + f_5) + f_2}{f_2\{(1 + f_1 + f_5)(1 + f_1/f_2 + f_5/f_4) - 1\}} \right]$$

$$\left[\frac{f_5}{f_4} + \frac{f_5}{1 + f_1 + f_5} \right] \tag{18}$$

The above equations can be used to predict rate of reaction for any given set of conditions.

RESULTS AND DISCUSSION

The model derived in this work [eq. (18)] can be used to evaluate the influence of different operating parameters on the rate of reaction. As an illustration, the effect of solid loading and the particle size of the solid reactant on reaction factor was calculated using eq. (18), and the results are presented in Figures 1 and 2 for different values of solubility ratios ($f_3 = A_w^*/A_B^*$). The reaction factor ϕ was found to increase with increase in solid loading (w) up to a certain limit, beyond which it was almost independent of w. This is indicating a transition from kinetic to mass transfer controlled regime. It is interesting to note that for values of $f_3 \simeq 1$, the contribution of reaction in both phases is significant and values of ϕ greater than 1 are observed. This is mainly due to the definition of ϕ in this analysis, wherein ϕ is the ratio of observed rate to that of maximum gas–liquid mass transfer rate in only one phase (e.g., benzene in this case).

The observation that ϕ decreases with increase in d_p indicates that the rate is retarded with increase in d_p. At higher particle size, the surface area of solid per unit volume of dispersion is reduced and liquid–particle mass transfer is likely to be a controlling regime. This leads to reduced rates at higher d_p.

In a similar manner, effect of other parameters on the rate can also be evaluated using the theoretical model proposed here.

APPENDIX: NOTATION

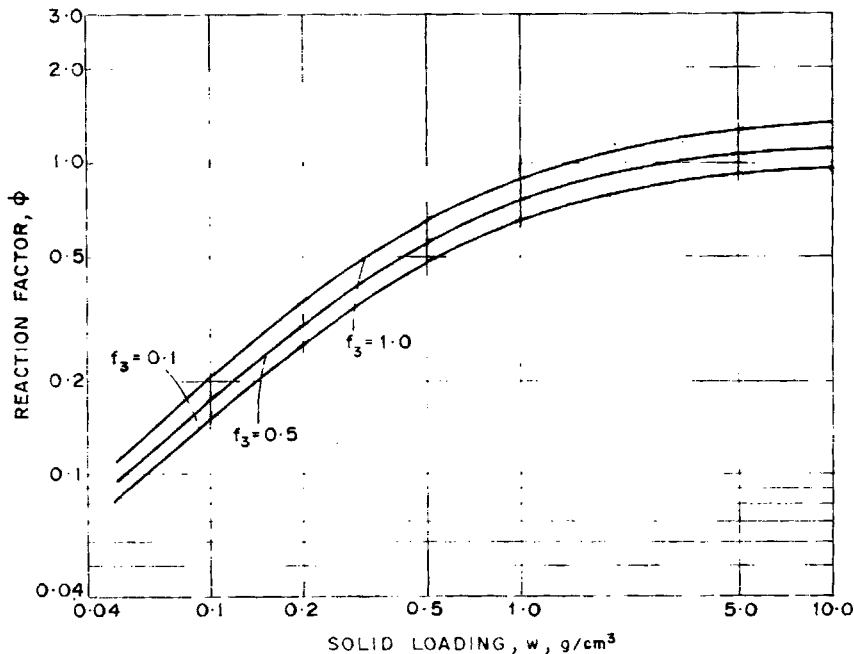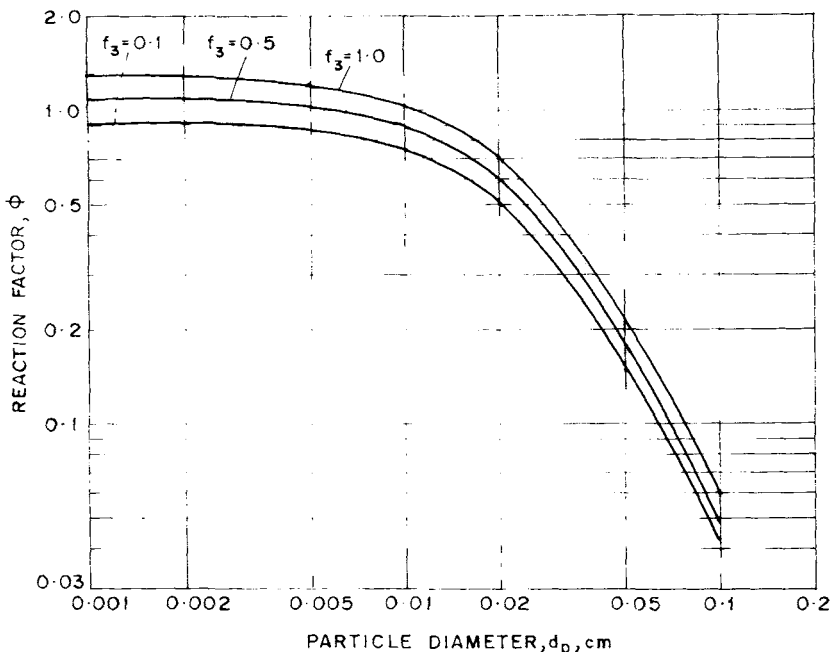|	
a_B	gas–liquid (benzene phase) interfacial area (cm^2/cm^3)
a_{ll}	liquid–liquid interfacial area (cm^2/cm^3)
a_w	gas–liquid (water phase) interfacial area (cm^2/cm^3)
A_B^*	solubility of A in benzene phase (mol/cm^3)

Fig. 1.   Effect of solid loading on reaction factor.

Fig. 2.   Effect of particle size on reaction factor.

A_{BL}	concentration of A in bulk benzene phase (mol/cm^3)
A_{B_s}	concentration of A solid surface in benzene (mol/cm^3)
A_W^*	solubility of A in water (mol/cm^3)
A_{Wl}	concentration of A in bulk water phase (mol/cm^3)
A_{Ws}	concentration of A on solid surface in water (mol/cm^3)
d_p	particle diameter (cm)
f	factor defined by eq. (9)
f_1	factor defined by eq. (11)
f_2	factor defined by eq. (12)
f_3	factor defined by eq. (13)
f_4	factor defined by eq. (14)
f_5	factor defined by eq. (15)
k	reaction rate constant (cm^3/g s)
k_{gl}	gas–liquid mass transfer coefficient (cm/s)
k_{ll}	liquid–liquid mass transfer coefficient (cm/s)
k_s	liquid–solid mass transfer coefficient (cm/s)
R_A	overall rate of reaction (mol/cm^3 s)
R_{AB}	rate of reaction in benzene phase (mol/cm^3 s)
R_{AW}	rate of reaction in water phase (mol/cm^3 s)
w	total solid loading (g/cm^3)
ϵ_B	benzene phase holdup
ϵ_W	water phase holdup
ρ_p	particle density (g/cm^3)

References

1. R. E. Kirk and D. F. Othmer, *Encyclopedia of Chemical Technology*, 3rd ed., Wiley-Interscience, New York, 1979, Vol. 5, p. 143.

2. C. G. Lawson, ERDE, U. K. Technical Memorandum No. 14/M/65, 1965.

3. P. A. Ramehandran and R. V. Chaudhari, *Three Phase Catalytic Reactors*, Gordon and Breach, New York, 1983.