

MODEL DEVELOPMENT FOR MULTICOMPONENT MASS TRANSFER WITH RAPID CHEMICAL REACTIONS IN A SMALL DROP

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(Received 17 November 1993 • accepted 1 August 1994)

Abstract—Multicomponent mass transfer accompanied by instantaneous chemical reactions in a small drop has been modeled and simulated for the case where two different solutes diffuse from a continuous phase into the drop and react rapidly with a third reactant in the drop. The computational results obtained by Galerkin's finite element method are reported in terms of concentration profiles, the locations of reaction front, the cumulative mass flux, and the enhancement factor. The effects of physical parameters, such as diffusivities of the solutes and the reactant, the interfacial concentration of solutes, and the relative amount of the reactant, on the calculated quantities are discussed.

Key words: Mass Transfer, Drop, Bubble, (Chemical) Reaction Front, Moving Boundary

INTRODUCTION

The simultaneous mass transfer and chemical reaction of soluble solutes in a rigid drop are of practical importance in various industrial gas-liquid and liquid-liquid contacting operations such as spray absorption, liquid-liquid extraction, separation using liquid membranes, and atmospheric scavenging. Numerous studies related to mass transfer accompanied with reversible or irreversible and isothermal or nonisothermal reactions in a simple geometry have been reported [1-4]. However, mass transfer to a drop or a bubble with chemical reactions has not been sufficiently investigated. This is because mass transfer to a drop is more restricted to solve than mass transfer to a simple geometry due to nonlinearity of the moving boundary. Ruckenstein et al. [5] studied mass transfer from a drop, accompanied by a first order reaction and obtained the concentration profile in the continuous phase and the rate of mass transfer, using a similarity solution scheme. Dang and Ruckenstein [6] obtained unsteady concentration profile and the mass transfer rate from a single or binary component drop with/without reaction for relatively large Reynolds number flow. Ramachandran et al. [7] investigated mass transfer into the core of drops with a liquid-phase first-order chemical reaction, using the boundary layer concept for the gas phase and film theory for the liquid phase. They showed their results in terms of concentration distribution of the gas solute, but did not report the parametric study on enhancement factor. Kleinstreuer et al. [8] extended Ramachandran's work to the case of adsorption in string of circulating drops. Dutta et al. [9] studied the simplest binary mass transfer in which a single gas solute diffuses into a liquid drop and reacts rapidly with a reactant present in the drop, using the finite difference method. They reported the reaction front positions, the rate of mass transfer, and the enhancement factor for different system parameters.

In many industrial situations, diffused solutes into a drop usual-

ly react instantaneously with a reactant in the drop. Therefore, there are two regions inside the drop, each containing only the solutes or the reactant. The boundary between these two regions is called reaction front and its location moves away from the surface of the drop toward the center of the drop as the reactions proceed.

Despite its practical importance, this moving-boundary problem is not understood satisfactorily for the general case in industrial processes, where more than one solute diffuse and react rapidly with a reactant in a drop. The goal of the present work is to theoretically analyze this multicomponent moving-boundary problem and develop a mathematical model. The developed mathematical model is simulated for absorption of two solutes from the continuous phase into the drop and instantaneous reactions with the third chemical component existing in the drop. The results of this study include concentration profiles of solutes and the reactant, reaction front position, and the cumulative mass flux and the enhancement factor of each diffusing solute for different values of the system parameters. For the development of the model proposed in this study, it is assumed that the drop is so small that it is considered to behave as a rigid particle [10].

MODEL DEVELOPMENT

Let us assume that the following irreversible instantaneous reactions occur between n diffusing solutes, A, B, ..., N, from the continuous phase into the non-circulating drop and a reactant, T, existing in the drop.



where γ_i is the ratio of stoichiometry coefficients of T to i. There

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are n chemical reactions described by the above equations because n diffusing solutes react with T independently. The reactions occur at the reaction front moving from the surface of the drop to its center. In the following mathematical treatment, it is assumed that the bulk concentrations of solutes are constant and the initial concentration of T is uniform in the drop. Also assumed are negligible mass transfer resistance in the continuous phase and the dilute system for no cross effects between mass fluxes of the solutes so that binary mass transfer coefficients can be used to describe the system. The governing equations are:

For region I ($x < r < R$)

$$\begin{aligned} \frac{D_A}{r^2} \frac{\partial}{\partial r} \left[r^2 \frac{\partial C_A}{\partial r} \right] &= \frac{\partial C_A}{\partial t} \\ \frac{D_B}{r^2} \frac{\partial}{\partial r} \left[r^2 \frac{\partial C_B}{\partial r} \right] &= \frac{\partial C_B}{\partial t} \\ &\vdots \\ \frac{D_N}{r^2} \frac{\partial}{\partial r} \left[r^2 \frac{\partial C_N}{\partial r} \right] &= \frac{\partial C_N}{\partial t} \end{aligned}$$

For region II ($0 < r < x$)

$$\frac{D_T}{r^2} \frac{\partial}{\partial r} \left[r^2 \frac{\partial C_T}{\partial r} \right] = \frac{\partial C_T}{\partial t} \quad (2)$$

and relevant initial and boundary conditions are;

$$\begin{aligned} t=0; C_A=C_B=\dots=C_N=0, C_T=C_{T_0} \text{ for } r>0 \\ r=R; C_A=C_{A_i}, C_B=C_{B_i}, \dots, C_N=C_{N_i}, \text{ for } t>0 \\ r=0; C_T=\text{finite} \text{ for } t>0 \\ r=x; C_A=C_B=\dots=C_T=0, \text{ for } t>0 \end{aligned} \quad (3)$$

where C_i 's and D_i 's are the concentrations and diffusivities of i , respectively; r is radius coordinate of the system measured from the drop center; R is drop radius; C_{ji} is the equilibrium concentration of j at the drop surface; C_{T_0} is the initial concentration of T ; x is the distance from the drop center to the location of the reaction front. The following compatibility condition relating the fluxes of all components at $r=x$ should be satisfied:

$$\gamma_A N_A + \gamma_B N_B + \dots + \gamma_N N_N = -N_T$$

that is

$$\begin{aligned} \frac{\partial C_A}{\partial r} + \frac{\gamma_B}{\gamma_A} \frac{D_B}{D_A} \frac{\partial C_B}{\partial r} + \dots + \frac{\gamma_N}{\gamma_A} \frac{\partial C_N}{\partial r} \\ = -\frac{1}{\gamma_A} \frac{D_T}{D_A} \frac{\partial C_T}{\partial r} \end{aligned} \quad (4)$$

There is no analytical method to solve the above set of equations. A direct application of any numerical technique becomes very complicated because the reaction front is moving and given as a function of time. Several studies have been reported on the analogous problem-solidification of a liquid sphere initially at the fusion temperature [11-13]. Those studies used a singular perturbation technique to find an asymptotic solution of the moving-boundary problem. However, such a technique may not be appropriate for the present problem which is more complicated. Instead, it is desired that the spherical coordinate be appropriately transformed in order to fix the reaction front.

If the following coordinate variables are introduced,

$$\omega_I = \frac{\rho - \phi}{1 - \phi} \quad \phi \leq \rho \leq 1 \quad (5)$$

$$\omega_{II} = \frac{\phi - \rho}{\phi} \quad 0 \leq \rho \leq \phi \quad (6)$$

$$\text{where } \rho = r/R, \quad \phi = x/R$$

the governing equations are transformed to contain the location of reaction front as follows:

$$\begin{aligned} \frac{1}{(1-\phi)^2} \frac{\partial^2 C_A^*}{\partial \omega_I^2} + \frac{1-\omega_I}{1-\phi} \frac{d\phi}{d\tau} \frac{\partial C_A^*}{\partial \omega_I} &= \frac{\partial C_A^*}{\partial \tau} \\ \frac{D_{BA}}{(1-\phi)^2} \frac{\partial^2 C_B^*}{\partial \omega_I^2} + \frac{1-\omega_I}{1-\phi} \frac{d\phi}{d\tau} \frac{\partial C_B^*}{\partial \omega_I} &= \frac{\partial C_B^*}{\partial \tau} \\ &\vdots \\ \frac{D_{NA}}{(1-\phi)^2} \frac{\partial^2 C_N^*}{\partial \omega_I^2} + \frac{1-\omega_I}{1-\phi} \frac{d\phi}{d\tau} \frac{\partial C_N^*}{\partial \omega_I} &= \frac{\partial C_N^*}{\partial \tau} \\ \frac{D_{TA}}{\phi^2} \frac{\partial^2 C_T^*}{\partial \omega_{II}^2} + \frac{1-\omega_{II}}{\phi} \frac{d\phi}{d\tau} \frac{\partial C_T^*}{\partial \omega_{II}} &= \frac{\partial C_T^*}{\partial \tau} \end{aligned} \quad (7)$$

$$\text{where } C_A^* = \rho \bar{C}_A = \rho \frac{C_A}{C_{A_i}}$$

$$C_B^* = \rho \bar{C}_B = \rho \alpha_B \frac{C_B}{C_{B_i}}$$

$$C_N^* = \rho \bar{C}_N = \rho \alpha_N \frac{C_N}{C_{N_i}}$$

$$C_T^* = \rho \bar{C}_T = \rho \frac{C_T}{C_{T_i}}$$

$$\tau = \frac{t D_A}{R^2}, \quad \alpha_j = \frac{C_{ji}}{C_{A_i}}, \quad \text{and } D_j = \frac{D_j}{D_j}$$

Accordingly, the initial and boundary conditions reduce to:

$$\begin{aligned} \tau=0; C_A^*=C_B^*=\dots=C_N^*=0, C_T^*=1-\omega_{II} \text{ for } \omega>0 \\ \omega_I=1; C_A^*=1, C_B^*=\alpha_B, \dots, C_N^*=\alpha_N, \text{ for } \tau>0 \\ \omega_{II}=1; C_T^*=0 \text{ for } \tau>0 \\ \omega_I=\omega_{II}=0; C_A^*=C_B^*=\dots=C_T^*=0, \text{ for } \tau>0 \end{aligned} \quad (8)$$

and the compatibility condition becomes

$$\begin{aligned} \frac{\partial C_A^*}{\partial \omega_I} + D_{BA} \gamma_{BA} \frac{\partial C_B^*}{\partial \omega_I} + \dots + D_{NA} \gamma_{NA} \frac{\partial C_N^*}{\partial \omega_I} \\ = \beta D_{TA} \left(\frac{1-\phi}{\phi} \right) \frac{\partial C_T^*}{\partial \omega_{II}} \end{aligned} \quad (9)$$

where $\gamma_j = \gamma_j / \gamma_A$ and $\beta = C_{T_0} / \gamma_A C_{A_i}$.

Thus, the new coordinate variables, ω_I and ω_{II} , always have the values between 0 and 1, even if they are functions of ϕ . One way to numerically solve Eq. (7) with Eqs. (8) and (9) is to use linear finite elements for the two regions of I and II.

COMPUTATIONAL METHOD

The transformed governing equations will be numerically solved using the usual Galerkin formula, which is easy and economic to apply on a regular grid such as ω_I and ω_{II} , over a fixed number of linear finite elements for the two regions in the drop.

For a fixed time, $i+1$, ϕ is assumed and then, Eq. (7) is developed into finite element equations, using the Galerkin's formula over the dimensionless distance grid and the lumped formulation followed by the backward difference method over dimensionless time grid. In order to solve the developed finite element equations, a delicate part of computer code is required to update the nodal values of the previous time step, i , because the reaction front moves with time. The element equations are then combined

with the other element equations and summed over all the elements using the Direct Stiffness Method [14]. The Gaussian elimination procedure is then used to solve the resulting set of equations. After solving equations for all components, the compatibility should be checked. If it is not satisfied, the Newton-Raphson method is used for another guess of ϕ and the process is repeated until the matching is satisfactory.

The cumulative mass flux, Q_i , and the enhancement factor, E_i , of i can be obtained by integrating the produced concentration profiles with various parametric values as follows [15]:

$$Q_i = \int_0^\tau \left(\frac{\partial C_i}{\partial \rho} \right)_{\rho=L, \text{chem}} d\tau \quad (10)$$

$$E_i = \frac{3Q_i}{1 - \frac{6}{\pi} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-n^2 \pi^2 \tau}} \quad (11)$$

The number of elements and the grid size in the directions of the dimensionless distance and time are chosen by trial and error for efficient convergence.

RESULTS AND DISCUSSION

The developed mathematical models are simulated for the case in which two gas components, A and B, are absorbed from the surrounding continuous phase into the liquid drop and react instantaneously with third reactant T, existing in the drop according to the following equations:



The computational results, which were obtained by using of the Galerkin's formula, are presented in terms of concentration profiles of all solutes in the drop, the reaction front position, the cumulative mass flux, and the enhancement factor of A. The discussion on the calculated quantities of B is omitted because their trend might be similar to those of A, although they must have different numerical values. The maximum matching error for the compatibility condition is below 0.1%.

The parametric studies are performed to evaluate the effects of the initial concentration ratio of T to A (β) and the diffusivity ratio of B and T to A (D_{BA} and D_{TA} , respectively). The ratio of stoichiometric coefficients of the two reactions is taken as unity for the simplicity of the calculation.

Figs. 1 and 2 show the concentration profiles of solutes in the drop with different values of D_{BA} and α , the interfacial concentration ratio of B to A, and constant D_{TA} as a function of time and radius. In Fig. 1, we can see that when the diffusivities of all reactants are the same, T reacts with A and B simultaneously, regardless of the interfacial concentrations of A and B. However, Fig. 2 shows that when B diffuses slower than A, the reaction takes place mainly between A and T as the reaction proceeds, although the same amount of A and B exists in the interface. Figs. 3 and 4 show the progress of the reaction front with time at constant α . As can be seen in Fig. 3, larger β with smaller D_{BA} at constant diffusivity ratio, D_{TA} , has a positive effect on the retardation of the reaction front, resulting in a sharper slope in a large time.

In Fig. 4, we can also see that as T diffuses faster and B slower at constant β , the reaction front initially moves slower and finally

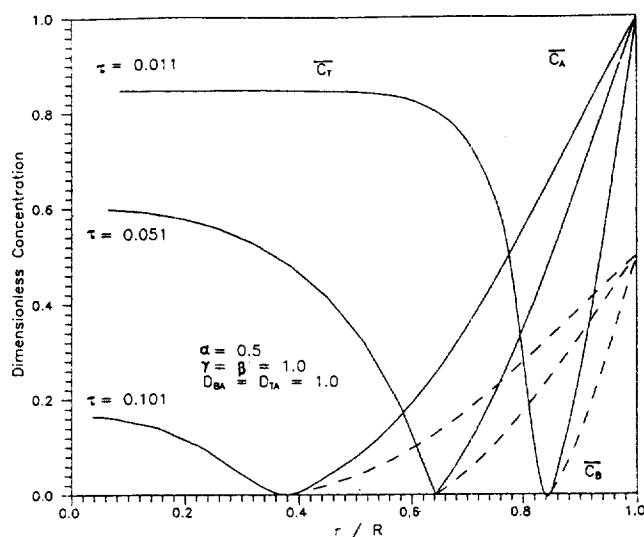


Fig. 1. Variation of concentration profiles (I).

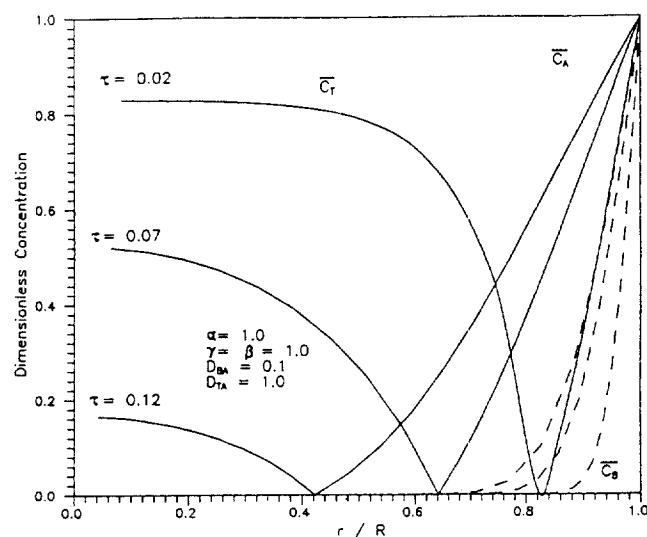


Fig. 2. Variation of concentration profiles (II).

faster. This confirms that if the diffusivity of T is very high, most amount of T must react with A and B, and consequently disappear at early stage, resulting in no more reaction at later time. For slower diffusing B, the disappearance rate of T will be lower because less amount of B diffuses and reacts with T. Therefore, the movement of the reaction front becomes slower for the entire reaction time.

The cumulative amount of A absorbed through unit surface area of the drop, which is obtained by integral of the concentration profile of A, is shown in Figs. 5 and 6. Fig. 5 shows that as β with smaller values of D_{BA} increases at constant D_{TA} , the more amount of A is absorbed. For constant β (Fig. 6), the faster diffusing T and the slower diffusing B cause the larger amount of A absorbed at a short time. However, the cumulative mass flux curves with constant β and D_{BA} tend toward the final limiting value no matter how fast T diffuses compared to A, and obviously the final limiting value increases as B moves slowly.

Fig. 7 shows the enhancement factor of A, which is obtained

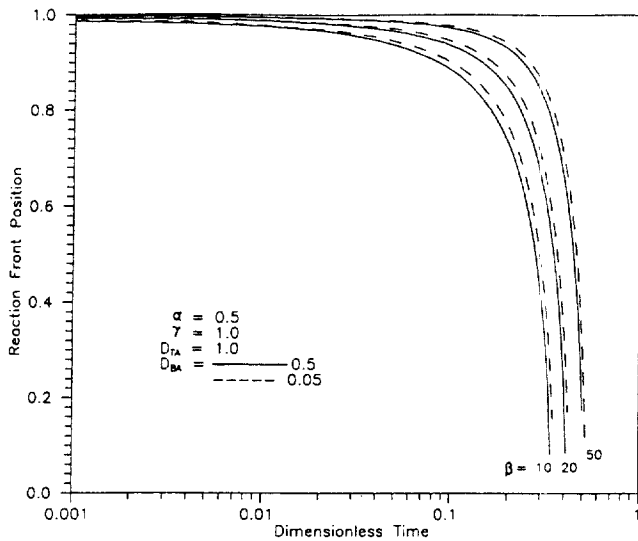


Fig. 3. Progress of reaction front (I).

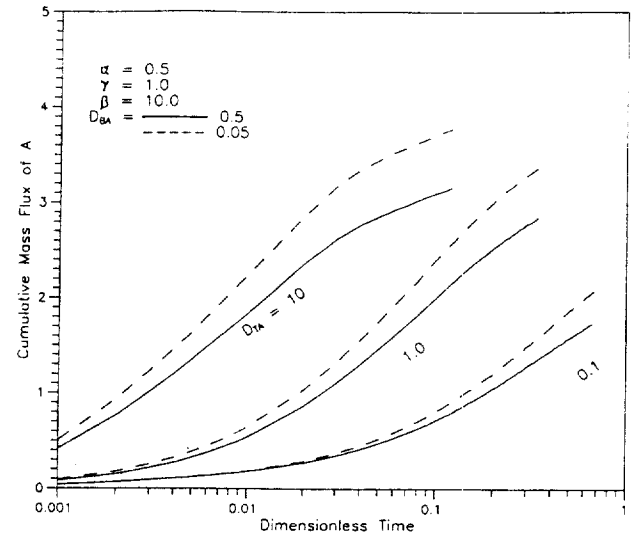


Fig. 6. Variation of cumulative mass flux of A (II).

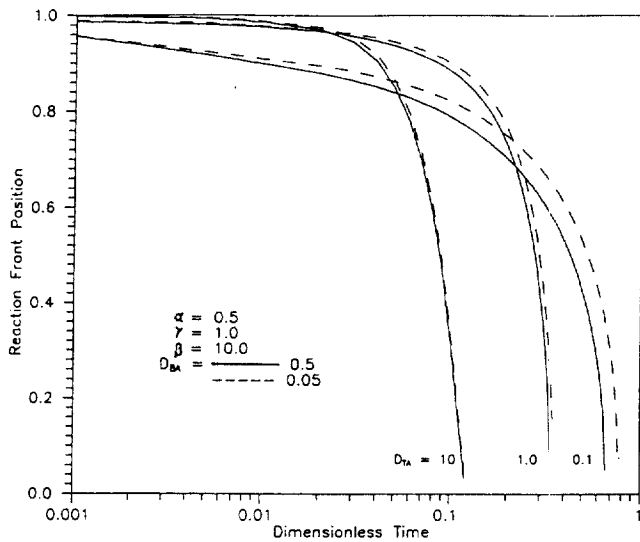


Fig. 4. Progress of reaction front (II).

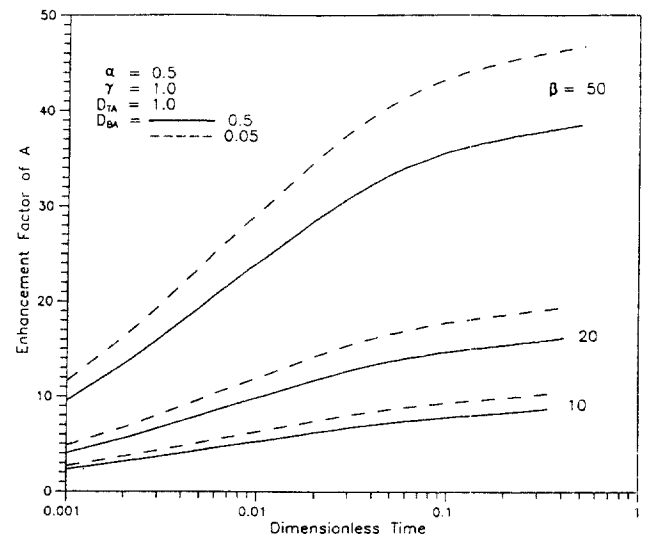


Fig. 7. Variation of enhancement factor of A (I).

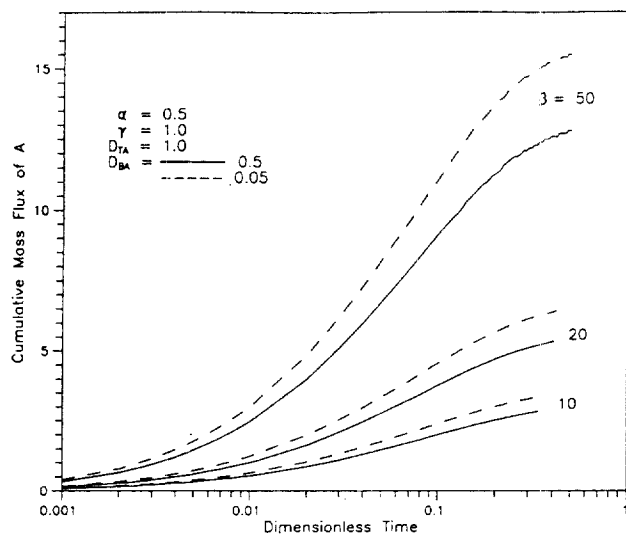


Fig. 5. Variation of cumulative mass flux of A (I).

by Eq. (11), with dimensionless time at constant α and D_{TA} . As expected, the larger β is and the slower B diffuses, the larger is the enhancement factor of A, if A and T move at the same diffusion rate. The effect of the slower moving B on the enhancement factor of A becomes obvious for larger time and β . All curves appear to reach their own asymptotic values as time proceeds.

The effect of the diffusivity ratio, D_{TA} , on the enhancement factor of A at constant β is shown in Fig. 8. The faster diffusing T compared to A results in the bigger enhancement factor of A at early stage. However, it becomes smaller after it reaches the maximum and approaches the final limiting value at final stage. This trend can be understood based on general considerations; A diffuses so fast at early stage due to the instantaneous reaction with the fast moving T and consequently most of T disappears during this period. Thereafter, there is only physical absorption because there is no more reaction in the drop. For slow moving T ($D_{TA}=0.1$), the curve remains constant for a while at early stage and gradually approaches the limiting value at final stage. The effect of the slower diffusing B compared to A becomes

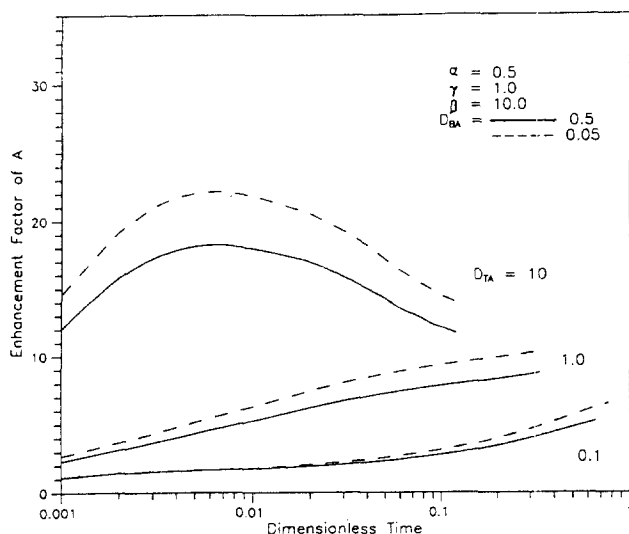


Fig. 8. Variation of enhancement factor of A (II).

obvious with larger value of D_{TA} . As expected, the final limiting value increases as B moves slow and is independent upon the diffusivity ratio of T to A. The effect of α is not discussed because it is likely to be replaced with the effect of D_{BA} , the diffusivity ratio of B to A.

CONCLUSIONS

Dilute multicomponent mass transfer with instantaneous chemical reactions in a small drop was modeled and simulated for the case of absorption of two solutes and their reactions with one component existing in the drop. After an appropriate coordinate transformation in order to fix the moving reaction front, the model was solved using the Galerkin's linear finite element method. The calculated results were presented in terms of the concentration profiles, the progress of the reaction front, the cumulative mass flux, and the enhancement factor with different system parameters. Parametric sensitivity studies showed the influences of the diffusivity ratios, the relative amount of the reactant in the drop, and the interfacial concentration of the diffusing solutes. The effects of those system parameters are in agreement with the general physical considerations; (1) the larger amount of the reactant in the drop causes the larger amount of solutes absorbed, and (2) the faster reactant in the drop moves, the faster solutes are absorbed from the surrounding fluid-approaching the final asymptotic value which is independent on the diffusion rates of solutes and the reactant.

NOMENCLATURE

A, B, T : solutes and reactant

C_i : concentration of i
 \bar{C}_i : dimensionless concentration of i
 C_i^* : transformed concentrations of i
 C_{ji} : concentration of j at drop surface
 C_{T0} : initial concentration of T in a drop
 D_{ij} : diffusivity ratio, D_i/D_j
 E_i : enhancement factor of i
 Q_i : cumulative mass flux of i

Greek Letters

α_j : C_{ji}/C_{Ai}
 β : $C_{T0}/\gamma_{TA} C_A$
 γ_i : ratio of stoichiometric coefficients of T to i
 γ_{ij} : ratio of stoichiometric coefficients, γ_{Ti}/γ_{Tj}
 ρ : dimensionless radial position, r/R
 τ : dimensionless time, tD_A/R^2
 ϕ : dimensionless position of reaction front, x/R
 ω_I, ω_{II} : transformed coordinate variables.

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