Onset of Solutal Marangoni Convection in a Suddenly Desorbing Liquid Layer

Kyoung H. Kang and Chang K. Choi
School of Chemical Engineering, Seoul National University, Seoul 151-742, Korea

In G. Hwang
Dept. of Chemical Engineering, The University of Suwon, Kyungki-Do 445-743, Korea

The onset of surface-tension-driven convection in an initially quiescent liquid layer experiencing sudden desorption from a free surface is analyzed using the linear stability theory. The propagation theory was developed for the basic time-dependent concentration profile, which is strongly nonlinear. Based on this theory, a new set of stability equations is derived in considering the effect of Gibbs adsorption and by neglecting the surface diffusion. It is found that the liquid layer becomes more stable by decreasing the Schmidt and Biot numbers. It is interesting that, during an initial period, the system is stable, depending on the Gibbs effect. The predictions agree favorably with the existing experimental results of triethylamine desorption in water in a wetted-wall and a liquid-jet column.

Introduction

Marangoni convection is often encountered in mass-transfer systems such as gas adsorption, solvent extraction, painting, drying and coating, and also in normal heat-transfer systems with a free surface experiencing surface-tension variations. It plays an important role even in an absorption heat pump involving both heat and mass transfer. Marangoni convection can enhance the mass-transfer rate, but incurs nonuniformities in product quality. Therefore, it becomes an important question to predict the critical conditions to mark the onset of Marangoni convection.

The convective instability problem in an initially quiescent, horizontal liquid layer heated under the constant surface-tension gradient was analyzed theoretically by Pearson (1958) and Scriven and Sternling (1964). Their work was extended to mass-transfer systems involving Gibbs adsorption (Brian, 1971). In their systems the basic conduction or concentration profile is time-independent and linear at a fully developed state and, therefore, the critical Marangoni number Ma_c, used to mark the onset of convection, becomes the most important problem to be known. The related solutions are well known. However, in many of practical systems, the Marangoni number Ma is large, that is, $Ma \gg Ma_c$ and the most important parameter becomes the critical time t_c to mark the onset of natural convection. This time-dependent instability problem, which is similar to those of infinite depth, remains unsolved. A kind of frozen-time model has been used for analyses in the system of pure liquid (Vidal and Acrivos, 1968), desorption (Brian and Ross, 1972), chemical reaction (Mendel-Tatsis and Perez de Ortiz, 1996), and absorption (Daiguji et al., 1997; Tan and Thorpe, 1999). In this model the unperturbed temperature or concentration profile is approximated by two linear segments and the initiated disturbances are analyzed like Currie's (1967) procedure under linear theory. For this purpose, the length scale representing the film or penetration theory at each instant is fixed and the disturbances are treated as time-independent ones. Another approach is the propagation theory that we have developed. In this model the time dependency of disturbances is assumed to keep the property of the unperturbed state. This means that, at the critical state of the onset of convection, the basic property of heat conduction or mass diffusion is still dominant due to infinitesimal magnitude of the disturbances. Also, the proper length scale is the conventional thermal or solutal penetration depth. This model has predicted the stability criteria reasonably well in connection with thermal convection (Hwang and Choi, 1996; Kang and Choi, 1997; Choi et al., 1998; Kim et al., 1999).

Correspondence concerning this article should be addressed to C. K. Choi.

In this article the problem of Brian and Ross (1972) is analyzed more rigorously under linear stability theory by using the propagation theory. They considered the Gibbs adsorption effect in a suddenly desorbing liquid layer and the related stability analysis was conducted by using the frozen-time model. They conducted experiments of triethylamine desorption from water in a wetted-wall column and showed the stabilizing effects of Gibbs adsorption. Also, Imaishi et al. (1982) conducted desorption experiments in a liquid-jet and a wetted-wall column. Their entry regions are analogous to an initially quiescent, horizontal liquid layer of infinite depth with an upper free boundary desorbed. In their analyses they defined the Marangoni number, the Biot number, and the adsorption number by using the time-dependent length scale. This means that these parameters involve the critical time implicitly, and the critical conditions are independent of the Schmidt number. Here, the above thin liquid film is analyzed based on the propagation theory involving the effect of the Schmidt number, and the resulting predictions are compared with their experimental and theoretical results. The present study concerns so-called Gibbs depth and, therefore, the relative depth, that is, the ratio of the Gibbs depth to the whole liquid-layer depth is newly introduced as the important parameter. With this relative depth, the limiting case of $Ma \to \infty$ is analyzed. If the Gibbs adsorption effect is neglected, the predicted critical conditions are the same as Kang and Choi's (1997) heat-transfer system when replacing their Prandtl number with the Schmidt number. In this article the critical time is shown explicitly for a given experimental condition of the fixed dimensionless parameters. The peculiar effect of the Gibbs depth will be illustrated more clearly, which is not exhibited in usual heat-transfer systems.

System Description

Governing equations

A horizontal thin liquid layer considered here is bounded by a free surface at $Z = 0$ and a rigid plane at $Z = d$, as shown in Figure 1. Z denotes the vertical distance and d is the whole liquid-layer depth. At time $t = 0$ a solute component begins to be desorbed suddenly from the lower liquid layer into the upper gas phase. The solute lowers the surface tension of the liquid and this can incur Marangoni convection. The bulk liquid is an initially stagnant, dilute solution at a uniform solute concentration C_B, and the solute concentration in the gas phase far from the interface is kept constant at C_G. The liquid-phase solubility in equilibrium with C_G is denoted by C_G^*. Both buoyant and thermal effects caused by desorption are assumed to be negligible. Now, the governing equations for surface-tension-driven convection are given as usual

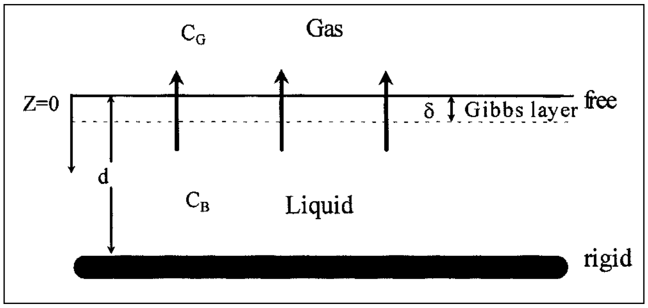

Figure 1. Present desorption system.

$$\nabla \cdot U = 0, \tag{1}$$

$$\rho\left(\frac{\partial}{\partial t} + U \cdot \nabla\right)U = -\nabla P + \mu \nabla^2 U, \tag{2}$$

$$\left(\frac{\partial}{\partial t} + U \cdot \nabla\right)C = D_B \nabla^2 C, \tag{3}$$

$$S = S_B - \gamma(C - C_B), \tag{4}$$

where U, ρ, P, μ, C, D_B, S, and γ denote the velocity vector, the liquid density, the pressure, the liquid viscosity, the solute concentration, the usual mass diffusivity of the solute in the liquid phase, the surface tension, and the negative surface-tension gradient with respect to the solute concentration, respectively. The subscript B represents the quantity based on the bulk liquid. Since the present study is restricted to dilute solutions, it is assumed that ρ and μ are constant. Equation 4 means that the surface tension of solution depends linearly on the solute concentration. The instability leading to surface-tension-driven convection will set in at the critical time t_c, depending on the mass flux of the solute $(= Hk_G(C_S - C_G^*))$. Here H denotes Henry's law constant for the solute, k_G denotes the gas-phase mass-transfer coefficient, and C_S denotes the solute concentration at the gas-liquid interface.

According to the Gibbs adsorption isotherm (Brian, 1971; Adamson and Gast, 1997), it is assumed that there is, in dilute solutions, a linear adsorption approximation between the surface excess concentration Γ and the interfacial concentration C_S

$$\Gamma = \left(\frac{\gamma}{\mathrm{RT}}\right)C_s = \delta C_s, \tag{5}$$

where R denotes the gas-law constant, T is the absolute temperature, and δ is the "Gibbs depth" having the dimension of length. δ may be considered as the fictitious depth of bulk liquid which contains the same quantity of the solute as that adsorbed at the surface, and here it is assumed to be constant. If the surface tension decreases with increasing the solute concentration, Γ is positive, that is, the solute tends to concentrate near the interface. Such solutes are called surfactants.

Basic state

In the present system the basic concentration profile of mass diffusion can be represented by the following dimensionless equations with solute storage in the Gibbs adsorption layer

$$\frac{\partial \phi_0}{\partial \tau} = \frac{\partial^2 \phi_0}{\partial z^2}, \tag{6}$$

with the proper initial and boundary conditions (Brian and

Ross, 1972)

$$\phi_0 = 1 \qquad \text{at} \quad \tau = 0, \tag{7}$$

$$\frac{\partial \phi_0}{\partial z} = Bi\phi_0 + G\frac{\partial \phi_{0S}}{\partial \tau} \qquad \text{at} \quad z = 0, \tag{8}$$

$$\frac{\partial \phi_0}{\partial z} = 0 \qquad \text{at} \quad z = 1, \tag{9}$$

where z, τ, and ϕ_0 denote the dimensionless vertical distance, the dimensionless time, and the dimensionless basic concentration of the solute, respectively. x and y denote the dimensionless horizontal coordinates. The subscript 0 denotes the basic quantity and ϕ_{0S} denotes the dimensionless basic concentration at the interface. Length has been nondimensionalized by the liquid depth d, the time by d^2/D_B, and the basic concentration excess $(C_0 - C_G^*)$ by $(C_B - C_G^*)$. The first term on the lefthand side of Eq. 8 represents the diffusion of the solute from the bulk liquid to the gas-liquid interface. The first term on the righthand side represents the transfer from the gas-liquid interface to the bulk gas containing the solute at the partial pressure corresponding to the liquid-phase concentration C_B. The last term in Eq. 8 represents the effect of Gibbs adsorption, which represents the solute accumulation at the interface. The surface diffusion in the adsorbed layer is neglected (Bragard et al., 1994). In the case of neglecting the effect of Gibbs adsorption, the term including G is dropped out and the problem reduces to that of Kang and Choi (1997). The dimensionless parameters Bi and G are defined by

$$\text{Biot number} \qquad Bi = \frac{Hk_G d}{D_B}, \tag{10}$$

$$\text{relative depth} \qquad G = \frac{\delta}{d}. \tag{11}$$

The Biot number Bi represents the ratio of the liquid-phase mass-transfer resistance to the gas-phase one. The dimensionless group G represents the relative depth of the Gibbs layer. Here Bi and G are assumed to be constant.

The solution of Eqs. 6–9 for small τ is known as

$$\phi_0 = \text{erf}\left(\frac{\zeta}{2}\right) - P\exp\left[\frac{J}{G^*}\zeta + \left(\frac{J}{G^*}\right)^2\right]\text{erfc}\left(\frac{\zeta}{2} + \frac{J}{G^*}\right) + Q\exp\left[\frac{F}{G^*}\zeta + \left(\frac{F}{G^*}\right)^2\right]\text{erfc}\left(\frac{\zeta}{2} + \frac{F}{G^*}\right), \tag{12}$$

where $\zeta = z/\sqrt{\tau}$ and $G^* = G/\sqrt{\tau}$ (Brian and Ross, 1972). The parameters in this equation are defined as follows

$$P = \frac{L_m/J + Y_s{}^0 J}{J - F}, \qquad Q = \frac{L_m/F + Y_s{}^0 F}{J - F},$$

$$Y_s{}^0 = \frac{C_B - \Gamma^0/\delta}{C_B - C_G^*}, \qquad L_m = \frac{Hk_G\delta}{D_L} = BiG,$$

$$J = \frac{1 - \sqrt{1 - 4L_m}}{2}, \qquad F = \frac{1 + \sqrt{1 - 4L_m}}{2}, \tag{13}$$

where Γ^0 represents the surface excess concentration in the Gibbs adsorption layer at the beginning of desorption, that is, $t = 0$. Here the case of $\Gamma^0 = 0$ corresponds to an absence of excess solute in the Gibbs layer, while that of $\Gamma^0 = \delta C_B$ corresponds to the Gibbs layer being in equilibrium with the bulk concentration C_B. It is noted that P, Q, J, and F are functions of L_m $(= BiG)$. Here C_G^* is assumed to be negligible.

Over a certain desorbing rate exceeding the critical value, surface-tension-driven convection will set in. The related important dimensionless parameters are identified as

$$\text{Marangoni number} \qquad Ma = \frac{\gamma(C_B - C_G^*)d}{\mu D_B}, \tag{14}$$

$$\text{Schmidt number} \qquad Sc = \frac{\nu}{D_B}, \tag{15}$$

$$\text{Adsorption number} \qquad A = \frac{\Gamma_0}{(C_B - C_G^*)d} = G\phi_{0S}, \tag{16}$$

where ν denotes the kinematic viscosity and the constant Γ_0 represents the surface excess concentration in the Gibbs adsorption layer in the unperturbed state. The adsorption number A has been considered as an important parameter showing the effect of the Gibbs layer (Brian and Ross, 1972; Imaishi et al., 1983). In the present system the adsorption number A is dependent on both the relative depth G and the dimensionless concentration at the interface ϕ_{0S}. Since ϕ_{0S} varies with time, G is used instead of A.

Linear Stability Theory

Under linear theory, the dimensionless disturbance quantities u_1^* and ϕ_1^* are assumed to have the form of

$$(u_1^*, \phi_1^*) = (u_1, \phi_1)\exp\left[i(a_x x + a_y y)\right], \tag{17}$$

which means that instabilities are periodic in the horizontal direction. u_1, ϕ_1, i, a_x, and a_y denote the velocity amplitude, the concentration amplitude, the imaginary number, the wave number in the x-direction, and the wave number in the y-direction, respectively. u_1 and ϕ_1 are functions of τ and z. The perturbed velocity has the scale of α/d and the perturbed concentration has that of $\Delta C/(a^2 Ma)$ with $\Delta C = C_B - C_G^*$ by using Ma defined by Eq. 14. Then, the dimensionless perturbed equations are obtained from Eqs. 1–4 and 17

$$\left[\frac{1}{Sc}\frac{\partial}{\partial \tau} - \left(\frac{\partial^2}{\partial z^2} - a^2\right)\right]\left(\frac{\partial^2}{\partial z^2} - a^2\right)w_1 = 0, \tag{18}$$

$$\frac{\partial \phi_1}{\partial \tau} + Ma\,a^2 w_1\frac{\partial \phi_0}{\partial z} = \left(\frac{\partial^2}{\partial z^2} - a^2\right)\phi_1, \tag{19}$$

where w_1 is the vertical velocity amplitude and a $(= (a_x^2 + a_y^2)^{1/2})$ is the horizontal wave number. When neglecting the surface diffusion, the proper boundary conditions, subjected to Eqs. 18 and 19, are given by

$$w_1 = \frac{\partial^2 w_1}{\partial z^2} - \phi_1 = 0 \qquad \text{at} \quad z = 0, \tag{20}$$

$$\frac{\partial \phi_1}{\partial z} - Bi\phi_1 - G\frac{\partial \phi_1}{\partial \tau} + G\phi_{0S}a^2 Ma\frac{\partial w_1}{\partial z} = 0 \qquad \text{at} \quad z = 0, \tag{21}$$

$$w_1 = \frac{\partial w_1}{\partial z} = \frac{\partial \phi_1}{\partial z} = 0 \qquad \text{at} \quad z = 1. \tag{22}$$

Equation 20 means that the upper free surface is flat and that the shear stress is balanced by surface tension effects. The terms involving G in Eq. 21 are related with Gibbs adsorption, and Eq. 22 represents the conditions of no-slip and no mass flux at the bottom boundary. With $G = Bi = 0$, Marangoni convection will set in at the critical Marangoni number $Ma_c = 48$ (Pearson, 1958) and with an increase in G and Bi, Ma_c increases. In this insulating case the system is stable for $A\ (= G\phi_{0S}) \geq 0.083$ (Brian, 1971). It is noted that if there is no concentration variation on the free surface, surface-tension-driven convection will not set in.

Now, consider the case of $Ma \gg Ma_c$. In this case the problem is to find the critical time τ_c to mark the onset of convective motion in the form of regular cells for a given Ma, Sc, Bi, and G. To solve Eqs. 18 and 19 subject to the boundary conditions (Eqs. 20–22), information on the initial conditions is required. Both the amplification theory (Foster, 1969) and the stochastic model (Jhaveri and Homsy, 1982) assume some initial conditions at $\tau = 0$ and require definition of the characteristic time to exhibit manifest convection. However, the frozen-time model and the propagation theory illustrated below follow the principle of the exchange of stabilities and τ_c is determined under the normal model analysis.

Frozen-time model

In the frozen-time model it is assumed that the disturbances represented by $w_1(\tau, z)$ and $\phi_1(\tau, z)$ grow exponentially with time, for example, $w_1 \propto \exp(\sigma\tau)$. Therefore, with $\sigma = 0$, the critical conditions are characterized by the minimum value of τ, that is, τ_c and its corresponding wave number a_c. In this case $\partial w_1/\partial\tau$ and $\partial\phi_1/\partial\tau$ in Eqs. 18, 19 and 21 disappear and, therefore, the system becomes independent of Sc.

Even though the terms involving $\partial(\cdot)/\partial\tau$ are removed, the resulting disturbance equations would not be solved analytically. Therefore, Brian and Ross (1972) approximated the basic concentration profiles by two linear segments, similar to the work of Currie (1967). In their model the characteristic length h is given by

$$h = \frac{2}{(C_B - C_S)}\int_0^d (C_B - C_0)\,dz \tag{23}$$

and based on h, the Maragoni number Ma_h and the adsorption number A_h are defined as

$$Ma_h = \frac{\gamma(C_B - C_S)h}{\mu D_B},\ A_h = \frac{\Gamma^0}{(C_B - C_S)h},\ Bi_h = \frac{Hk_G h}{D_B}, \tag{24}$$

and, therefore, the above parameters result in

$$Ma_h = Ma(1 - \phi_{0S})\frac{h}{d},\ A_h = G\frac{\phi_{0S}}{(1 - \phi_{0S})}\frac{h}{d},\ Bi_h = Bi\frac{h}{d} \tag{25}$$

(see Eqs. 10, 11, 14 and 16). Ma_h, A_h and Bi_h having the length scale h are rather complicated in comparison with the present parameters Ma, G, and Bi. Now, the basic concentration profile (Eq. 12) is replaced by $\phi_0 = 1 - zd/h$ for $0 \leq z \leq h/d$ and $\phi_0 = 0$ for $h/d \leq z \leq 1$. Based on these two linear concentration profiles, Brian and Ross conducted the stability analysis and showed that for $A_h \geq 0.5$ the system would be stable due to Gibbs adsorption.

Propagation theory

The propagation theory employed here is based on the assumption that the disturbances at the onset of the convective motion are propagated mainly to the solutal penetration depth of diffusion. Therefore, this depth is a proper length-scaling factor. For small τ, the basic concentration field is nonlinear and the similarity variable $\zeta = z/\tau^{1/2}$ is introduced to take into account the positional and temporal dependencies of disturbances. For large Ma, incipient surface-tension-driven convection will occupy only part near the upper free surface and, therefore, the critical time τ_c to mark the incipient instability of a most dangerous mode for a given physical condition would be independent of the whole layer thickness d. It is assumed that for a large Ma, the dimensionless disturbance amplitudes have the following relation near $\tau = \tau_c$

$$[w_1(\tau, z), \phi_1(\tau, z)] = [\tau w^*(\zeta), \phi^*(\zeta)], \tag{26}$$

of which validity will be discussed later. The above relationships mean that $w_1/\phi_1 = O(\delta_c^2)$. δ_c denotes the dimensionless solutal penetration depth, which is approximately proportional to $\tau^{1/2}$ in the present system of small τ. The above transformation is verified to a certain degree from the scale analysis (Hwang and Choi, 1996; Kang and Choi, 1997). With the above relation, it is known that $\partial(\tau w^*)/\partial\tau$, that is, $\partial w_1/\partial\tau$ is a function of ζ only. Since $\partial/\partial\tau = -(\zeta/2\tau)(\partial/\partial\zeta)$ and $\partial^2/\partial z^2 = (1/\tau)(\partial^2/\partial\zeta^2)$ with ϕ^* and w^* and $\partial\phi_1/\partial\tau = 0$ at $z = 0$ in Eq. 21, the following stability equations are produced from Eqs. 18–22

$$\left[(D^2 - a^{*2})^2 + \frac{1}{2Sc}(\zeta D^3 - a^{*2}\zeta D + 2a^{*2})\right]w^* = 0, \tag{27}$$

$$\left[D^2 + \frac{1}{2}\zeta D - a^{*2}\right]\phi^* - Ma^* a^{*2} w^* D\phi_0 = 0, \tag{28}$$

with the boundary conditions

$$w^* = D^2 w^* - \phi^* = 0 \qquad \text{at} \quad \zeta = 0, \tag{29}$$

$$D\phi^* - Bi^*\phi^* + G^*\phi_{0S}Ma^* a^{*2} Dw^* = 0 \qquad \text{at} \quad \zeta = 0, \tag{30}$$

$$w^* = Dw^* = D\phi^* = 0 \qquad \text{for} \quad \zeta \to \infty, \tag{31}$$

where $D = d/d\zeta$, $a^* = \tau^{1/2}a$, $Ma^* = \tau^{1/2}Ma$, $Bi^* = \tau^{1/2}Bi$, and $G^* = \tau^{-1/2}G$. All these dimensionless groups having the superscript* are assumed to be eigenvalues through τ. ϕ_{0S} is a function of G^* and Bi^* since $GBi = G^*Bi^*$. Because the system of small τ is concerned, the lower boundary of $z = 1$ in Eq. 22 has been replaced with $\zeta \to \infty$ in Eq. 31. For a given Sc, Ma, Bi, and G the minimum τ-value, that is, τ_c and its corresponding wave number a_c should be found. This procedure is equivalent to that for finding the minimum Ma for a given τ_c, Sc, Bi, and G. The resulting instability mode is assumed to represent a most dangerous one.

At the critical time t_c, the following relation on the concentration disturbance C_1 is possible

$$\frac{\partial C_1}{\partial t} \sim - D_B \frac{C_1}{\Delta_C^2} \qquad (32)$$

if the diffusive processes are still dominant. Δ_C represents the solutal penetration depth $(\propto (D_B t)^{1/2})$ and Δ_C^2 implies the surface area of whatever solution element is concerned. It is noted that $\pi d/a_c \sim \Delta_C$ at $t = t_c$ since the wavelength is equal to $2\pi d/a$. The above relation means that the incipient, positive concentration disturbance will decrease with time for $\gamma > 0$. This decrease will bring an increase in surface tension and enhance convective motion. Now, it is known that the dimensionless amplitude ϕ_1 of the incipient C_1-quantity at $t = t_c$ can be represented by Eq. 26, which shows the characteristics of Eq. 32. In the present system of small time, there are three length scales: $(D_B t)^{1/2}$, $\mu D_B/(\gamma \Delta C)$, and d. The ratio of the first to the second scale is Ma^*, which is independent of d like Bi^*, G^*, and ζ. Once Bi^* and G^* are given, ϕ_0, $D\phi_0$, and ϕ_{0S} are functions of ζ only. Therefore, Eqs. 27–31 can produce the stability criteria.

The propagation theory may be called the relaxed frozen-time model by letting $\partial(\cdot)/\partial\tau \neq 0$, but freezing τ in the time-scaled parameters. τ involves dual meaning of time and length. Because there exist the terms involving $\partial(\cdot)/\partial\tau$, the Sc-effect is exhibited in Eq. 27, similar to the work of Lick (1965), and for large Sc, the terms involving $1/Sc$ in Eq. 27 can be neglected. This is the case of an ordinary liquid system since its Sc-value is the order of 10^3. The related trend will be discussed later, based on the numerical results. Here, it is noted that this kind of treatment on time-dependent parameters has been successful both theoretically and experimentally in many of time-dependent, thermal instability analyses (Goldstein and Volino, 1995; Hwang and Choi, 1996; Kang and Choi, 1997; Tan and Thorpe, 1999). This whole procedure is the essence of the propagation theory that we have developed.

Solution procedure

For small τ, the basic concentration profiles are strongly nonlinear and it may be assumed that the outer boundary is infinity. Therefore, the shooting method (Press et al., 1992) is applied to the present problem. Since the governing equations and the boundary conditions are all homogeneous, the value of Dw^* at $\zeta = 0$ can be assigned arbitrarily (Chen, 1981). For a specified τ, Sc, Ma, G and Bi, two initial guesses on D^3w^* and ϕ^* at $\zeta = 0$ are given and a is determined. A is obtained from Eqs. 12 and 16. As a result, this problem is completely converted to an initial value problem. The method employed to integrate the disturbance Eqs. 27–31 is the fifth-order Runge-Kutta method with monitoring of the local truncation error to ensure the accuracy and adjust the step size. The Newton-Raphson iteration modifies the guessed values at $\zeta = 0$ until the integration results agree with the outer boundary conditions within the error tolerance of 10^{-7}.

Results and Discussion

In the present study the parameters controlling the behavior of surface-tension-driven convection (Marangoni convection) in the present mass-transfer system are Γ^0, Ma, Sc, Bi, and G. First, the case of $\Gamma^0 = 0$ is examined with the propagation theory. With fresh solution at $t = 0$, the surface-tension-decreasing solute of $\gamma > 0$, such as a surfactant, begins to experience desorption from the interface to the gas phase and also diffusion from the bulk liquid phase to the interface. At $t = t_c$, Marangoni convection will set in. The marginal stability curve to characterize the onset of convective motion in the form of regular cellular motion is obtained, as shown in Figure 2. It is assumed that in this figure the minimum τ-value τ_c and the corresponding a-value a_c constitute the critical conditions to mark a most dangerous disturbance. Numerical calculation of the base concentration profile shows that the time domain obtained with $Bi = 100$ is valid for $\tau < 0.05$. With decreasing Bi, the valid time domain increases.

Figure 3 shows that τ_c decreases with an increase in Sc for the other fixed parameters. It becomes almost independent of Sc for $Sc > 10$. For large Sc, the mass diffusivity is so small that the solutal penetration depth is also small and natural convection initiated due to the concentration gradient near the boundary is weak. Therefore, convective acceleration including the inertia effect is neglected, that is, $|Du/Dt| \ll \mu|\nabla^2 u|$. This relation is similar to the effect of Pr on the critical conditions of analogous heat-transfer systems (Choi et al., 1998). From this figure, it is known that τ_c decreases

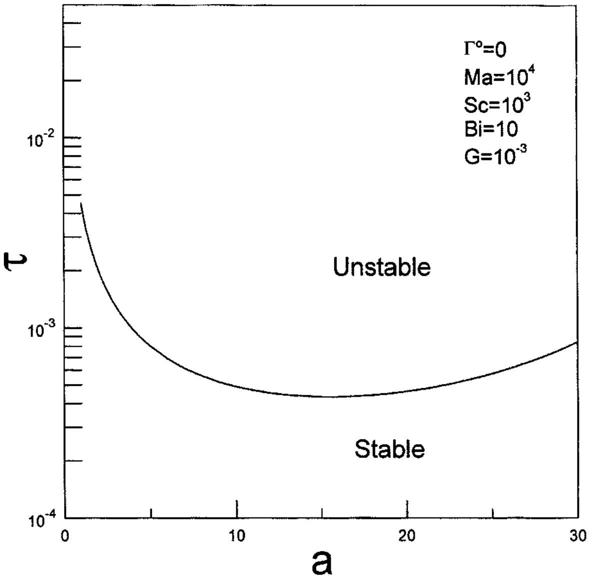

Figure 2. Marginal stability curve for $\Gamma^0 = 0$, $Ma = 10^4$, $Sc = 10^3$, $Bi = 10$, and $G = 10^{-3}$.

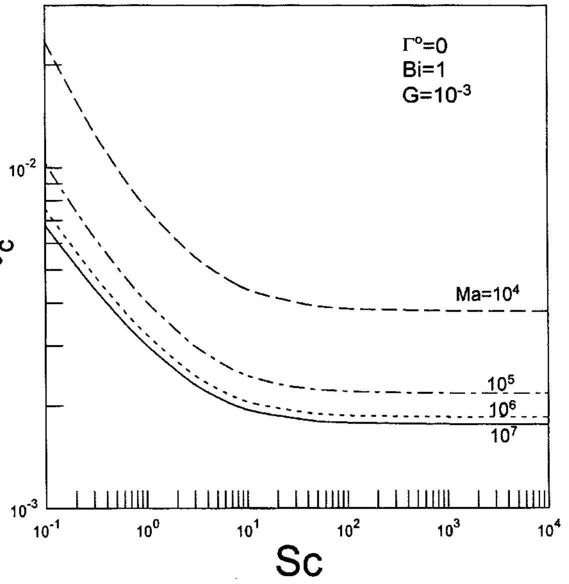

Figure 3. Effect of Schmidt number *Sc* on critical conditions for various Marangoni numbers *Ma*.

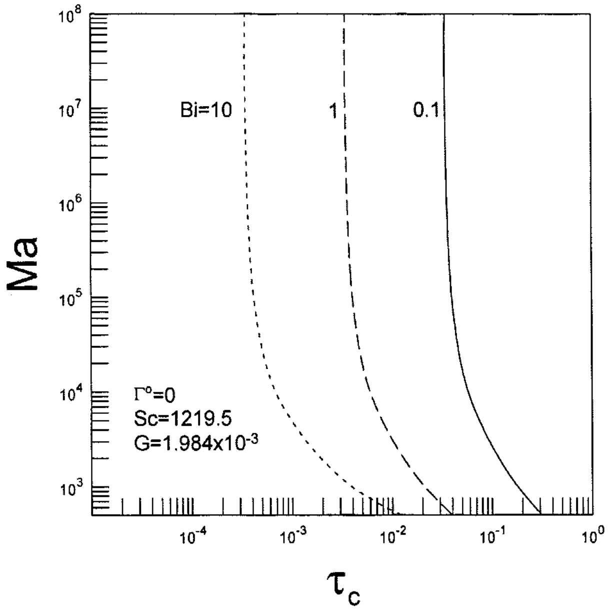

Figure 5. Effect of Marangoni number *Ma* on critical time τ_c for various Biot numbers *Bi*.

with increasing *Ma*, as expected. However, Figure 4 shows that, for $Ma > 10^6$, the critical time τ_c is almost constant. This means that Marangoni convection is insignificant during a certain initial period for a given *Sc*, *Bi*, and *G*, bringing some delay time even though $Ma \gg Ma_c$.

While increasing the Biot number *Bi*, the mass-transfer rate from the free interface to the ambient gas phase increases and the concentration profile changes faster in the vicinity of the interface. Therefore, τ_c decreases with increasing *Bi*, as shown in Figure 5. In this figure the values of $Sc = 1219.5$ and $G = 1.984 \times 10^{-3}$ correspond to those of Brian et al.'s (1971) experiment of triethylamine desorption from water. Figure 6 shows that τ_c approaches a certain asymptotic value with an increase in *Ma* for a given *Bi*. This interesting trend seen commonly in Figures 4–6 is illustrated more clearly as a function of *G* in Figure 7. When $G = 0$, that is, no Gibbs adsorption, the minimum τ_c-bound corresponds to the results of Kang and Choi (1997).

The Gibbs adsorption layer represents a capacity for the gas-liquid interface to store solute molecules, and for positive

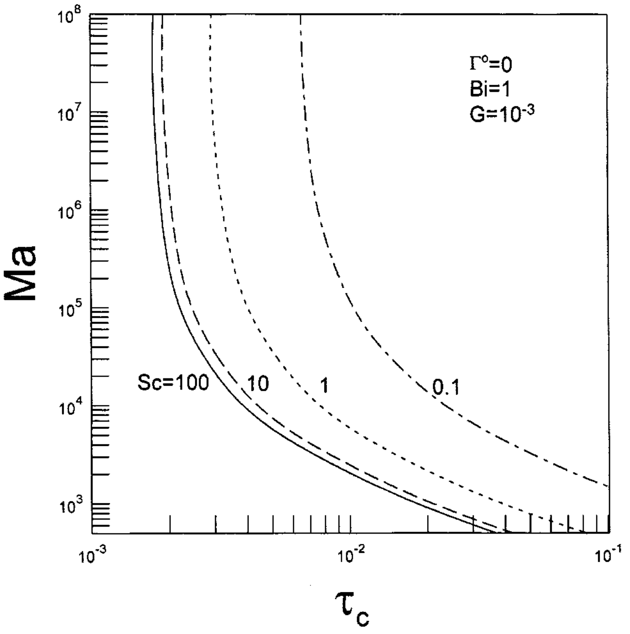

Figure 4. Effect of Marangoni number *Ma* on critical conditions for various Schmidt numbers *Sc*.

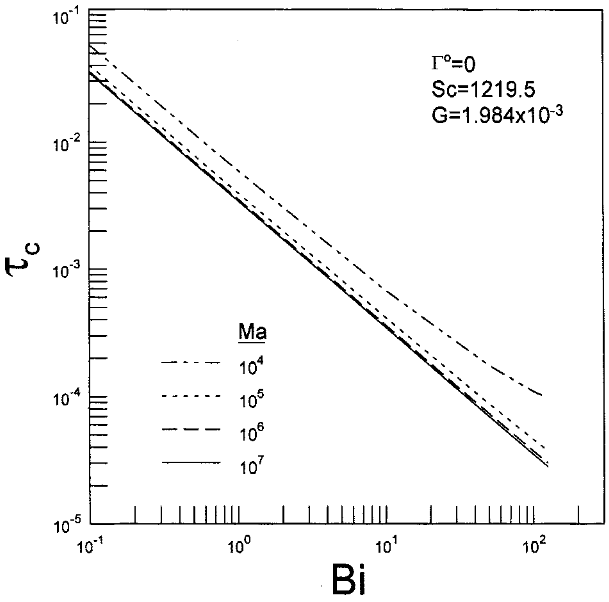

Figure 6. Effect of Biot number *Bi* on critical time τ_c for various Marangoni numbers *Ma*.

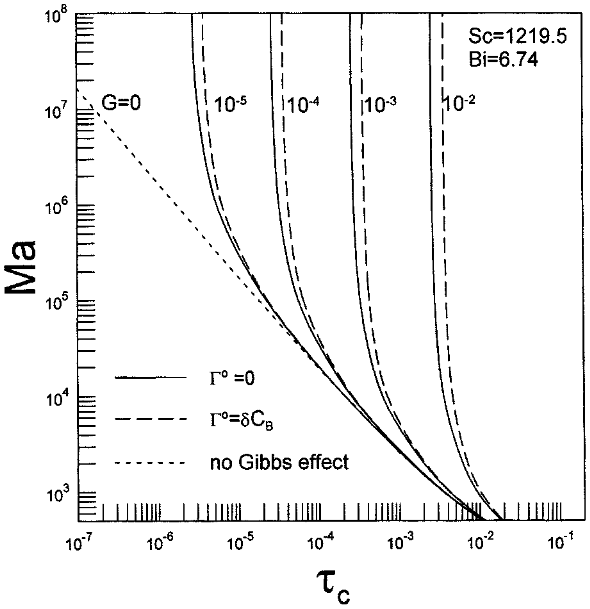

Figure 7. Effect of parameter *G* on critical conditions.

Ma, both solute accumulation and surface convection on the interface stabilize the system (Brian, 1971; Brian and Ross, 1972). In the present system, the Gibbs effect is described by *G*, *J* and *F* in Eqs. 12 and 21, and surface convection is described by the term involving *Ma* in Eq. 21. Surface convection contributes significantly to stabilization of the system like the linear case of $\partial\phi_0/\partial z = 1$. For this linear concentration profile of large τ_c, the critical Marangoni number Ma_c subject to the adiabatic boundary condition (Eq. 22) is 48 with $G = 0$, and Ma_c increases with an increase in *Bi*, as aforementioned. However, the *Bi*-effect is reversed in the present nonlinear system of small τ_c, as shown above. However, the stabilizing effect of *G* is common in the whole time domain. For the linear case, the adsorption number *A*, defined by Eq. 16 is fixed. From Eqs. 18–22, it is found analytically that for $A \geq 1/12$ the system is stable, that is, $Ma \to \infty$, independently of *Bi* and *Sc*. Brian (1971) reported that, in this case of the adiabatic bottom boundary, the characteristic *A*-value is 0.083. In the above limiting case of $Ma \to \infty$, it has been assumed that $Ma|w_1| \sim |\phi_1|$, and, therefore, $w_1 = \phi_1 = 0$ at $z =$ 0. This order of magnitude seems valid even in the present nonlinear developing concentration field. In the case of Figure 7 ($Sc = 1219.5$; $Bi = 6.74$), it is obtained that for $Ma \to \infty$, $\tau_c = 0.26\ G$ with $\Gamma^0 = 0$, and $\tau_c = 0.35\ G$ with $\Gamma^0 = \delta C_B$. The system of $\Gamma^0 = 0$ is more unstable than that of $\Gamma^0 = \delta C_B$, for the former system initially requires solute accumulation in the Gibbs layer. For example, with $G = 1.984 \times 10^{-3}$, its unperturbed interface concentration ϕ_{0S} increases up to $\tau = 10^{-4}$ and then decreases like that of $\Gamma^0 = \delta C_B$. At $\tau \geq 5 \times 10^{-3}$, its concentration profile becomes the same as the latter one and their critical conditions are also the same, as shown in Figure 7. This means that, in this time domain, solute accumulation in the Gibbs layer does not affect the mass transfer.

In Figure 8, where $G = 1.984 \times 10^{-3}$, the present predictions are compared with those of Brian and Ross (1972). In their experiment, *d* is 0.025 cm; hence, $\delta = 4.96 \times 10^{-5}$ cm. Their Ma_h and A_h have been converted to *Ma* and *A* (see Eqs. 23–25) by using their experimental data of triethylamine. Brian et al. (1971) conducted the experiment of *Ma* $\approx 2 \times 10^{-6}$ with a wetted-wall column, wherein Γ^0 would exist between 0 and δC_B. Figure 8 shows that the present predictions are closer to the experimental value than those of their frozen-time model using two linear segments, and the present $4\tau_c$-values agree very well with the experimental point. This supports the viewpoint that the times predicted with correct dimensional relations for the onset of convective motion in an initially quiescent fluid layer would be short by a factor of about 4 (Foster, 1969; Lee et al., 1990; Kim et al., 1991; Kang and Choi, 1997). The critical time predicted in the present study is that time at which disturbances of a most dangerous mode set in, and, therefore, a certain time would be required until manifest convection is detected experimentally. We plan to solve the full Navier-Stokes equations in the future in order to understand this peculiar behavior in the diffusion systems. In this figure it is known that, with $\Gamma^0 = 0$, the difference between Brian and Ross' (1972) predictions and the present ones becomes more significant with increasing *Ma*. It is seen that their prediction by the frozen-time model is more sensitive to the value of Γ^0 than the present prediction when τ_c is smaller than 10^{-3}. The reason can be found from the effect of solute accumulation in the Gibbs layer. For example, with $\Gamma^0 = 0$, the interface concentration ϕ_{0S} initially increases with time, as aforementioned, and the maximum $\partial\theta_0/\partial z$-value appears below the interface while with $\Gamma^0 = \delta C_B$, ϕ_{0S} decreases continuously with time and the maximum $\partial\theta_0/\partial z$-value always appears on the interface. The frozen-time model using two linear segments (see Eq. 23) does not represent the above initial behavior when $\Gamma^0 = 0$.

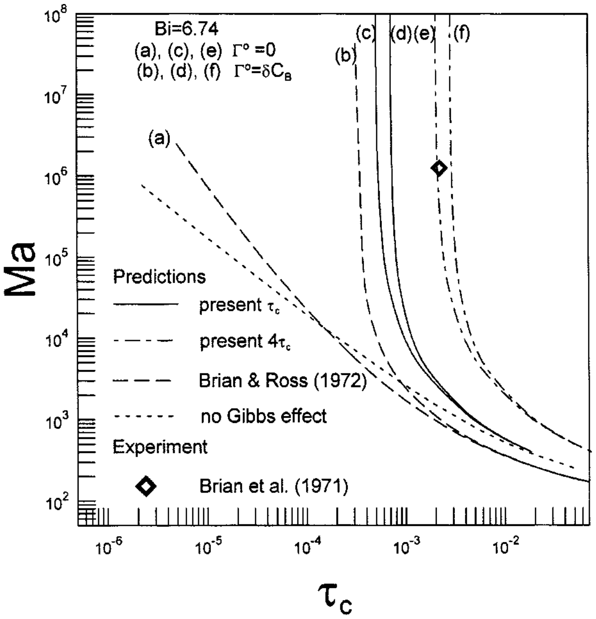

Figure 8. Comparison of present predictions with Brian et al.'s (1971) experiment of triethylamine desorption from water.

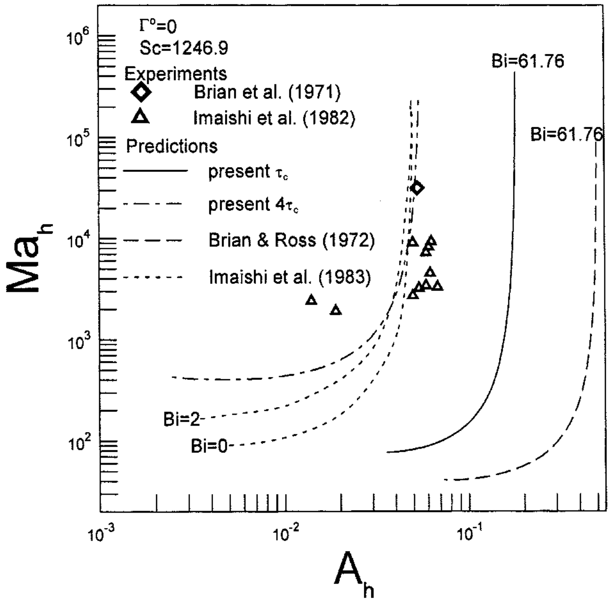

Figure 9. Comparison of predictions with Imaishi et al.'s (1982, 1983) results for triethylamine desorption from water.

There is another set of experimental data comparable with the present predictions. Imaishi et al. (1982, 1983) conducted the experiment of triethyamine using a liquid-jet column and the theoretical analysis by applying Brian's (1971) results for the case of a linear, basic concentration profile. Unfortunately, their Bi-value is unknown and, therefore, the value of $Bi = 61.76$ is assumed here by taking the nozzle radius of the liquid-jet column as the characteristic liquid depth. The present predictions with $G = 1.984 \times 10^{-3}$ are compared with their experimental data in Figure 9. For this purpose, the present theoretical Ma- and A-values have been converted to Ma_h and A_h. In the figure the lefthand side region of the line predicted by each model represents the unstable state, while the righthand side region represents the stable state. Imaishi et al. (1983) compared their experimental data of triethylamine with predictions based on Brian's (1971) linear case for $Bi = 0$ and 2. They argued that there would exist the paradox, because many experimental data are located in the region of $A_h > 0.05$. According to Brian's analysis and the aforementioned analytical solution, the system of the conducting case ($\phi_1 = 0$ at $z = 1$) with a linear concentration profile is stable for $A \geq 1/20$ ($= 0.05$). However, according to Brian and Ross' (1972) predictions, the stable region is that of $A_h \geq 0.5$ because the basic concentration profile is developing. The former case corresponds to the system of large time, while the latter one corresponds to small time. Therefore, it is believed that there is no paradox in Brian et al.'s predictions. With $Bi = 6.74$, the Ma_h-values are a little lower than those of $Bi = 61.76$ for a given A_h, but the maximum A_h-value is almost the same for each model. This trend is the same as that of $Bi = 0$ and $Bi = 2$ in Figure 9. It is noted that a plot of Ma_h vs. A_h should be interpreted very carefully, because they implicitly involve the critical time. For example, case (a) in Figure 8 represents that $Ma_h = 2125$ and $A_h = 0.4865$ at $\tau_c = 10^{-5}$, and $Ma_h = 100.5$ and $A_h = 0.3799$ at $\tau_c = 10^{-4}$. However, the predicted values in Figure 8 explicitly illustrate the relation of Ma vs. τ_c. The linear stability analysis is to predict the critical time to mark a most dangerous mode of instability and its growth time will be required until detected. With this viewpoint, the agreement between experimental values and the present $4\tau_c$-values in Figure 9 looks reasonable.

Conclusions

In the present study the onset of surface-tension-driven convection in a horizontal liquid layer undergoing desorbing from a free surface has been investigated. The related stability analysis has been conducted numerically by employing the propagation theory. In the small time domain it is shown that the Schmidt number Sc strongly influences the onset of instability in the form of regular cells for $Sc < 10$. For small τ_c, a smaller-Sc liquid layer becomes more stable while a larger-Bi one becomes more unstable. The effect of Gibbs adsorption delays the onset of convection and the present predictions are compared well with the existing experimental results of triethylamine desorption in water.

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