Mass Transfer Accompanied by a Chemical Reaction in an Emulsion Foam Bed Reactor

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Introduction

Experimental studies on foam bed reactors have variously employed a homogeneous liquid (Biswas and Kumar, 1981; Bhaskarwar and Kumar, 1984; Shah and Mahalingam, 1984), a slurry of catalyst (Bhaskarwar and Kumar, 1986), or an emulsion as the absorbing medium (Nakamura, 1975). The first two of these situations have been modeled. An emulsion foam bed contactor, found effective by Nakamura (1975) in decontaminating polluted gas streams, has however not been analyzed. This paper presents a model for an emulsion foam bed reactor. The model, which is an extension of the single-stage model by Bhaskarwar and Kumar (1984), incorporates a submodel for evaluating the mass transfer of a reactive component from a limited volume of the gaseous mixture into an emulsion foam film of finite thickness.

The Model

An emulsion foam bed reactor comprises a pool of foamable emulsion above a distributor plate through which a gas is continuously passed, resulting in a bed of foam above the pool. In accord with previous terminology, these parts of the reactor are referred to as the emulsion storage and foam sections, respectively. The reactor can be operated either continuously or in a semibatch mode. In continuous operation, a stream of emulsion continuously enters and leaves the reactor such that a constant volume of emulsion is maintained in the storage section. In semibatch operation, a batch of emulsion is initially introduced above the distributor through which the gas is passed continuously. In either of the operations, a constant height of emulsion foam is maintained over the storage section.

During the upward passage of bubbles through the column, the active component of the gas is absorbed in the emulsion in the storage and foam sections. The extent of absorption of the gas in the storage section is known to be negligible (Bhaskarwar and Kumar, 1986). Thus, the analysis of gas absorption in the emulsion foam bed reactor is essentially that for the emulsion foam section.

Generally, foams made from homogeneous liquids have polyhedral bubbles separated from each other by thin films, which offer most of the interfacial area for mass transfer accompanied by chemical reaction. Three such films of the adjacent bubbles join together to form a nonrigid pipelike structure called a Plateau border. As the foam bubbles move up in the foam column, their films drain into the adjoining Plateau borders. The Plateau borders constitute a newtork through which the emulsion from the films drains by the action of gravity. The drainage of films in foams made of low-viscosity liquids occurs mostly near the liquid-foam interface (Desai and Kumar, 1983). The films thin down rapidly in the first few centimeters of the height of foam near this interface and then maintain a nearly constant thickness for the rest of their passage through the foam section. This thickness may be found from experimental measurements. These general hydrodynamic considerations are expected to be valid for emulsion foams also, especially in view of the very slight observed difference between the drainage rates of the homogeneous and emulsion foam films (Trykov et al., 1977).

Following Biswas and Kumar (1981), the polyhedral foam bubbles are idealized in the present model by regular pentagonal dodecahedrons, each of which shares its emulsion film with other bubbles. The submodel of gas absorption in the foam section involves an analysis of diffusion, accompanied by a chemical reaction, of the gas into a single emulsion film surrounded by limited gas pockets. The gas absorption process for emulsion

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films is different from that for homogeneous liquid films in that, besides the chemical reaction in the aqueous phase, there is an additional path for mass transfer of the dissolved gas, namely, the physical absorption in the dispersed phase sink. The present model embodies the following assumptions:

1. The polyhedral foam bubbles are idealized by regular pentagonal dodecahedrons.
2. The dispersed phase is uniformly distributed as equal-size spherical droplets that are well-mixed internally and are surrounded completely by the aqueous phase.
3. The gas phase resistance is negligible and the gaseous reactant is the limiting component.
4. The kinetics of reaction between the dissolved gas A and the aqueous phase component B is irreversible pseudofirst-order, and component A does not react with the dispersed phase.
5. The gas and liquid are in physical equilibrium at the interface.
6. The surface resistance due to surfactant is negligible.

With these assumptions, the gas absorption in an emulsion film surrounded by limited gas pockets, as illustrated in Figure 1, is described by the following equations.

Continuous Aqueous Phase:

$$\frac{\partial C_A}{\partial t_c} = D_A \frac{\partial^2 C_A}{\partial x^2} - \lambda(1 - \phi_o)C_A - K_{AO}A_p n_p\left(C_A - \frac{C_{AO}}{D_o}\right) \quad (1)$$

Dispersed Organic Phase:

$$V_o \frac{\partial C_{AO}}{\partial t_c} = K_{AO}A_p\left(C_A - \frac{C_{AO}}{D_o}\right) \quad (2)$$

Initial and boundary conditions:

$$t_c = 0, \quad -a \le x \le +a; \quad C_A = C_{Ai}, \quad C_{AO} = C_{AOi} \quad (\mathrm{I})$$

$$-a - L_p \le x \le -a \quad \text{and}$$

$$a \le x \le a + L_p; \; C_{Ag} = C_{Agi} \quad (\mathrm{II})$$

$$t_c > 0, \quad x = \pm a; \quad -\frac{V_b}{12}\frac{\partial C_{Ag}}{\partial t_c} = \pm D_A S \frac{\partial C_A}{\partial x} \quad (\mathrm{III})$$

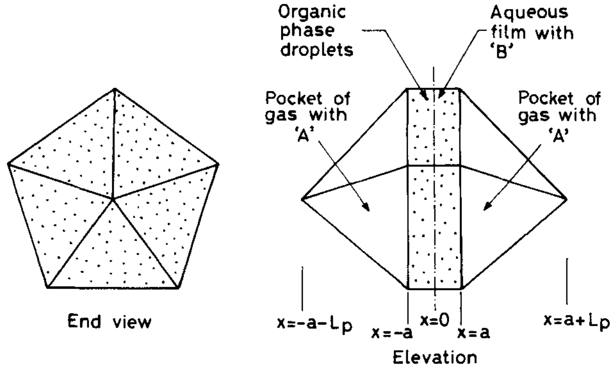

Figure 1. Emulsion foam unit: emulsion film and associated gas pockets.

$$t_c > 0, \quad x = \pm a; \quad C_A = K_e C_{Ag} \quad (\mathrm{IV})$$

$$t_c \ge 0, \quad x = 0; \quad \frac{\partial C_A}{\partial x} = 0 \quad (\mathrm{V})$$

The above model equations have been solved by Laplace transform technique to obtain the concentration profiles $C_A(x, t_c)$ and $C_{AO}(x, t_c)$. The amount of component A absorbed by the emulsion film during the total time of contact is

$$M_t = \int_o^{t_c^*} D_A \left.\frac{\partial C_A}{\partial x}\right|_{x=+a} dt_c \quad (3)$$

This is obtained as

$$\mathrm{M_t} = L \sum_{n=1}^{\infty}\left(K_e C_{Agi} + \frac{V_o C_{AOi}}{K_{AO}A_p} P_n + \frac{P_n}{K_n^2 D_A} \cdot \left\{C_{Ai} + \frac{V_o C_{AOi}[(1 - \phi_o)\lambda + K_{AO}A_p n_p + P_n]}{K_{AO}A_p}\right\}\right) \frac{(1 - e^{P_n t_c^*})}{G_3(P_n)} \quad (4)$$

where

$$G_3(P_n) = 1 + \frac{1}{2}\left(\frac{a}{L} + \left(1 + \frac{aLP_n}{D_A}\right)\frac{\tan(K_n a)}{K_n L} \cdot \left\{1 + \frac{V_o n_p}{D_o[(1/D_o) + (V_o P_n)/(K_{AO}A_p)]^2}\right\}\right) \quad (5)$$

where P_n's are the nonzero roots of the following transcendental equations:

$$\frac{LP_n}{D_A} = K_n \tan(K_n a) \quad (6)$$

and

$$K_n^2 = \frac{(K_{AO}A_p n_p / D_o D_A)}{\left(\frac{V_o P_n}{K_{AO}A_p} + \frac{1}{D_o}\right)} - \frac{1}{D_A} \cdot [(1 - \phi_o)\lambda + K_{AO}A_p n_p + P_n] \quad (7)$$

The fractional absorption of gaseous component A is

$$M_f = \frac{M_t}{M_\infty} \quad (8)$$

where

$$M_\infty = \frac{C_{Agi}V_b}{12S} = LK_e C_{Agi} = L_p C_{Agi} \quad (9)$$

For a foam bed reactor operating in a fast reaction regime, the concentration of component A in either of the phases of emulsion in the storage section is zero, and the fractional absorption is given by

$$M_f = 1 - \sum_{n=1}^{\infty} \frac{e^{P_n t_c^*}}{G_3(P_n)} \tag{10}$$

This expression has been used to compute the fractional absorption in the foam section and to simulate the performance of the reactor.

Following Bhaskarwar and Kumar (1984), the material balance for liquid phase component B is written over the storage section as

$$-V\frac{dC_B}{dt} = (Q_1 + Q)C_B - QC_{BO} - Q_1C_{B1} \tag{11}$$

The concentration of the unreacted B in the drainage stream from the foam section is

$$C_{B1} = C_B - \frac{2Y_AM_t}{V_1} \tag{12}$$

Combining Eqs. 11 and 12, we obtain

$$\frac{dC_B}{dt} + P_1C_B = P_2 \tag{13}$$

where $P_1 = Q/V$ and $P_2 = Q(QC_{BO} - 2Y_AQ_1M_t/V_1)/V$.

The above nonlinear ordinary differential equation has been solved, using the method of solution described previously (Bhaskarwar and Kumar, 1984), to obtain a solution valid in the time interval $[t_i, t_{i+1}]$ as

$$C_B = C_{B,t_i}e^{P_1(t_i-t)} - P_2(t_i - t) - \frac{P_1P_2(t_i - t)^2}{2!} - \frac{P_1^2P_2(t_i - t)^3}{3!} - \cdots \tag{14}$$

which, for a semibatch operation ($Q = 0$), reduces to

$$C_B = C_{B,t_i} - \frac{2Y_AQ_1M_t}{VV_1}(t - t_i) \tag{15}$$

This equation has been used in the manner explained earlier by Bhaskarwar and Kumar (1984), for simulation of the effect of various parameters of emulsion on the performance of the reactor. The expressions for the foam parameters have also been given in previous work (Biswas and Kumar, 1981; Bhaskarwar and Kumar, 1984).

Results and Discussion

Figure 2 shows the effect of the distribution coefficient on the fractional absorption of A by an emulsion film, for four specific reaction velocities. It is seen that the effect of the distribution coefficient on the absorption is negligible in the entire feasible range corresponding to real organic liquids if the reaction is very fast ($K_2 \geq 10^2$ m^3/kmol · s) since the aqueous sink for A is much more powerful than the dispersed organic sink and the presence of the latter is tantamount to having a dead space. However, for slower reactions an enhancement in the rate of gas absorption is possible through the use of organic liquids with distribution coefficients greater than about 10. It is also seen that the rate of a slower chemical reaction is more strongly enhanced than that of a faster reaction.

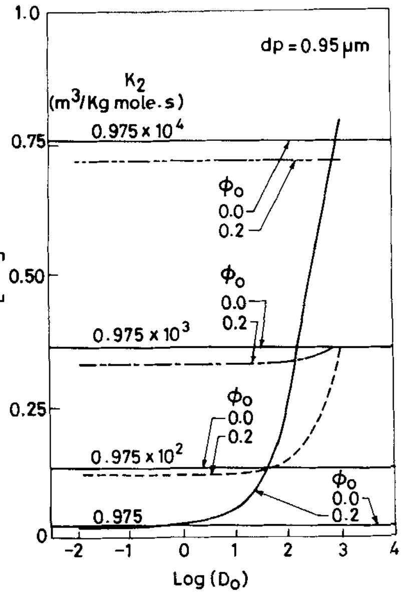

Figure 2. Effect of distribution coefficient of organic phase on fractional gas absorption in emulsion film.

Figure 3 shows the effect of the volume fraction of the dispersed phase on the fractional gas absorption by an emulsion film for three distribution coefficients and four reaction velocities. It is seen that for physical absorption or absorption accompanied by a slow chemical reaction, the fractional absorption increases with the volume fraction of the dispersed phase, showing that the organic phase provides a more effective sink than

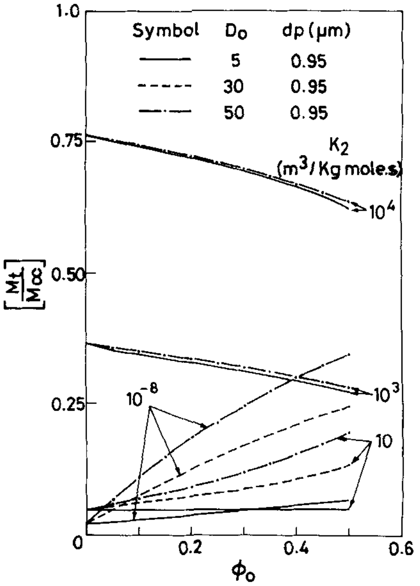

Figure 3. Effect of volume fraction of organic phase on fractional gas absorption in emulsion film.

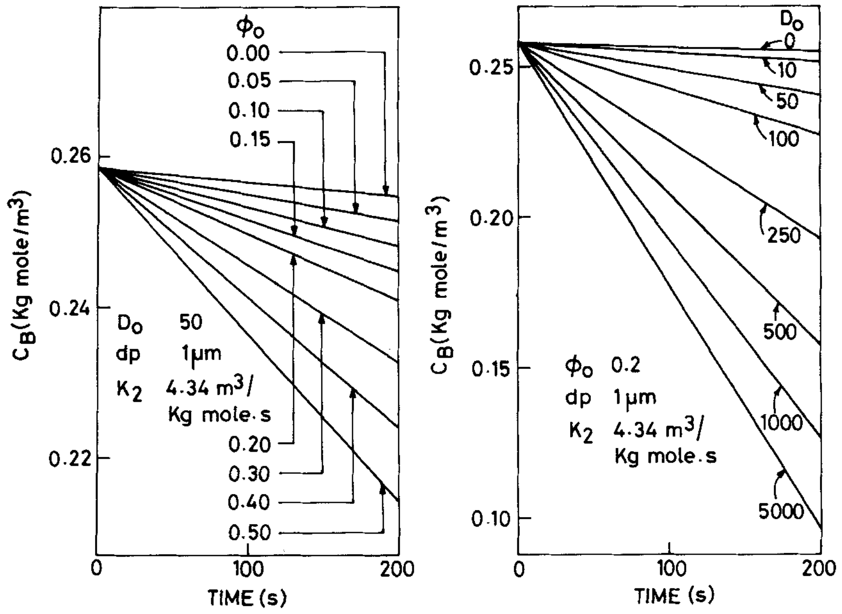

Figure 4. Simulated effect of volume fraction and distribution coefficient of dispersed organic phase on performance of emulsion foam bed reactor.

the aqueous one. On the other hand, the very fast reactions show the opposite trend, which is more pronounced the faster the chemical reaction. The sensitivity of the absorption fraction to the distribution coefficient at lower reaction speeds is again seen at all volume fractions of the organic phase. It also shows that with a proper choice of the volume fraction and distribution coefficient of the dispersed phase, a higher absorption capacity may be obtained with a slower reaction.

Figure 4 shows the effect of the volume fraction and distribution coefficient of the dispersed organic phase on the performance of an emulsion foam bed reactor. The results indicate that the rate of depletion of the liquid phase reactant B increases as the volume fraction of the dispersed phase is raised. The enhancement obtained in the average rate of reaction is 11.75 for the emulsion with $\phi_o = 0.5$ as compared to the rate for a homogeneous reaction ($\phi_o = 0$). As regards the effect of the distribution coefficient, it is clear that a considerable enhancement results in the rate of reaction on increasing the value of D_o. The average rate of reaction for a distribution coefficient of 5,000 is 44.2 times higher than that for the datum value of $D_o = 10^{-8}$, which corresponds to nearly no mass transport to the dispersed-phase droplets.

Simulations of the effect of the droplet size on the fractional gas absorption in a single emulsion foam film and on the performance of the emulsion foam bed reactor show:

- There is practically no effect of this parameter if the accompanying reaction is fast.
- The effect is relatively mild if the reaction is slow, say, when $K_2 \leq 1$ m³/kmol · s.

Where there is some effect, the fractional absorption and the reactor performance become worse as the droplet size is increased, as expected from the interfacial area considerations.

In conclusion, the presence of a dispersed organic phase in the absorbing medium of foam appears to be more advantageous for reactions with lower magnitudes of the rate constant. The emulsion foam bed reactor may be found useful for absorption of a gas if the accompanying reaction has an inherently slow kinetics.

Notation

A = gaseous reactant species
A_p = average surface area of a droplet of dispersed phase in emulsion, m²
$2a$ = thickness of emulsion foam film, m
B = reactant solute dissolved in aqueous phase in emulsion
C_A = concentration of reactant A in aqueous phase in emulsion film, kmol/m³
C_{Ai} = initial concentration of reactant A in aqueous phase in emulsion film, kmol/m³
C_{Ag} = concentration of reactant A in gas pockets surrounding emulsion film, kmol/m³
C_{Agi} = initial concentration of reactant A in gas entering foam section, kmol/m³
C_{AO} = concentration of reactant A in dispersed organic phase in emulsion foam film, kmol/m³
C_{AOi} = initial concentration of reactant A in dispersed organic phase in emulsion foam film, kmol/m³
C_B = concentration of reactant B in aqueous phase in emulsion in storage section at time t, kmol/m³
C_{BO} = concentration of reactant B in aqueous phase in emulsion stream entering storage section, kmol/m³
C_{B1} = concentration of reactant B in aqueous phase in emulsion draining into storage section from foam section, kmol/m³
C_{B,t_i} = concentration of reactant B in aqueous phase in emulsion in storage section at time node t_i, kmol/m³
D_A = diffusion coefficient of reactant A in aqueous phase, m²/s
D_o = distribution coefficient of reactant A between organic phase and aqueous phase
G_3 = function, Eq. 5
K_{AO} = mass transfer coefficient for aqueous film surrounding a dispersed organic phase droplet ($= 2D_A/dp$), m/s
K_e = equilibrium distribution factor for reactant A between gas and aqueous phase
K_n = defined in Eq. 6 and 7, m^{-1}
K_2 = second-order reaction rate constant, m³/kmol · s
L = representative length of an idealized gas pocket ($= V_b/12K_eS$), m
L_p = actual length of an idealized gas pocket ($= V_b/12S$), m

M_f = fractional absorption of gas A in half the emulsion foam film

M_t = total amount of reactant A, both free to diffuse and immobilized, in half the emulsion film per unit area at contact time t_c^*, kmol/m^2

M_∞ = total amount of reactant A, both free to diffuse and immobilized, in half the emulsion film per unit area after infinite time, kmol/m^2

n_p = number of droplets of organic phase per unit volume of emulsion film, m^{-3}

$P_1 = Q/V$

P_2 = defined in text

P_n = defined in Eqs. 6 and 7, s^{-1}

Q = flow rate of emulsion entering foam bed reactor, m^3/s

Q_1 = flow rate of emulsion draining into storage section from foam section, m^3/s

S = surface area of emulsion foam film, m^2

t = time of operation of emulsion foam bed contactor, s

t_c = time of contact between emulsion film and gas pockets in foam section, s

t_c^* = total time of contact between emulsion film and gas pockets in foam section, s

t_i, t_{i+1} = time nodes corresponding to ith interval, s

Δt_i = ith time interval after which λ from $(i - 1)$th interval is corrected, s

V = volume of emulsion in storage section, m^3

V_b = average volume of an emulsion foam bubble, m^3

V_o = average volume of a dispersed organic phase droplet, m^3

V_1 = volume of emulsion film in foam section, m^3

x = spatial coordinate of a system with origin placed at center of foam film, m

Y_A = stoichiometric factor, i.e., moles of aqueous phase reactant B consumed per mole of gaseous reactant A

Greek letters

λ = pseudofirst-order kinetic constant for aqueous phase reaction of dissolved free A with B, s^{-1}

ϕ_o = volume fraction of dispersed organic phase in emulsion

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