Facilitated Diffusion of Carbon-Dioxide in a Living Body Liquid Film

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SYNOPSIS

A numerical study is performed for the facilitated diffusion of carbon-dioxide in an ultrapure water film flowing downward along a vertical surface. The model adopted for the present work includes the effects of the reaction rate for the hydration of CO_2 in a liquid. Comparison of the total concentration of CO_2 for different film thickness indicates that the effects of the hydration is more remarkable for the thinner liquid film.

1 INTRODUCTION

Transport of carbon-dioxide in liquids has received considerable attention in connection with the biological and industrial systems. The transport of CO_2 through solutions is augmented by the hydration of CO_2. The hydrated CO_2, in the form of bicarbonate ion, diffuses with CO_2 dissolved physically in the liquid. Previous results for the behavior of CO_2 in liquids have shown that the dissociation of CO_2 is far from chemical equilibrium, and the kinetics of the reactions have been revealed [1~3]. However, little study can be observed for the hydration of CO_2 in a flowing liquid film. The present work was undertaken to provide a model for predicting the behavior of CO_2 absorbed in a living body liquid film.

2 FORMULATION AND NUMERICAL METHOD

The problem is formulated in corresponding to the coordinate system shown in Fig. 1. A gravity-controlled liquid film with thickness δ flows downward along a vertical surface. In Fig.1, x and y show the coordinates parallel and normal to the

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surface at y = 0, respectively. Ultrapure water is
adopted as a solvent. To simplify the treatment the
following assumptions are made:

   (a) Rate of CO_2 absorbed by the film is substantially
small compared to the film flow rate so that the film
thickness is unchanged along x-direction.

   (b) The film thickness is so small compared to the
plate length that the relation $\partial/\partial y \gg \partial/\partial x$ holds.

   (c) Velocity profile in the film is written as

$$u = \frac{g\delta^2(\eta - \eta^2)}{2\nu} \qquad (1)$$

where u is the liquid velocity in x-direction, g the
gravitational acceleration, ν the kinematic viscosity
and $\eta = y/\delta$. The profile given by equation (1) was
derived from the gravity-controlled film flow model with
negligible shear-force at the liquid-gas interface.

   (d) Undissociated carbonic-acid contributes
negligibly to both the total CO_2 in the film and the
transport of gas [1].

Fig.1 Physical model
and coordinate system

   (e) Concentration of metal ions in the film can be neglected in comparison with
that of hydrogen ion. This assumption is possible for the wall surface polished
using the electrolytic-abrasive combined method.

   Diffusion process is characterized by the gradient of the electrochemical
potential. The potential of species j, μ_j, is defined as

$$\mu_j = \mu_j^0 + RT\ln[c_j] + z_j F\phi \qquad (2)$$

where μ_j^0 is the standard electrochemical potential, R the universal gas constant, T
the absolute temperature, $[c_j]$ the concentration, z_j the charge number, F the
Faraday constant and ϕ the electrical potential. The diffusion flux in y-direction,
N_j, is obtained from

$$N_j = -(D_j/RT)[c_j](d\mu_j/dy) \qquad (3)$$

where D_j is the diffusion or ionic self-diffusion coefficient of species j in a
liquid.

   In order to evaluate the rate expression showing the depletion of CO_2 by
dissociation reaction, the equilibrium and kinetic properties of the carbon dioxide-
bicarbonate system must be examined. Several reactions taking place in the system
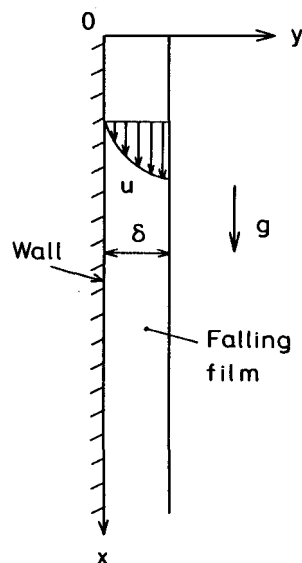have been observed, in which the next two steps for the present problem are rate
limiting [2].

$$CO_2 + H_2O \overset{k_1}{\underset{k_1^*}{\rightleftarrows}} H_2CO_3 \tag{4}$$

and

$$CO_2 + OH^- \overset{k_2}{\underset{k_2^*}{\rightleftarrows}} HCO_3^- \tag{5}$$

where $k_{1,2}$ and $k_{1,2}^*$ denote the forward and reverse rate constants for the above reactions, respectively. In comparison to these reactions, the dissociation of water and also the second dissociation of carbonic-acid are sufficiently rapid so that the dissociation equilibria can be assumed as

$$K_w = [H^+][OH^-] \tag{6}$$

and

$$K_{H2CO3} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} \tag{7}$$

where K_w and K_{H2CO3} denote the equilibrium constants for water and carbonic-acid, respectively.

On the basis of the rate law of the reactions given by equations (4) and (5) and also the dissociation equilibria by equations (6) and (7), the conservation of CO_2 dissolved physically in the film can be written as

$$u\frac{\partial[CO_2]}{\partial x} = D_{CO2}\frac{\partial^2[CO_2]}{\partial y^2} - \left\{(k_1 + k_2[OH^-])[CO_2] - (k_1^*\frac{[H^+]}{K_{H2CO3}} + k_2^*)[HCO3^-]\right\} \tag{8}$$

Neglecting the effects of H_2CO_3, a total carbon balance in the film gives

$$u\frac{\partial([CO_2] + [HCO_3^-])}{\partial x} = D_{CO2}\frac{\partial^2[CO_2]}{\partial y^2} + D_{HCO3-}\frac{\partial}{\partial y}\left\{\frac{\partial[HCO_3^-]}{\partial y} - [HCO_3^-]\frac{F}{RT}\left(\frac{d\phi}{dy}\right)\right\} \tag{9}$$

Electrical neutrality requires the following conditions:

$$N_{H+} = N_{HCO3-} + N_{OH-} \tag{10}$$

and

$$[H^+] = [HCO_3^-] + [OH^-] \tag{11}$$

Combining equations (6) and (11) yields

$$[H^+] = \{[HCO_3^-] + \sqrt{[HCO_3^-]^2 + 4K_w}\}/2 \tag{12}$$

and

$$[OH^-] = 2K_w/\{[HCO_3^-] + \sqrt{[HCO_3^-]^2 + 4K_w}\} \tag{13}$$

When the flux of each ionic species is formulated in terms of equation (3) and substituted into equation (10) then introducing equation (11), we get
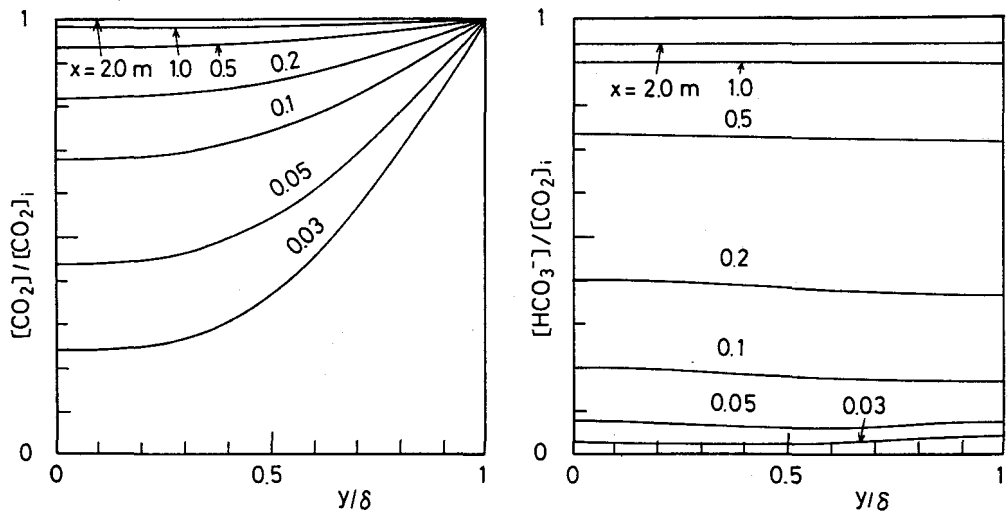
Fig.2 Variations of $[CO_2]$ and $[HCO_3^-]$ with y, $\delta = 0.1$ mm

$$\frac{d\phi}{dy} = \frac{RT}{F} \frac{(\mathcal{D}_{HCO3-} - \mathcal{D}_{OH-}) \partial[HCO_3^-]/\partial y + (\mathcal{D}_{OH-} - \mathcal{D}_{H+}) \partial[H^+]/\partial y}{(\mathcal{D}_{HCO3-} - \mathcal{D}_{OH-})[HCO_3^-] + (\mathcal{D}_{OH-} + \mathcal{D}_{H+})[H^+]} \tag{14}$$

Equations (8) and (9) were solved to provide the concentration distributions of CO_2 and HCO_3^-. Initial and boundary conditions are

$$[CO_2] = 0, \qquad [HCO_3^-] = 0 \qquad\qquad \text{at } x = 0 \qquad\qquad (15a,b)$$

$$N_{CO2} = 0, \qquad N_{HCO3-} = 0 \qquad\qquad \text{at } y = 0 \qquad\qquad (16a,b)$$

$$[CO_2] = [CO_2]_i, \quad N_{HCO3-} = 0 \qquad\qquad \text{at } y = \delta \qquad\qquad (17a,b)$$

Solutions of equations (8) and (9) subject to the initial and boundary conditions (15) $\sim$ (17) were obtained numerically. A finite difference scheme marching in x-direction were employed to solve them simultaneously and iteratively at each x-step.

3 RESULTS AND DISCUSSION

Numerical calculations were conducted under the conditions of $[CO_2]_i = 10^{-8}$ M and T = 353.15 K for $\delta = 0.1$ and 0.2 mm. Figures 2 and 3 show the variations of $[CO_2]$ and $[HCO_3^-]$ with y at various x-locations for $\delta = 0.1$ mm and 0.2 mm, respectively. A rapid penetration of CO_2 into the film can be observed with increasing x, whereas the production of HCO_3^- proceeds gradually. In both cases, the $[HCO_3^-]$ value near the liquid-gas interface is larger than that near the wall surface at smaller x, whereas the $[HCO_3^-]$ is seen to be almost unchanged along y at larger x. This indicates that the production rate of HCO_3^- in the film is
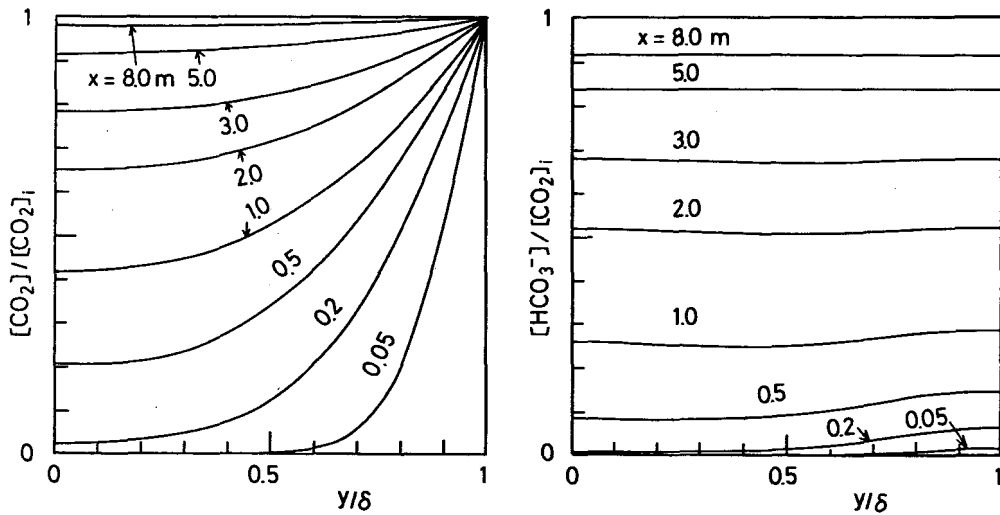
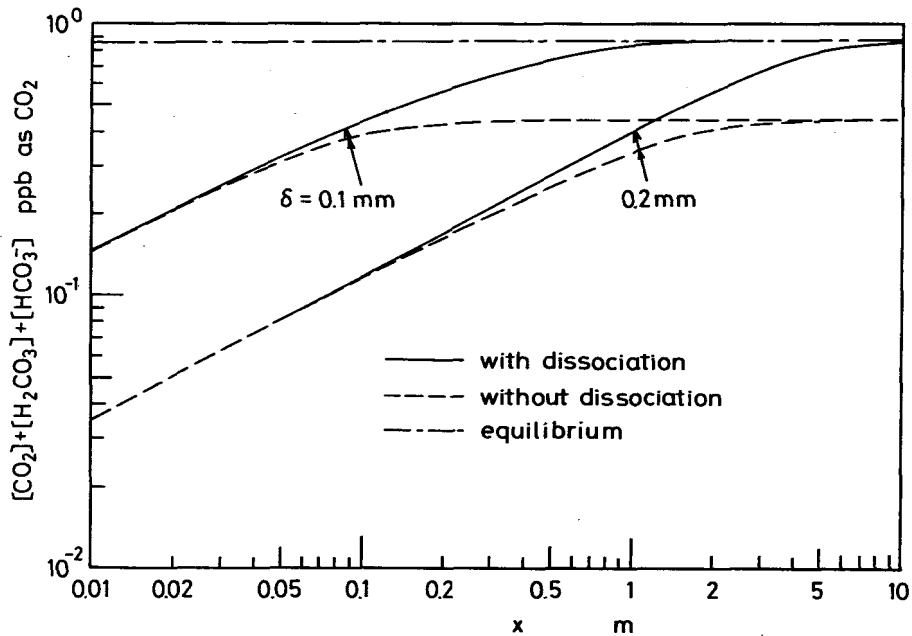Fig.3 Variations of $[CO_2]$ and $[HCO_3^-]$ with y, $\delta = 0.2$ mm

Fig.4 Variation of $[CO_2]+[H_2CO_3]+[HCO_3^-]$ with x

controlled by the fluid velocity along with the values of $[CO_2]$, $[HCO_3^-]$ and $[OH^-]$, and the rate constants of the reactions.

Figure 4 presents the axial variations of the total $[CO_2]$ in the film, $[CO_2]+[H_2CO_3]+[HCO_3^-]$, for $\delta = 0.1$ and 0.2 mm. The results obtained on the basis of the model without dissociation are also shown for comparison. The $[CO_2]+[H_2CO_3]+[HCO_3^-]$

value increases monotonically with x, then reaches gradually the prediction obtained from an equilibrium analysis. Comparison of the results with and without dissociation indicates that the effects of the facilitated diffusion is more remarkable for the thinner film at larger x. This is in accord with the results shown in Figs.2 and 3.

   The present model can be extended to a biological system with slow chemical reactions. Also, it can be adopted to study the facilitated diffusion of carbon-dioxide in a condensate film by taking the effects of the variation of film thickness into consideration.

REFERENCES

[1] Meldon,J.H., Chem. Engng. Commun., 16, (1982), pp.263-300.

[2] Kern,D.M., J. Chem. Education, 37, (1960), pp.14-23.

[3] Otto,N.C., and Quinn,J.A., Chem. Engng. Sci., 26, (1971), pp.949-961.