Dynamic Model for Mass Transfer and Reaction in Liquid/Liquid Phase-Transfer Catalysis

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In this study, a mathematical model of liquid/liquid phase-transfer catalysis concerning mass transfer with reaction in a single organic droplet was developed. The diffusion resistance of an active phase-transfer catalyst in the organic phase and mass-transfer resistance between the droplet and the bulk aqueous phase were all considered. The film conversion parameter (ϕ) and mass Biot number of QY (Bi_{QY}) were defined to interpret their relative importance with respect to the organic reaction rate. Using this model, simulation results were consistent with the experimental data. From the simulation results, the organic phase reaction of QY with RX occurs mostly in the region close to the surface of the liquid droplet, depending on the film conversion parameter and the mass Biot number of QY. The reaction rate is influenced by the diffusion resistance as $\phi > 2$, while the reaction rate is limited mainly by reaction and weakly by diffusion resistance as $\phi < 1$. The amount of QY existing in the organic phase increases with increasing distribution coefficient of QY and mass-transfer coefficient from aqueous to organic phase, thus enhancing the overall reaction rate. The liquid/liquid phase-transfer catalysis can be well demonstrated by the present model.

Introduction

The reaction between two mutually insoluble phases can be promoted by a phase transfer catalyst (PTC) under mild operating conditions to give a high yield of products (Starks and Liotta, 1978; Starks et al., 1994; Weber and Gokel, 1977). The catalyst first reacts with the reactant in the aqueous phase to form an active intermediate that then transfers into the organic phase to react with the other organic reactant. During such a process, the organic phase reaction is generally the rate-determining step under sufficient agitation (Dehmlow and Dehmlow, 1983). Phase-transfer catalysis is usually conducted in an agitated system in which the main organic reaction generally takes place in the dispersed phase. Several investigators have been engaged in developing a theory for systems of a two-liquid phase with chemical reactions. Rietema calculated the residence time required to obtain a given conversion for no mixing and complete mixing of the dispersed phase of a reactor for a zero-order reaction (Rietema, 1968). Curl studied a zero-order reaction in the dispersed phase of a well-stirred flow reactor by using a simplified population method and assuming equal size drops with equal coalescence and breakage rate (Curl, 1963). Zeitlin and Tavlarides analyzed the dispersed-phase volume concentration distributions to ascertain the effect of the degree of mixing on conversion and interphase transfer (Zeitlin et al., 1972). Sada et al. used film theory to develop the diffusion equation with chemical reaction in a two-liquid phase (Sada et al., 1977). They obtained the concentration profiles of reactants in the film on either side of the flat interface to describe the effect of mass transfer by directly assuming the chemical reaction occurred in the film.

Inoue et al. investigated mass transfer accompanied by chemical reaction at the surface of a single droplet. They studied the mass-transfer effect for both neglecting and accounting for the mass-transfer resistance in the continuous phase (Inoue and Nakashio, 1979). Cruz-Pinto et al. developed the numerical algorithms for the simultaneous solutions of mass transfer and hydrodynamic equations for swarms of liquid drops in a counter current flow liquid/liquid extraction column including the changing continuous-phase concentration (Cruz-Pinto and Korchinsky, 1983). Asai et al. measured the liquid/liquid mass-transfer coefficients in an agitated vessel with a flat interface (Asai et al., 1983). In their later works, the overall reaction rate of phase-transfer catalysis with mass transfer for the alkaline hydrolysis of *n*-butyl acetate and oxidation of benzyl alcohol in an agitated vessel with a flat interface was analyzed. They concluded that the observed overall reaction rate was proportional to the interfacial concentration of the actual reactant (Asai et al., 1992, 1994). Wang and Yang investigated the dynamic behavior of phase-transfer-catalyzed reactions by determining the parameters accounting for mass transfer and the kinetics in a two-phase system (Wang and Yang, 1991). However, the analysis for the effects of mass transfer on phase-transfer catalysis in a dispersed system is still lacking. The role of diffusion for the active intermediate or the phase-transfer catalyst in such a system is little understood. Hence, it is useful to realize which parameter dominates in the overall reaction. In the present study, a theoretical analysis for phase-transfer catalysis was developed to investigate the effects of mass transfer and diffusion for the active catalyst on the conversion of organic reactant in the dispersed system.

Mathematical Model

For a liquid/liquid agitated system, several phenomena appear, i.e., (1) formation of a droplet in the continuous phase by stirring, (2) free rise or fall of a droplet through the continuous phase, and (3) coalescence of a droplet at the end of the free rise period. In a liquid/liquid phase-transfer-catalyzed system, the

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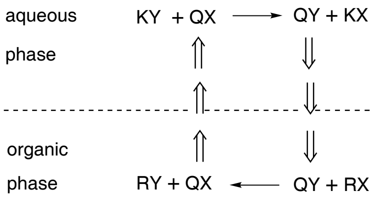
extractions of catalyst and active component between these phases are important because the extracting agents are the main components conducting the organic reaction.

Consider the typical phase-transfer-catalytic reaction system as follows. A reactant KY reacts with a catalyst QX to form the active intermediate QY reversibly or irreversibly in the aqueous phase, in which the reversibility generally depends on the characteristics of QY produced. If QY is a more lipophilic compound, the equilibrium constant of this ion-exchange reaction will be large, and the reversibility can be neglected. In this analysis, the aqueous reaction is assumed irreversible. The produced active intermediate QY then transfers into the organic phase due to its distribution behavior between the two phases. The intrinsic reaction of QY with organic phase reactant RX is conducted to produce the desired product RY. The catalyst QX is regenerated and transfers back to the aqueous phase. This system is shown as the following scheme.



Each step with its appropriate velocity constant is listed below.

(1) Reaction in the aqueous phase

$$\mathrm{KY} + \mathrm{QX} \xrightarrow{k_{\mathrm{aq}}} \mathrm{QY} + \mathrm{KX} \qquad (1)$$

(2) Mass transfer of QY from the aqueous phase to the organic phase

$$\mathrm{QY(aq)} \xrightarrow{K_{\mathrm{QY}}} \mathrm{QY(org)} \qquad (2)$$

(3) Reaction in the organic phase

$$\mathrm{RX} + \mathrm{QY} \xrightarrow{k_{\mathrm{org}}} \mathrm{RY} + \mathrm{QX} \qquad (3)$$

(4) Mass transfer of QX from the organic phase to the aqueous phase

$$\mathrm{QX(org)} \xrightarrow{K_{\mathrm{QX}}} \mathrm{QX(aq)} \qquad (4)$$

In the above equations, k_{org} is the reaction rate constant in the organic phase, k_{aq} is the reaction rate constant in the aqueous phase, K_{QY} is the mass-transfer coefficient of QY from the aqueous phase to the organic phase, and K_{QX} is the mass-transfer coefficient of QX from the organic phase to the aqueous phase. In formulating the equations for diffusion and reaction in a phase-transfer-catalyzed system, consider the organic phase to be dispersed. The organic droplet is assumed as a rigid sphere with equal mean radius R. Since the molar flux of the organic phase reactant equals that of the product either in the organic droplet or in the bulk aqueous phase, the product (RY) is not necessarily taken into account in the formulation. The rates of change of RX, QX, and QY in an organic droplet are described by the combination of diffusion and reaction rate as follows:

$$\frac{\partial C_{\mathrm{RX}}^{\mathrm{org}}}{\partial t} = \frac{D_{\mathrm{RX}}}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_{\mathrm{RX}}^{\mathrm{org}}}{\partial r}\right) - R_{\mathrm{org}} \qquad (5)$$

$$\frac{\partial C_{\mathrm{QX}}^{\mathrm{org}}}{\partial t} = \frac{D_{\mathrm{QX}}}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_{\mathrm{QX}}^{\mathrm{org}}}{\partial r}\right) + R_{\mathrm{org}} \qquad (6)$$

$$\frac{\partial C_{\mathrm{QY}}^{\mathrm{org}}}{\partial t} = \frac{D_{\mathrm{QY}}}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial C_{\mathrm{QY}}^{\mathrm{org}}}{\partial r}\right) - R_{\mathrm{org}} \qquad (7)$$

where $R_{\mathrm{RX}}^{\mathrm{org}}$ denotes the organic phase reaction rate.

$$R_{\mathrm{RX}}^{\mathrm{org}} = k_{\mathrm{org}} C_{\mathrm{RX}}^{\mathrm{org}} C_{\mathrm{QY}}^{\mathrm{org}} \qquad (8)$$

The diffusion coefficients for RX, QX, and QY are designated as D_{RX}, D_{QX}, and D_{QY}, respectively, and r is the spatial coordinate in the radial direction for a spherical droplet. Initially, only RX exists in the organic phase; hence, the initial conditions for eqs 5−7 are

$$\text{at } t = 0, \quad C_{\mathrm{RX}}^{\mathrm{org}} = C_{\mathrm{RX},0},\ C_{\mathrm{QY}}^{\mathrm{org}} = 0,\ C_{\mathrm{QX}}^{\mathrm{org}} = 0 \qquad (9)$$

The boundary conditions at the center of the droplet are

$$\text{at } r = 0, \quad \frac{\partial C_{\mathrm{RX}}^{\mathrm{org}}}{\partial r} = \frac{\partial C_{\mathrm{QY}}^{\mathrm{org}}}{\partial r} = \frac{\partial C_{\mathrm{QX}}^{\mathrm{org}}}{\partial r} = 0 \qquad (10)$$

At the droplet surface, RX should react with QY that transfers from the aqueous phase; thus, the diffusion rate of RX equals its reaction rate in this model. However, if the droplet is in a situation with high internal turbulence, the concentration gradient of RX at the surface may be approximated to zero. For QY and QX, the flux of mass transfer between the aqueous phase and the organic droplet should be considered. Thus, the other boundary conditions for RX, QY, and QX are

$$\text{at } r = R, \quad \frac{3D_{\mathrm{RX}}}{R}\frac{\partial C_{\mathrm{RX}}^{\mathrm{org}}}{\partial r} = -R_{\mathrm{org}}$$

$$\frac{3D_{\mathrm{QY}}}{R}\frac{\partial C_{\mathrm{QY}}^{\mathrm{org}}}{\partial r} = \frac{3K_{\mathrm{QY}}}{R}\left(C_{\mathrm{QY}}^{\mathrm{aq}} - \frac{1}{m_{\mathrm{QY}}}C_{\mathrm{QY}}^{\mathrm{org}}\right) - R_{\mathrm{org}}$$

$$\frac{3D_{\mathrm{QX}}}{R}\frac{\partial C_{\mathrm{QX}}^{\mathrm{org}}}{\partial r} = -\frac{3K_{\mathrm{QX}}}{R}(C_{\mathrm{QX}}^{\mathrm{org}} - m_{\mathrm{QX}}C_{\mathrm{QX}}^{\mathrm{aq}}) + R_{\mathrm{org}} \qquad (11)$$

In eq 11, K_{QX} and K_{QY} represent the mass-transfer coefficients of QX and QY, respectively. m_{QY} and m_{QX} are the distribution coefficients of QY and QX, representing the equilibrium partition between the two phases, and are defined as the ratio of concentration in the organic phase side to that in the aqueous phase side at the interface.

$$m_{\mathrm{QY}} = \frac{C_{\mathrm{QY}}^{\mathrm{org(s)}}}{C_{\mathrm{QY}}^{\mathrm{aq(s)}}} \quad \text{and} \quad m_{\mathrm{QX}} = \frac{C_{\mathrm{QX}}^{\mathrm{org(s)}}}{C_{\mathrm{QX}}^{\mathrm{aq(s)}}} \qquad (12)$$

In the aqueous phase, the rates of change of QY, QX, and KY are expressed by the following equations:

$$\frac{\mathrm{d}C_{\mathrm{QY}}^{\mathrm{aq}}}{\mathrm{d}t} = k_{\mathrm{aq}} C_{\mathrm{KY}}^{\mathrm{aq}} C_{\mathrm{QX}}^{\mathrm{aq}} - K_{\mathrm{QY}}\alpha\left(\frac{V_{\mathrm{org}}}{V_{\mathrm{aq}}}\right)\left(C_{\mathrm{QY}}^{\mathrm{aq}} - \frac{1}{m_{\mathrm{QY}}}C_{\mathrm{QY}}^{\mathrm{org(s)}}\right) \qquad (13)$$

$$\frac{\mathrm{d}C_{\mathrm{QX}}^{\mathrm{aq}}}{\mathrm{d}t} = K_{\mathrm{QX}}\alpha\left(\frac{V_{\mathrm{org}}}{V_{\mathrm{aq}}}\right)(C_{\mathrm{QX}}^{\mathrm{org(s)}} - m_{\mathrm{QX}}C_{\mathrm{QX}}^{\mathrm{aq}}) - k_{\mathrm{aq}}C_{\mathrm{KY}}^{\mathrm{aq}}\,C_{\mathrm{QX}}^{\mathrm{aq}} \tag{14}$$

$$\frac{\mathrm{d}C_{\mathrm{KY}}^{\mathrm{aq}}}{\mathrm{d}t} = -k_{\mathrm{aq}}C_{\mathrm{KY}}^{\mathrm{aq}}C_{\mathrm{QX}}^{\mathrm{aq}} \tag{15}$$

In eqs 13 and 14, the rate of change of QY or QX equals the difference of the reaction rate and the interphase mass-transfer rate. The interfacial area per unit volume between the droplet and the aqueous bulk phase is designated as *a* and equals to 3/*R*. Initially, only KY and QX exist. The initial conditions for eqs 13−15 are

$$\text{at } t = 0, \quad C_{\mathrm{QY}}^{\mathrm{aq}} = 0,\ C_{\mathrm{KY}}^{\mathrm{aq}} = C_{\mathrm{KY,0}},\ C_{\mathrm{QX}}^{\mathrm{aq}} = C_{\mathrm{QX,0}} \tag{16}$$

The average concentration of component *i* within the droplet is

$$\bar{C}_i^{\mathrm{org}} = \frac{3}{R^3}\int_0^R r^2 C_i^{\mathrm{org}}\,\mathrm{d}r \tag{17}$$

The conversion of RX in the organic phase is then calculated from its average concentration in a droplet as

$$X = 1 - \bar{C}_{\mathrm{RX}}^{\mathrm{org}}/C_{\mathrm{RX,0}} \tag{18}$$

The conservation of phase-transfer catalyst Q is the sum of QX and QY in both phases at any reaction time.

$$N_{\mathrm{QX,0}} = N_{\mathrm{QX}}^{\mathrm{aq}} + N_{\mathrm{QX}}^{\mathrm{org}} + N_{\mathrm{QY}}^{\mathrm{aq}} + N_{\mathrm{QY}}^{\mathrm{org}} \tag{19}$$

$$V_{\mathrm{aq}}C_{\mathrm{QX,0}} = V_{\mathrm{aq}}(C_{\mathrm{QX}}^{\mathrm{aq}} + C_{\mathrm{QY}}^{\mathrm{aq}}) + V_{\mathrm{org}}(\bar{C}_{\mathrm{QY}}^{\mathrm{org}} + \bar{C}_{\mathrm{QX}}^{\mathrm{org}}) \tag{20}$$

Equations 5−20 characterize the phenomena of phase transfer catalysis with the organic phase reaction occurring in a rigid droplet. These equations can be further rendered dimensionless by defining appropriate dimensionless groups as follows.

$$\tau = \frac{D_{\mathrm{RX}}t}{R^2},\ \delta = \frac{V_{\mathrm{org}}}{V_{\mathrm{aq}}},\ \xi = \frac{r}{R},\ \beta = \frac{k_{\mathrm{aq}}}{k_{\mathrm{org}}},\ \phi = R\sqrt{\frac{k_{\mathrm{org}}C_{\mathrm{QX,0}}}{D_{\mathrm{RX}}}},\ \gamma_{\mathrm{QX}} = \frac{D_{\mathrm{QX}}}{D_{\mathrm{RX}}},\ \gamma_{\mathrm{QY}} = \frac{D_{\mathrm{QY}}}{D_{\mathrm{RX}}},\ Bi_{\mathrm{QY}} = \frac{K_{\mathrm{QY}}R}{D_{\mathrm{QY}}},\ Bi_{\mathrm{QX}} = \frac{K_{\mathrm{QX}}R}{D_{\mathrm{QX}}},\ q_{\mathrm{RX}} = \frac{C_{\mathrm{RX,0}}}{C_{\mathrm{QX,0}}},\ q_{\mathrm{KY}} = \frac{C_{\mathrm{KY,0}}}{C_{\mathrm{QX,0}}},\ f_{\mathrm{QX}}^{\,i} = \frac{C_{\mathrm{QX}}^{i}}{C_{\mathrm{QX,0}}},\ f_{\mathrm{QX}}^{\,\mathrm{org(s)}} = \frac{C_{\mathrm{QX}}^{\mathrm{org(s)}}}{C_{\mathrm{QX,0}}},\ f_{\mathrm{QY}}^{\,\mathrm{org(s)}} = \frac{C_{\mathrm{QY}}^{\mathrm{org(s)}}}{C_{\mathrm{QX,0}}},\ f_{\mathrm{QY}}^{\,i} = \frac{C_{\mathrm{QY}}^{i}}{C_{\mathrm{QX,0}}},\ f_{\mathrm{RX}}^{\,\mathrm{org}} = \frac{C_{\mathrm{RX}}^{\mathrm{org}}}{C_{\mathrm{RX,0}}},\ f_{\mathrm{KY}}^{\,\mathrm{aq}} = \frac{C_{\mathrm{KY}}^{\mathrm{aq}}}{C_{\mathrm{KY,0}}} \tag{21}$$

When the above dimensionless groups are used, the dimensionless equations (5)−(7) are

$$\frac{\partial f_{\mathrm{RX}}^{\,\mathrm{org}}}{\partial\tau} = \frac{1}{\xi^2}\frac{\partial}{\partial\xi}\left(\xi^2\frac{\partial f_{\mathrm{RX}}^{\,\mathrm{org}}}{\partial\xi}\right) - \phi^2 f_{\mathrm{RX}}^{\,\mathrm{org}}\,f_{\mathrm{QY}}^{\,\mathrm{org}} \tag{22}$$

$$\frac{\partial f_{\mathrm{QY}}^{\,\mathrm{org}}}{\partial\tau} = \frac{\gamma_{\mathrm{QY}}}{\xi^2}\frac{\partial}{\partial\xi}\left(\xi^2\frac{\partial f_{\mathrm{QY}}^{\,\mathrm{org}}}{\partial\xi}\right) - q_{\mathrm{RX}}\phi^2 f_{\mathrm{RX}}^{\,\mathrm{org}}\,f_{\mathrm{QY}}^{\,\mathrm{org}} \tag{23}$$

$$\frac{\partial f_{\mathrm{QX}}^{\,\mathrm{org}}}{\partial\tau} = \frac{\gamma_{\mathrm{QX}}}{\xi^2}\frac{\partial}{\partial\xi}\left(\xi^2\frac{\partial f_{\mathrm{QX}}^{\,\mathrm{org}}}{\partial\xi}\right) + q_{\mathrm{RX}}\phi^2 f_{\mathrm{RX}}^{\,\mathrm{org}}\,f_{\mathrm{QY}}^{\,\mathrm{org}} \tag{24}$$

The initial and boundary conditions are

$$\text{at } \tau = 0, \quad f_{\mathrm{RX}}^{\,\mathrm{org}} = 1,\ f_{\mathrm{QY}}^{\,\mathrm{org}} = f_{\mathrm{QX}}^{\,\mathrm{org}} = 0 \tag{25}$$

$$\text{at } \xi = 0, \quad \frac{\partial f_{\mathrm{RX}}^{\,\mathrm{org}}}{\partial\xi} = \frac{\partial f_{\mathrm{QY}}^{\,\mathrm{org}}}{\partial\xi} = \frac{\partial f_{\mathrm{QX}}^{\,\mathrm{org}}}{\partial\xi} = 0 \tag{26}$$

$$\text{at } \xi = 1, \quad \frac{\partial f_{\mathrm{RX}}^{\,\mathrm{org}}}{\partial\xi} = -\frac{1}{3}\phi^2 f_{\mathrm{RX}}^{\,\mathrm{org}}\,f_{\mathrm{QY}}^{\,\mathrm{org}}$$

$$\frac{\partial f_{\mathrm{QY}}^{\mathrm{org}}}{\partial\xi} = -\frac{1}{3}\frac{q_{\mathrm{RX}}}{\gamma_{\mathrm{QY}}}\phi^2 f_{\mathrm{RX}}^{\,\mathrm{org}}\,f_{\mathrm{QY}}^{\mathrm{org}} + Bi_{\mathrm{QY}}\left(f_{\mathrm{QY}}^{\,\mathrm{aq}} - \frac{1}{m_{\mathrm{QY}}}f_{\mathrm{QY}}^{\,\mathrm{org}}\right) \tag{27}$$

$$\frac{\partial f_{\mathrm{QX}}^{\,\mathrm{org}}}{\partial\xi} = \frac{1}{3}\frac{q_{\mathrm{RX}}}{\gamma_{\mathrm{QX}}}\phi^2 f_{\mathrm{RX}}^{\,\mathrm{org}}\,f_{\mathrm{QY}}^{\,\mathrm{org}} - Bi_{\mathrm{QX}}(f_{\mathrm{QX}}^{\,\mathrm{org}} - m_{\mathrm{QX}}f_{\mathrm{QX}}^{\,\mathrm{aq}})$$

In eqs 22−24, the dimensionless group ϕ is defined as a film conversion parameter, indicating the ratio of diffusion resistance to kinetic resistance, which is similar to the Thiele modulus in a fluid−solid reaction. When ϕ is greater than 2, the organic phase reaction proceeds mainly in the region near the droplet surface. The rate of reaction is limited by the internal diffusion. The parameters Bi_{QY} and Bi_{QX} represent the relative importance of diffusion resistance and mass-transfer resistance between phases for QY and QX, respectively.

In the aqueous phase, the governing dimensionless equations and initial conditions for QY, QX, and KY are

$$\frac{\mathrm{d}f_{\mathrm{QY}}^{\mathrm{aq}}}{\mathrm{d}\tau} = \beta q_{\mathrm{KY}}\phi^2 f_{\mathrm{KY}}^{\mathrm{aq}}\,f_{\mathrm{QX}}^{\mathrm{aq}} - 3Bi_{\mathrm{QY}}\gamma_{\mathrm{QY}}\delta\left(f_{\mathrm{QY}}^{\mathrm{aq}} - \frac{1}{m_{\mathrm{QY}}}f_{\mathrm{QY}}^{\mathrm{org,s}}\right) \tag{28}$$

$$\frac{\mathrm{d}f_{\mathrm{QX}}^{\,\mathrm{aq}}}{\mathrm{d}\tau} = 3Bi_{\mathrm{QX}}\gamma_{\mathrm{QX}}\delta(f_{\mathrm{QX}}^{\,\mathrm{org,s}} - m_{\mathrm{QX}}f_{\mathrm{QX}}^{\,\mathrm{aq}}) - \beta q_{\mathrm{KY}}\phi^2 f_{\mathrm{KY}}^{\,\mathrm{aq}}\,f_{\mathrm{QX}}^{\,\mathrm{aq}} \tag{29}$$

$$\frac{\mathrm{d}f_{\mathrm{KY}}^{\,\mathrm{aq}}}{\mathrm{d}\tau} = -\beta\phi^2 f_{\mathrm{KY}}^{\,\mathrm{aq}}\,f_{\mathrm{QX}}^{\,\mathrm{aq}} \tag{30}$$

$$\text{at } \tau = 0, \quad f_{\mathrm{QY}}^{\,\mathrm{aq}} = 0,\ f_{\mathrm{QX}}^{\,\mathrm{aq}} = 1,\ f_{\mathrm{KY}}^{\,\mathrm{aq}} = 1 \tag{31}$$

The dimensionless average concentration for component *i* within droplets and the conversion of RX become

$$\bar{f}_i^{\,\mathrm{org}} = 3\int_0^1 \xi^2 f_i^{\,\mathrm{org}}\,\mathrm{d}\xi \tag{32}$$

$$X = 1 - \bar{f}_{\mathrm{RX}}^{\,\mathrm{org}} \tag{33}$$

Results and Discussion

Equations 22−33 were solved simultaneously by finite difference and Runge−Kutta fourth-order methods for different values of parameters. The molar concentrations of reactants and phase-transfer catalyst are all set at $C_{\mathrm{QX,0}} = 0.01$ M, $C_{\mathrm{RX,0}} = 0.1$ M, and $C_{\mathrm{KY,0}} = 0.2$ M with the same volume of organic and aqueous phases. The simulation results shown in Figure 1 are the profiles of average dimensionless concentrations for RX and QY in the organic phase and QX and KY in the

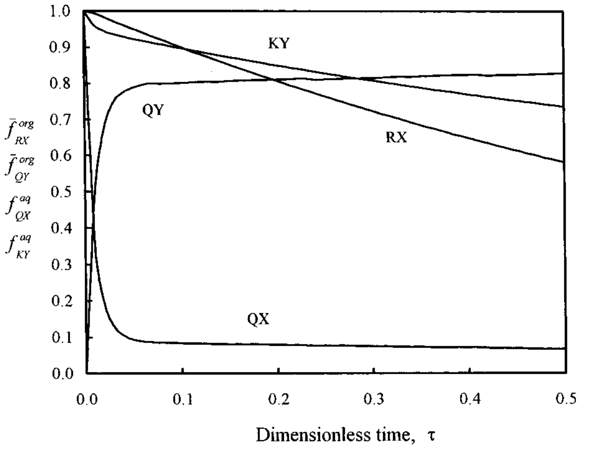


Figure 1. Variation for concentrations of QY and RX in the organic phase as well as those of QX and KY in the aqueous phase: $Bi_{QY} = 100$, $\phi = 0.816$, $D_{QY}/D_{RX} = 5$, $D_{QX}/D_{QY} = 10$, $k_{aq}/k_{org} = 10$, $k_{org} = 1.0\ M^{-1}\ min^{-1}$, $m_{QY} = 10$, $m_{QX} = 0.05$, $C_{QX,0} = 0.01$ M, $C_{RX,0} = 0.1$ M, $C_{KY,0} = 0.2$ M.

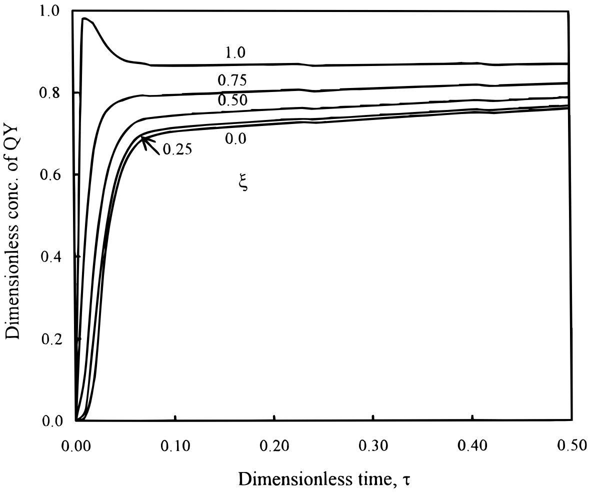


Figure 2. Dimensionless concentration profile of QY in the organic droplet at different reaction times: $Bi_{QY} = 100$, $\phi = 0.816$, $D_{QY}/D_{RX} = 5$, $D_{QX}/D_{QY} = 10$, $k_{aq}/k_{org} = 10$, $k_{org} = 1.0\ M^{-1}$ min^{-1}, $m_{QY} = 10$, $m_{QX} = 0.05$, $C_{QX,0} = 0.01$ M, $C_{RX,0} = 0.1$ M, $C_{KY,0} = 0.2$ M.

aqueous phase at various τ for $Bi_{QY} = 100$, $\phi = 0.816$, $D_{QY}/D_{RX} = 5$, and $D_{QX}/D_{QY} = 10$. The average dimensionless concentration of QY in the droplet rises from zero to a value of about 0.8 during early reaction time and then gradually increases to its equilibrium due to higher mass-transfer rate. The early reaction time after which QY accumulates sharply from zero to some value of concentration in the organic phase can be designated as the induction period. After the induction period, a sufficient amount of QY can conduct the intrinsic organic reaction. In such cases, the main resistance of the reaction occurs within the droplet. However, since the film conversion parameter is less than unity ($\phi = 0.816$), the reaction is only weakly influenced by the internal diffusion. Thus, the chemical reaction within the droplet dominates as the rate-determining step. It is seen that the profile of QY along the radial direction does not drop sharply after the induction period as shown in Figure 2. The highest value of f^{org}_{QY} is approaching 0.95 and is located at the surface of the droplet in the induction period.

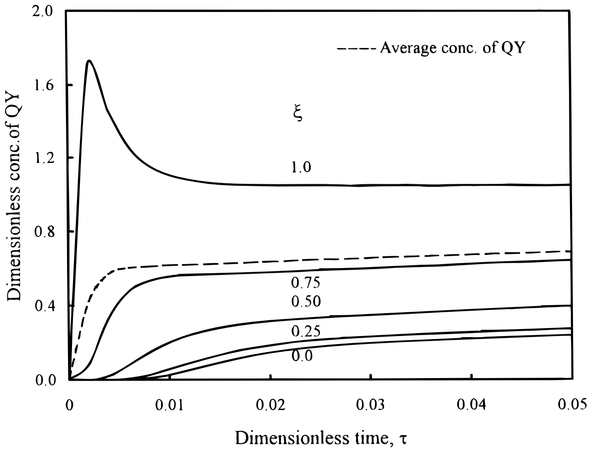


Figure 3. Dimensionless concentration profile of QY in the organic droplet at different reaction times: $Bi_{QY} = 100$, $\phi = 2.582$, $D_{QY}/D_{RX} = 5$, $D_{QX}/D_{QY} = 10$, $k_{aq}/k_{org} = 10$, $k_{org} = 1.0\ M^{-1}\ min^{-1}$, $m_{QY} = 10$, $m_{QX} = 0.05$, $C_{QX,0} = 0.01$ M, $C_{RX,0} = 0.1$ M, $C_{KY,0} = 0.2$ M.

Figure 3 shows the dimensionless concentration profile of QY at a higher value of the film conversion parameter ($\phi = 2.582$), with the other conditions the same as in Figure 2. For this condition, the fraction of phase-transfer catalyst in the form of QY in the organic phase rises up to about 0.6 after the induction period. The total amount of QY within the droplet for $\phi = 2.582$ is about 25% less than that for $\phi = 0.816$. This will cause the overall reaction rate to be reduced. The diffusion resistance within the droplet indeed influences the overall reaction rate. This effect can be demonstrated from the profile of QY along the radial direction at various τ as shown in Figure 3. It is seen that QY mainly exists within the zone close to the interface. Surprisingly, at small τ (less than 0.01 as the induction period), the dimensionless concentration of QY at the droplet surface can be as high as 1.6 times the initial concentration of catalyst, although the average QY concentration in the organic phase is about 0.6 times the initial catalyst concentration. This exhibits that QY will concentrate near the droplet surface for larger ϕ. It also demonstrates that the reaction is mainly conducted near the surface of the droplet for $\phi > 2$. Moreover, the fraction of phase transfer catalyst QX in the aqueous phase is less than 0.1 after the induction period for both higher and lower ϕ and is affected by the distribution coefficient.

The effective diffusivity ratio of QY to that of RX also affects the overall reaction rate. Figure 4 shows the profiles of QY in the organic phase and conversion of RX at various τ. From the plot, QY increases as the diffusivity ratio of QY to RX increases, which thus increases the overall reaction rate. As D_{QY}/D_{RX} raises from 0.5 to 5.0, the fraction of QY increases from 0.2 to about 0.6. At a higher value of D_{QY}/D_{RX}, the diffusion rate of QY is faster than its reaction rate during the induction period.

Figure 5 compares the effect of ϕ on the fraction of QY in the organic phase with an equal effective diffusivity of QY and RX. There is no doubt that the fraction of QY increases as ϕ decreases. This indicates that the operating conditions of phase-transfer catalysis are better set on the situation of as low diffusion resistance as possible. From the results in Figure 5, the higher film conversion parameter provides the more concen-

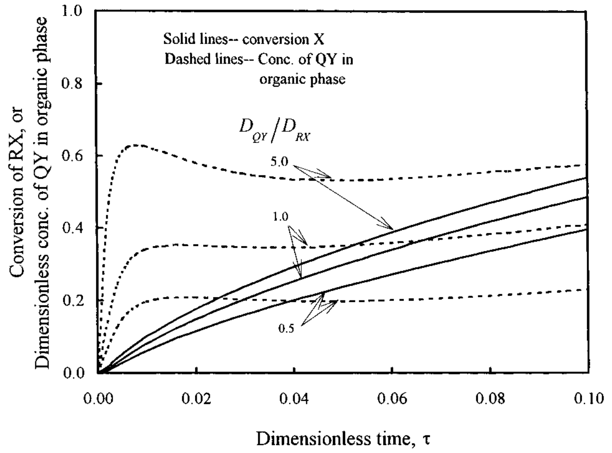


Figure 4. Concentration profile of QY and conversion of RX vs τ at different D_{QY}/D_{RX}: $Bi_{QY} = 100$, $D_{QX}/D_{RX} = 5$, $k_{aq}/k_{org} = 10$, $k_{org} = 1.0\ M^{-1}\ min^{-1}$, $D_{RX} = 6.0 \times 10^{-9}\ m^2/min$, $m_{QY} = 10$, $m_{QX} = 0.05$, $C_{QX,0} = 0.01$ M, $C_{RX,0} = 0.1$ M, $C_{KY,0} = 0.2$ M.

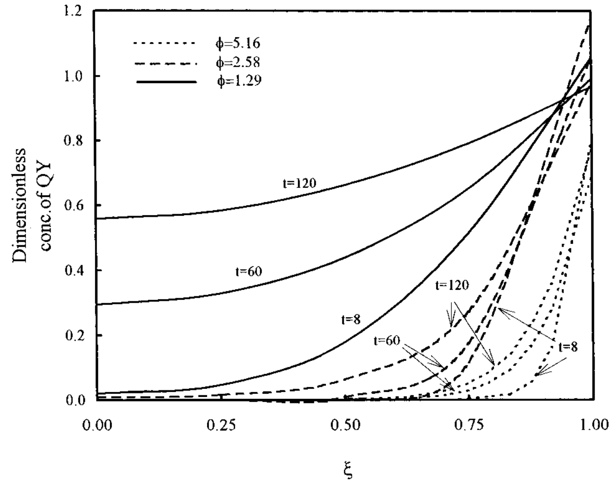


Figure 5. Dependence of QY concentration in the radial direction of the droplet on ϕ and t: $Bi_{QY} = 100$, $D_{QX}/D_{RX} = 5$, $k_{aq}/k_{org} = 10$, $k_{org} = 1.0\ M^{-1}\ min^{-1}$, $D_{RX} = 6.0 \times 10^{-9}\ m^2/min$, $m_{QY} = 10$, $m_{QX} = 0.05$, $C_{QX,0} = 0.01$ M, $D_{QY}/D_{RX} = 1$, $C_{RX,0} = 0.1$ M, $C_{KY,0} = 0.2$ M.

trated QY near the droplet surface. When ϕ is smaller than 2, a near flat profile of QY is obtained as the reaction proceeds.

External mass-transfer resistance also affects the overall reaction rate. A higher value of Bi_{QY} exhibits a lower transfer resistance of QY into the organic phase. Figure 6 depicts the effect of mass transfer at various Bi_{QY} for $\phi = 0.816$. A higher stirring speed leads to higher mass-transfer rates of QX and QY, thus enhancing the reaction rate. However, the mass-transfer rate of QY does not influence the shape of the profile within the droplet, as shown in Figure 6 for different values of Bi_{QY} at various τ. The only difference is the amount of QY in the organic phase. The distribution of QX and QY between the two phases is important in evaluating suitable catalysts. The effect of the distribution coefficient on QY concentration in the organic phase is revealed in Figure 7. From the results, one can see that a lower distribution coefficient of QX and a higher one of QY would lead to more of QY in the organic phase, thus enhancing the intrinsic organic reaction.

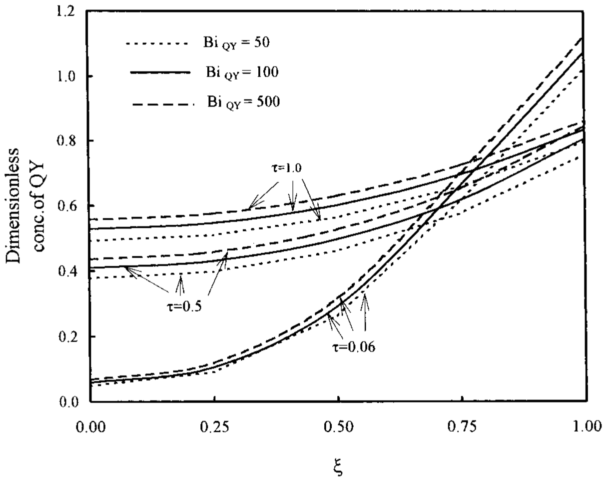


Figure 6. Dependence of QY concentration in the radial direction of the droplet on Bi_{QY}: $D_{QX}/D_{RX} = 1$, $k_{aq}/k_{org} = 10$, $k_{org} = 1.0\ M^{-1}\ min^{-1}$, $D_{RX} = 6.0 \times 10^{-8}\ m^2/min$, $\phi = 0.816$, $m_{QY} = 10$, $D_{QY}/D_{RX} = 1$, $m_{QX} = 0.05$, $C_{QX,0} = 0.01$ M, $C_{RX,0} = 0.1$ M, $C_{KY,0} = 0.2$ M.

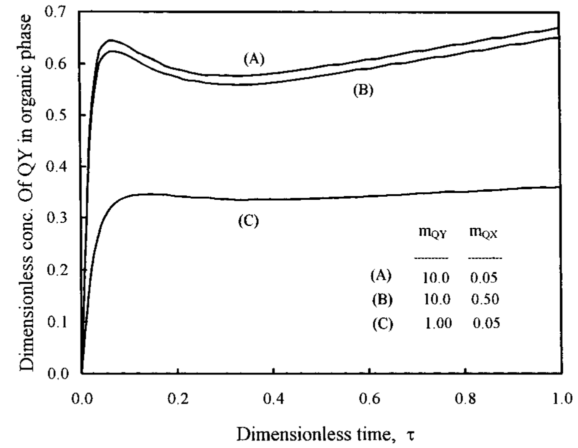


Figure 7. Dependence of distribution coefficients of QX and QY on the variation of QY concentration in the organic phase: $Bi_{QY} = 50$, $D_{QX}/D_{RX} = 1$, $k_{aq}/k_{org} = 10$, $k_{org} = 1.0\ M^{-1}\ min^{-1}$, $D_{RX} = 6.0 \times 10^{-8}\ m^2/min$, $\phi = 0.816$, $C_{QX,0} = 0.01$ M, $D_{QY}/D_{RX} = 1$, $C_{RX,0} = 0.1$ M, $C_{KY,0} = 0.2$ M.

In order to compare the simulation results with the experimental data, the data of 2,4,6-tribromophenol reacted with allyl bromide in an alkaline solution/chlorobenzene under the action of various amounts of tetrabutylammonium bromide in a batch reactor (Wang and Yang, 1991) were used. The comparison is shown in Figure 8. The necessary parameters for simulation, such as reaction rate constants and mass-transfer coefficients were obtained from the literature (Wang and Yang, 1991). By adjusting the effective diffusivity of the components within the droplet, the estimated concentration of QY can be quite consistent with the experimental data for cases A–D.

Conclusion

In the present study, a dynamic model concerning the mass transfer and reaction in a single droplet for a liquid/liquid phase-transfer-catalyzed system was developed. The role of active intermediate was investigated to interpret its effects on the overall reaction rate. The solutions of system equations were solved by the finite difference and Runge–Kutta fourth-order

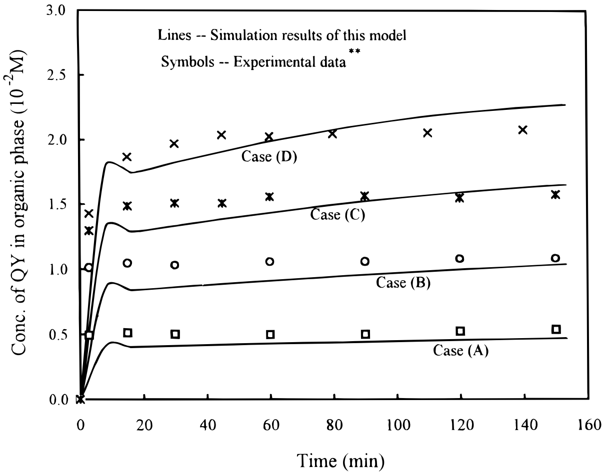


Figure 8. Comparison of the estimated concentration of QY in the organic phase with the experimental data (**Wang and Yang, 1991). Experimental conditions: 3.0 g of 2,4,6-tribromophenol; 0.7 g of allyl bromide; 1.0 g of KOH; 50 mL of chlorobenzene; 50 mL of water; temperature 50 °C; Bu_4NBr: (A) 0.0062 M, (B) 0.0124 M, (C) 0.0186 M, (D) 0.0248 M. Simulation conditions: $k_{aq}/k_{org} = 8.281$, $k_{org} = 1.194\ M^{-1}\ min^{-1}$, $D_{RX} = 1.5 \times 10^{-10}\ m^2/min$, $D_{QY} = 9.0 \times 10^{-8}\ m^2/min$, $D_{QX} = 1.5 \times 10^{-7}\ m^2/min$, $Bi_{QY} = 125$, $m_{QY} = 12.8$, $m_{QX} = 0.07$, $R = 2.2$ mm.

methods. The simulation results can successfully describe the two-phase system in a batch reactor. Film conversion parameter ϕ was used to describe the relative importance of diffusion and chemical reaction in a single droplet. The effect of external mass-transfer resistance of a phase-transfer catalyst was also considered. The key reacting component for phase-transfer catalysis is the active intermediate. It is found that the concentration and profile of the active intermediate in organic droplets depend on the film conversion parameter, mass Biot number, and kinetics. A higher film conversion parameter would lead to a lower reaction rate, with the active intermediate concentrated in the interface. The present study provides an analysis to understand the behavior of phase-transfer catalysis. Therefore, the selection of catalysts and reactor design for the liquid/liquid system can be more properly obtained.

Nomenclature

a = interfacial area per unit volume
Bi_{QY} = mass Biot number of QY
Bi_{QX} = mass Biot number of QX
C_i^j = concentration of component i in phase j (j = org, aq)
$C_{RX,0}$ = initial concentration of RX in the organic phase, M
$C_{KY,0}$ = initial concentration of KY in the aqueous phase, M
$C_{QX,0}$ = initial concentration of QX in the aqueous phase, M
$\bar{C}_i^{org}$ = average concentration of component i in the droplet, M
D_i = diffusion coefficient of component i in the droplet, m²/min
f_i^j = dimensionless concentration of component i in phase j
$f_{RX,0}$ = dimensionless concentration of RX at initial condition
$f_{KY,0}$ = dimensionless concentration of KY at initial condition
$f_{QX,0}$ = dimensionless concentration of QX at initial condition
$\bar{f}_i^{org}$ = average dimensionless concentration of component i in an organic droplet, M
k_{aq} = reaction rate constant in the aqueous phase, 1/(M min)
k_{org} = reaction rate constant in the organic phase, 1/(M min)
K_{QX} = mass-transfer coefficient of QX in the aqueous phase, m/min
K_{QY} = mass-transfer coefficient of QY in the organic phase, m/min
m_{QX} = distribution constant of QX between the organic and aqueous phases
m_{QY} = distribution constant of QY between the organic and aqueous phases
q_{RX} = initial concentration ratio of RX to QX
q_{KY} = initial concentration ratio of KY to QX
r = spatial coordinate in the radial direction
R = mean radius of the organic droplet, m
t = time, min
V_{aq} = volume of the aqueous phase, l
V_{org} = volume of the organic phase, l
X = conversion of RX in the organic phase

Greek Symbols

β = ratio of k_{aq}/k_{org}
γ_i = ratio of D_i/D_{RX}
δ = volume ratio of the organic phase to the aqueous phase
ξ = dimensionless spatial coordinate in the radial direction
ϕ_{RX} = Thiele modulus of RX in the two-liquid phase system, defined as $R(k_{org}C_{QX,0})^{1/2}/D_{RX}^{1/2}$
τ = dimensionless time, defined as $D_{RX}t/R^2$

Superscripts

aq = aqueous phase
j = j phase (j = org, aq)
org = organic phase
s = surface of liquid droplet

Subscripts

RX = organic phase reactant
KY = aqueous phase reactant
QX = phase transfer catalyst
QY = active phase-transfer intermediate
i = component i

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