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Lévêque Model for Mass Transfer with an Irreversible Second-Order Chemical Reaction

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The effect of an irreversible second-order chemical reaction on the rate of mass transfer has been studied theoretically on the basis of the Lévêque model. The approximate and numerical solutions for the reaction factor have been presented and compared with each other. It has been shown that the approximate solution agrees well with the numerical solution.

1. Introduction

In mass transfer operations, such as gas absorption, liquid-liquid extraction, solid dissolution, etc., mass transfer is frequently accompanied by chemical reaction. Therefore the theoretical analysis of mass transfer with chemical reaction is believed to be of great importance for the reasonable interpretation of the experimental data or the rational design of the equipment for such operations. Most works in this area have dealt with gas absorption with chemical reaction on the basis of the film model[1] or the penetration model[2], and simultaneous mass transfer and chemical reaction between a solid wall and a flowing fluid has received somewhat less attention.

In this paper mass transfer accompanied by an irreversible second-order chemical reaction has been studied theoretically on the basis of the Lévêque model[3] in which mass transfer is assumed to take place in a flow with a constant velocity gradient.

2. Mass Transfer without Chemical Reaction

The flow situation in the Lévêque model[3] is shown in Fig. 1. The fluid with a steady velocity profile flows along a solid boundary, the velocity gradient being constant. In this paper we consider the case in which a solute A dissolves into the liquid from the solid wall.

When chemical reaction is absent, the basic differential equation describing the diffusion of solute A in the liquid phase can be written as:

$$D_A \frac{\partial^2 A}{\partial x^2} - ax\frac{\partial A}{\partial y} = 0 \tag{1}$$

with the boundary conditions:

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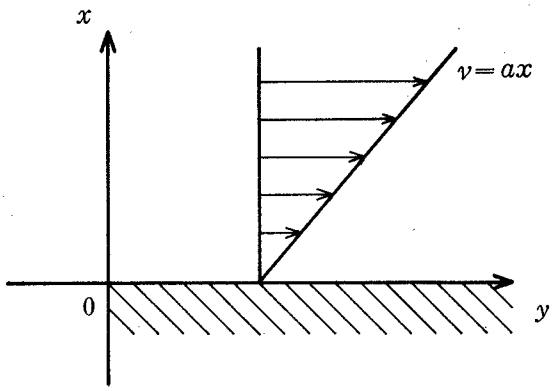

Fig. 1. Flow pattern based on Lévêque model

$$\left.\begin{array}{lll} x=0, & y>0; & A=A_i \\ x=\infty, & y\geq 0; & A=0 \\ y=0, & x>0; & A=0 \end{array}\right\} \tag{2}$$

This problem has been solved by Kramers and Kreyger[4], Hikita et al.[5] and Den Hartog and Beek[6]. The solution for the concentration profile of solute A is:

$$\frac{A}{A_i}=1-\frac{3}{\Gamma(1/3,\infty)}\int_0^{(a/9D_A y)^{1/3}x}\exp(-p^3)\mathrm{d}p \tag{3}$$

Then the average rate of mass transfer over the entire length from 0 to y is given by:

$$N_A{}^*=\frac{1}{y}\int_0^y[-D_A(\partial A/\partial x)_{x=0}]\mathrm{d}y=\frac{3^{4/3}}{2\Gamma(1/3,\infty)}(aD_A{}^2/y)^{1/3}A_i \tag{4}$$

The liquid-phase mass transfer coefficient $k_L{}^*$ for diffusion without chemical reaction is defined as:

$$N_A{}^*=k_L{}^*A_i \tag{5}$$

whence

$$k_L{}^*=\frac{3^{4/3}}{2\Gamma(1/3,\infty)}(aD_A{}^2/y)^{1/3} \tag{6}$$

From Eq. (6) it can be seen that in the absence of chemical reaction, the mass transfer coefficient is proportional to the 2/3 power of the liquid-phase diffusivity of solute A. This dependence of $k_L{}^*$ on D_A is the same as that derived from the laminar boundary-layer theory[7].

3. Mass Transfer with an Irreversible Pseudo First-Order Reaction

Let us consider the case where a solute A dissolves into the liquid from the solid wall and reacts irreversibly with a reactant B which is already present in the liquid phase according to the following reaction:

$$\mathrm{A}+\nu\mathrm{B}\longrightarrow\mathrm{Products} \tag{7}$$

with the reaction rate represented by

$$r=k_2AB \tag{8}$$

If the concentration of reactant B is much greater than that of solute A, the reaction can be regarded as pseudo first-order with respect to solute A and the concentration of B is constant throughout the liquid phase at the value B_0 which is the bulk concentration of B. The reaction rate is then given by:

$$r=(k_2B_0)A \tag{9}$$

In this case, the basic differential equation for the diffusion of solute A can be represented as:

$$D_A\frac{\partial^2 A}{\partial x^2}-ax\frac{\partial A}{\partial y}=(k_2B_0)A \tag{10}$$

with the boundary conditions, Eq. (2).

Eqs. (10) and (2) can be solved[6] by Laplace transformation. The solution giving the concentration profile of solute A is represented as:

$$\frac{A}{A_i}=\mathscr{L}^{-1}\left[\frac{\sqrt{k_2B_0+asx}}{s\sqrt{k_2B_0}}\frac{K_{1/3}(2\sqrt{(k_2B_0+asx)^3/D_Aa^2}/3s)}{K_{1/3}(2\sqrt{(k_2B_0)^3/D_Aa^2}/3s)}\right] \tag{11}$$

and then the average mass transfer rate is given by

$$N_A=\frac{\sqrt{k_2B_0D_A}A_i}{y}\mathscr{L}^{-1}\left[\frac{1}{s^2}\frac{K_{2/3}(2\sqrt{(k_2B_0)^3/D_Aa^2}/3s)}{K_{1/3}(2\sqrt{(k_2B_0)^3/D_Aa^2}/3s)}\right] \tag{12}$$

Thus the reaction factor β, which is defined as the ratio of the rates of mass transfer with and without chemical reaction, is obtained from Eqs. (4) and (12) as:

$$\beta=\frac{2\Gamma(1/3,\infty)\sqrt{k_2B_0}A_i}{3^{4/3}(a\sqrt{D_A}y^2)^{1/3}}\mathscr{L}^{-1}\left[\frac{1}{s^2}\frac{K_{2/3}(2\sqrt{(k_2B_0)^3/D_Aa^2}/3s)}{K_{1/3}(2\sqrt{(k_2B_0)^3/D_Aa^2}/3s)}\right] \tag{13}$$

The inverse transformation is difficult, but it is possible to find the asymptotic expressions for small and large values of y by expanding the right-hand side of Eq. (13) in series for large and small values of s, respectively. For large values of y ($r\geq 2.4$), the solution of β is

$$\beta=r+0.474715/r^2 \tag{14}$$

while for small values of y ($r\leq 2.4$), the solution is

$$\beta=1+\sum_{j=1}^{\infty}b_jr^{2j} \tag{15}$$

where r is a dimensionless parameter defined by

$$\begin{aligned} r&=(2/3^{4/3})\Gamma(1/3,\infty)\sqrt{k_2B_0}(y/a\sqrt{D_A})^{1/3}\\ &=\sqrt{k_2B_0D_A}/k_L{}^* \end{aligned} \tag{16}$$

and b_1, b_2, $\cdots$ b_j are the numerical constants, which are given in Table 1. Table 2 shows the value of the reaction factor β calculated from Eqs. (14) and (15) as a function of r. As can be seen from Eq. (14), when the value of r is very large the reaction factor β approaches the value given by the following expression

$$\beta=r \tag{17}$$

and the mass transfer rate is represented by:

$$N_A=\sqrt{k_2B_0D_A}A_i \tag{18}$$

This situation corresponds to the case of a fast pseudo first-order reaction and the

Table 1 Values of b_j in Eq. (15)

j	b_j	j	b_j
1	3.60459×10^{-1}	8	-2.71339×10^{-8}
2	-2.96396×10^{-2}	9	2.09426×10^{-9}
3	3.37614×10^{-3}	10	-1.54920×10^{-10}
4	-3.75698×10^{-4}	11	1.01279×10^{-11}
5	3.88808×10^{-5}	12	-7.17765×10^{-13}
6	-3.71726×10^{-6}	13	4.01924×10^{-14}
7	3.29083×10^{-7}	14	-2.65455×10^{-15}

Table 2 Values of reaction factor for mass transfer with pseudo first-order reaction

γ	β	γ	β
0.10	1.004	1.5	1.692
0.15	1.008	2.0	2.116
0.20	1.014	2.5	2.576
0.25	1.022	3.0	3.053
0.30	1.032	4.0	4.030
0.40	1.057	5.0	5.019
0.50	1.088	6.0	6.013
0.60	1.126	7.0	7.010
0.70	1.170	8.0	8.007
0.80	1.219	9.0	9.006
0.90	1.274	10.0	10.005
1.00	1.334		

mass transfer rate in this case is independent of k_L^*, i.e. the hydrodynamic conditions. When the value of γ is very small, $\beta=1$, corresponding to physical mass transfer.

Fig. 2 shows the comparison between the Lévêque-model, film-model[8] and penetration-model[9] solutions of the reaction factor for mass transfer with a pseudo first-order reaction. The Lévêque-model curve lies between the film-model curve and the penetration-model curve, and the maximum deviation between the upper and lower curves is only 7%. The curve representing the numerical solution of β based on the laminar boundary-layer model[10] also agrees with the Lévêque-model curve within less than 2%. (this curve is omitted from Fig. 2 for brevity.) From these results we can conclude that the effect of chemical reaction on the rate of mass transfer is insensitive to the flow situation, when the value of β is compared at the same value of γ.

4. Mass Transfer with an Irreversible Instantaneous Reaction

In this case solute A reacts instantaneously and irreversibly with reactant B. The reaction takes place at a reaction plane beneath the solid surface where the concentrations of A and B are zero, and the reaction rate is equal to the rate at

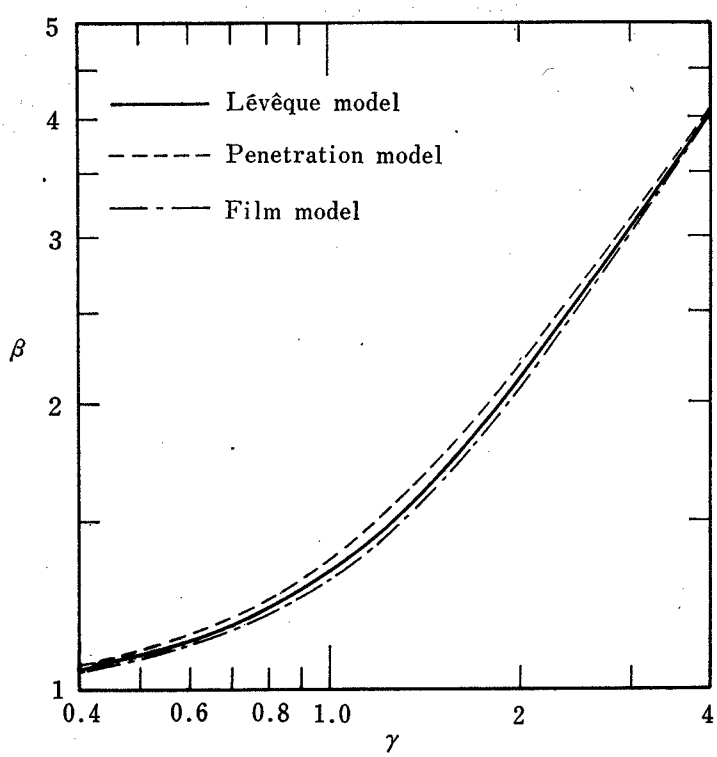

Fig. 2. Comparison between Lévêque-, film- and penetration-model solutions of reaction factor for mass transfer with an irreversible pseudo first-order reaction

which the two substances can diffuse to the reaction plane. The basic differential equations governing the diffusion of A and B can be written as:

$$D_A\frac{\partial^2 A}{\partial x^2}-ax\frac{\partial A}{\partial y}=0 \quad (0<x<x_r) \tag{19}$$

$$D_B\frac{\partial^2 B}{\partial x^2}-ax\frac{\partial B}{\partial y}=0 \quad (x_r<x<\infty) \tag{20}$$

with the boundary conditions:

$$\left.\begin{array}{ll} x=0, \ y>0; & A=A_i \\ x=\infty, \ y\geq 0; & B=B_0 \\ y=0, \ x>0; & B=B_0 \\ x=x_r, \ y>0; & A=B=0, \ D_A(\partial A/\partial x)+(D_B/\nu)(\partial B/\partial x)=0 \end{array}\right\} \tag{21}$$

where x_r represents the location of the reaction plane. The solutions of Eqs. (19) to (21) are:

$$\frac{A}{A_i}=1-\frac{\Gamma(1/3,ax^3/9D_Ay)}{\Gamma(1/3,\sigma)} \quad (0<x<x_r) \tag{22}$$

$$\frac{B}{B_0}=\frac{\Gamma(1/3,ax^3/9D_By)-\Gamma(1/3,\sigma D_A/D_B)}{\Gamma(1/3,\infty)-\Gamma(1/3,\sigma D_A/D_B)} \quad (x_r<x<\infty) \tag{23}$$

where σ is the root of the following equation:

$$\left(\frac{D_B}{D_A}\right)^{2/3}\frac{B_0}{\nu A_i}=\exp\left[\left(\frac{D_A}{D_B}-1\right)\sigma\right]\frac{\Gamma(1/3,\infty)-\Gamma(1/3,\sigma D_A/D_B)}{\Gamma(1/3,\sigma)} \tag{24}$$

The average rate of mass transfer of solute A is obtained from Eq. (22) as:

$$N_A=\frac{3^{4/3}}{2\Gamma(1/3,\sigma)}(aD_A{}^2/y)^{1/3}A_i \tag{25}$$

The reaction factor is then expressed as:

$$\beta=\Gamma(1/3,\infty)/\Gamma(1/3,\sigma) \tag{26}$$

It should be noted that Eqs. (26) and (24) are the same as those obtained by Acrivos[11] on the basis of the laminar boundary-layer model. The solutions obtained above were also derived by Den Hartog and Beek[6] and the solution giving the concentration profile of reaction product was presented by Hikita et al[12].

When $D_A=D_B$, Eqs. (24) and (26) can be simplified to

$$\beta=1+\frac{B_0}{\nu A_i} \tag{27}$$

which is identical to the film-model[13] and penetration-model[9] solutions with $D_A=D_B$. When D_A and D_B are not widely different and the value of $B_0/\nu A_i$ is large, the following approximations can be permissible:

$$\exp\left[\left(\frac{D_A}{D_B}-1\right)\sigma\right]\approx 1 \tag{28}$$

$$\Gamma(1/3,\sigma D_A/D_B)/\Gamma(1/3,\sigma)\approx(D_A/D_B)^{1/3} \tag{29}$$

Making these approximations in Eqs. (24) and (26), the expression for the reaction factor now becomes:

$$\beta=\left(\frac{D_A}{D_B}\right)^{1/3}+\left(\frac{D_B}{D_A}\right)^{2/3}\frac{B_0}{\nu A_i} \tag{30}$$

This is the same equation as obtained by Potter[14] based on the laminar boundary-layer model. For the case where $B_0=0$ which corresponds to the physical mass transfer of solute A, Eq. (30) reduces to $\beta=(D_A/D_B)^{1/3}$. Therefore, in order to obtain an approximate expression of the reaction factor which is valid when $B_0=0$, the first term of the right-hand side of Eq. (30) should be replaced by unity. Thus:

$$\beta=1+\left(\frac{D_B}{D_A}\right)^{2/3}\frac{B_0}{\nu A_i} \tag{31}$$

Eq. (31) agrees with the exact solution to within a maximum deviation of 15%, if the value of D_B/D_A lies between 4 and 1/4, and the agreement between the approximate and exact solutions is much better at very large and small values of $B_0/\nu A_i$.

5. Mass Transfer with an Irreversible Second-Order Reaction

Here we consider the case where mass transfer is accompanied by an irreversible second-order reaction between solute A and reactant B, with the reaction rate given by Eq. (8). The basic differential equations describing the diffusion of A and B can be written as:

$$D_A\frac{\partial^2 A}{\partial x^2}-ax\frac{\partial A}{\partial y}=k_2AB \tag{32}$$

$$D_B \frac{\partial^2 B}{\partial x^2} - ax\frac{\partial B}{\partial y} = \nu k_2 AB \tag{33}$$

with the boundary conditions:

$$\left.\begin{array}{ll} x=0, & y>0\,;\ A=A_i,\ \partial B/\partial x=0 \\ x=\infty, & y\geq 0\,;\ A=0,\quad B=B_0 \\ y=0, & x>0\,;\ A=0,\quad B=B_0 \end{array}\right\} \tag{34}$$

Eqs. (32) and (33) with Eq. (34) cannot be solved analytically. Then these equations were solved numerically by a finite-difference method similar to that used by Brian et al[15,16]. Convergence tests and comparison of the computed results with known asymptotes indicated that the error of the computed results was less than 1%. The computed results of reaction factor for four given values of β_∞ which represents the reaction factor for the case of an instantaneous reaction are shown as solid curves in Fig. 3, where the values of β are plotted against r with the diffusivity ratio D_B/D_A as parameter. The three solid curves for each value of β_∞ approach the pseudo first-order reaction curve at low values of r, and they approach an

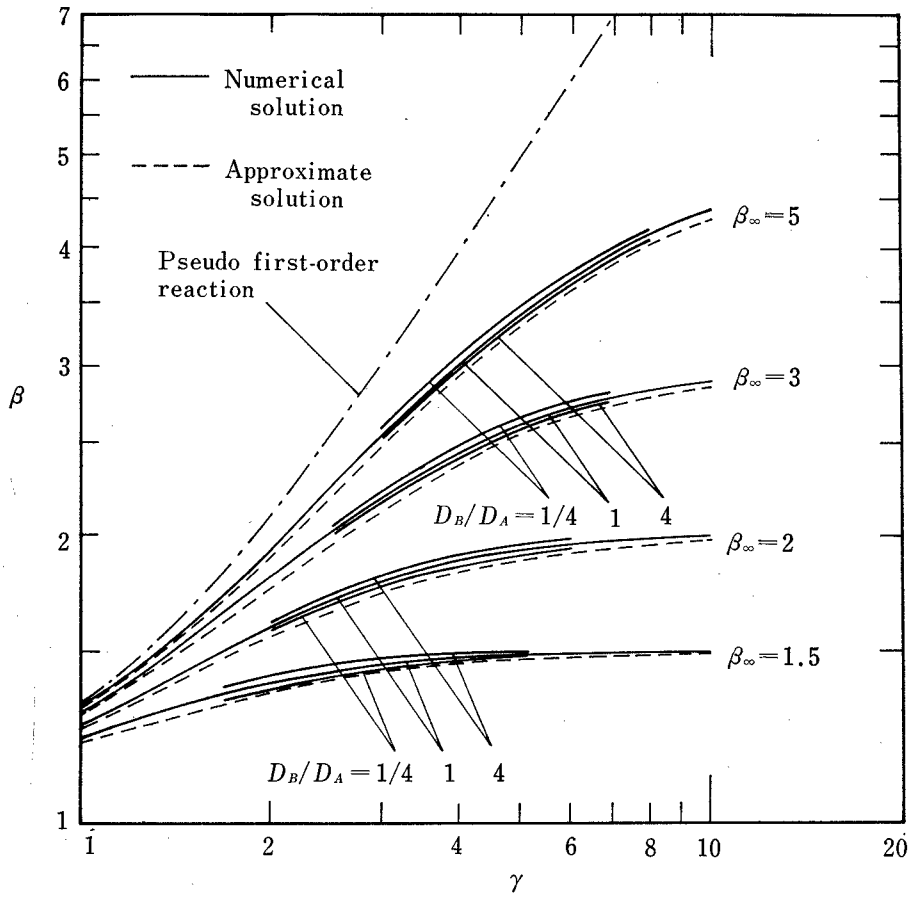

Fig. 3. Numerical and approximate solutions of reaction factor for mass transfer with an irreversible second-order reaction based on Lévêque model

asymptotic value β_∞ at high values of r. These three curves agree well with each other within 4% over the range of the D_B/D_A values from 1/4 to 4. Thus it may be concluded that the reaction factor is quite insensitive to the diffusivity ratio D_B/D_A. The numerical solutions of the reaction factor were also obtained by Den Hartog and Beek[6] for $D_B/D_A=1$ and $\beta_\infty=2$, 3 and 6.

In the present work, the approximate solution of the reaction factor has also been derived using the method similar to that used by van Krevelen and Hoftijzer[17] and Hikita and Asai[18]. In the following treatment, it is assumed that the concentration of reactant B in the liquid-phase is uniform and equal to B_i, the concentration of B at the solid wall, and that the value of B_i is independent of y, the distance in the flow direction. The reaction rate is then given by

$$r=(k_2B_i)A \tag{35}$$

and Eq. (32) can be written as

$$D_A\frac{\partial^2 A}{\partial x^2}-ax\frac{\partial A}{\partial y}=(k_2B_i)A \tag{36}$$

Since Eq. (36) has the same form as Eq. (10), the solution giving β in this case is represented by the following equations

$$\beta=r\eta+0.474715/(r\eta)^2 \quad (r\eta\geq 2.4) \tag{37}$$

$$\beta=1+\sum_{j=1}^{\infty}b_j(r\eta)^{2j} \qquad (r\eta\leq 2.4) \tag{38}$$

which are the same forms as Eqs. (14) and (15). Here b_1, b_2, $\cdots b_j$ are the numerical constants given in Table 1, r is the same parameter as Eq. (16), and η is a dimensionless parameter defined by

$$\eta=\sqrt{B_i/B_0}=\sqrt{(\beta_\infty-\beta)/(\beta_\infty-1)} \tag{39}$$

where β_∞ is the reaction factor for an instantaneous irreversible reaction and given by Eqs. (24) and (26). Thus the approximate solution of β for the case of an irreversible second-order reaction is composed of Eqs. (16), (24), (26) and (37) to (39).

The approximate solutions of the reaction factor calculated for the cases of $\beta_\infty=1.5$, 2, 3 and 5 are shown in Fig. 3 as dotted curves and compared with the numerical solutions. As can be seen in this figure, the agreement between the numerical and approximate solutions is good for large and small values of r. For intermediate values of r, the approximate solutions are slightly lower than the numerical solutions. However, the maximum deviations between the approximate solutions and the numerical solutions for $D_B/D_A=1$ are only about 3%.

Fig. 4 shows the comparison of the Lévêque-model approximate solution of the reaction factor with the film-model and the penetration-model approximate solutions at the constant values of $\beta_\infty=2$ and 5. The solid curves in this figure represent the Lévêque-model approximate solution calculated from Eqs. (37) to (39), while the chain curves show the film-model approximate solution of van Krevelen and Hoftijzer[17] given by:

$$\beta=r\eta/\tanh(r\eta) \tag{40}$$

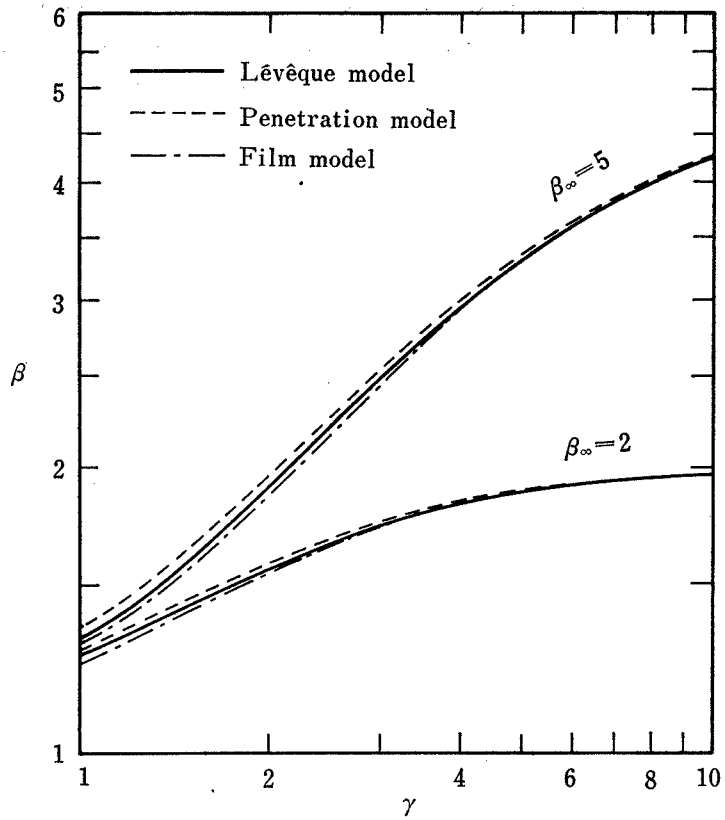

Fig. 4 Comparison between Lévêque-, film- and penetration-model approximate solutions of reaction factor for mass transfer with an irreversible second-order reaction

Further, the dotted curves represent the penetration-model approximate solution derived by Hikita and Asai[18], which is given by:

$$\beta=(r\eta+\frac{\pi}{8r\eta})\mathrm{erf}(2r\eta/\sqrt{\pi})+\frac{1}{2}\exp(-4r^2\eta^2/\pi) \tag{41}$$

The values of β based on these three models agree well with each other within 10%, when compared at the same values of β_∞ and r. This indicates that the effect of chemical reaction on the rate of mass transfer is insensitive to the hydrodynamic conditions.

Acknowledgement

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Notation

A : concentration of solute A, g-mol/cm^3
A_i : concentration of solute A at the solid wall, g-mol/cm^3
a : velocity gradient of the flowing liquid at the solid wall, 1/sec
B : concentration of liquid-phase reactant B, g-mol/cm^3
B_i, B_0 : concentrations of liquid-phase reactant B at the solid wall and in the bulk of liquid, respectively, g-mol/cm^3
b_j : coefficient in Eq. (15), ——
D_A, D_B : liquid-phase diffusivities of solute A and reactant B, respectively, cm^2/sec
$K_p(z)$: modified Bessel function of the second-kind of order p, ——
k_L^* : liquid-phase mass transfer coefficient in the absence of chemical reaction for solute A, cm/sec
k_2 : rate constant for irreversible second-order reaction, cm^3/g-mol sec
N_A^*, N_A : average rates of mass transfer of solute A without and with chemical reaction, respectively, g-mol/cm^2 sec
x : distance from the solid wall into liquid, cm
x_r : distance from the solid wall to the reaction plane, cm
y : distance in the flow direction, cm

Greek letters

β : reaction factor, ——
β_∞ : reaction factor for mass transfer with an instantaneous irreversible reaction, ——
γ : dimensionless parameter defined by Eq. (16), ——
$\Gamma(p, q)$: incomplete gamma function, $\int_0^q t^{p-1}e^{-t}dt$, ——
η : dimensionless parameter defined by Eq. (39), ——
ν : number of moles of liquid-phase reactant B reacting with each mole of solute A, ——
σ : dimensionless parameter defined by Eq. (24), ——

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