Influence of Gibbs Adsorption on Oscillatory Marangoni Instability

P. L. T. BRIAN and K. A. SMITH

Department of Chemical Engineering
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

In a recent paper (*1*) it has been shown that Gibbs adsorption can have a profound stabilizing influence upon Marangoni convection caused by the desorption of a surface tension-lowering solute from a liquid layer. The surface flow accompanying the cellular convection results in surface convection in the Gibbs layer, removing the surface tension-lowering solute from the points of low surface tension and convecting it to the points of high surface tension in the gas-liquid interface, creating a negative feedback effect which opposes the Marangoni instability. The importance of this phenomenon was assessed by incorporating these effects into the small disturbance hydrodynamic stability analysis of Pearson (*2*), in which the gas phase fluid mechanics are not considered but rather are modeled by a constant gas phase mass transfer coefficient and in which deformation of the liquid surface is assumed to be negligible. The results showed that surface diffusion within the Gibbs layer had little effect but that surface convection stabilized the system completely, raising the critical Marangoni number to infinity, at a critical value of an adsorption number $\mathcal{A}$.

In performing this analysis (*1*) it was assumed that the state of neutral stability was stationary rather than oscillatory, an assumption which had been justified for the Pearson problem by Vidal and Acrivos (*3*). This assumption, referred to as the principle of exchange of stabilities, would appear to require additional justification for the case in which the effects of Gibbs adsorption are introduced into the concentration boundary condition at the free surface. As the adsorption number $\mathcal{A}$ approaches its critical value, found to be 0.05 and 0.083 for the two cases treated in (*1*), the critical value of the Marangoni number approaches infinity, and the entire positive branch of the neutral stability curve is confined to wave numbers less than a crossover value which approaches zero in this limit. This behavior, described in (*1*), raises the question of whether or not values of $\mathcal{A}$ above the critical do indeed completely stabilize the system or whether oscillatory modes of instability will develop at large values of the Marangoni number. The fact that the stationary modes of instability are confined to wave numbers approaching zero suggests that oscillatory modes of instability may exist at the more expected wave numbers in the vicinity of unity. Furthermore, since the stabilizing effect of surface convection in the Gibbs layer results from the negative feedback effect of surface convection mitigating the positive feedback effect of convection in the bulk liquid, the possibility of developing sufficient phase shift to produce oscillatory negative feedback instability appears real.

It is therefore the purpose of this work to determine whether the neutral state is indeed a stationary one or whether oscillatory modes of instability exist. The development will follow closely those in references *1* and *2*, and their nomenclature will be adopted here.

ANALYSIS

The velocity and concentration perturbations are assumed to be of the form

$$v = -\,(\mathcal{D}/d)\; F(\xi, \zeta)\; f(\eta)\; e^{p\tau} \tag{1}$$

$$C = (\beta d)\; F(\xi, \zeta)\; g(\eta)\; e^{p\tau} \tag{2}$$

and the governing linearized differential equations are

$$[p - N_{Sc}\,(D^2 - \alpha^2)]\,[D^2 - \alpha^2]\, f = 0 \tag{3}$$

$$[p - (D^2 - \alpha^2)]\; g = -\, f \tag{4}$$

The solution to Equation (3), subject to the boundary conditions

$$f(1) = f(0) = f'(0) = 0 \tag{5}$$

is found to be

$$f(\eta) = a\left[\frac{\alpha \sinh \Omega\eta - \Omega \sinh \alpha\eta}{\alpha \sinh \Omega - \Omega \sinh \alpha} - \frac{\cosh \Omega\eta - \cosh \alpha\eta}{\cosh \Omega - \cosh \alpha}\right] \tag{6}$$

where a is an arbitrary constant representing the magnitude of the perturbation and

$$\Omega \equiv \sqrt{\alpha^2 + p/N_{Sc}} \tag{7}$$

The solution to Equation (4) then becomes

$$g(\eta) = a\,[c_1 \sinh \lambda\eta + c_2 \cosh \lambda\eta + \Phi(\eta)] \tag{8}$$

where

$$\lambda \equiv \sqrt{\alpha^2 + p} \tag{9}$$

and

$$\Phi(\eta) \equiv \left[\frac{\alpha/(\Omega^2 - \lambda^2)}{\alpha \sinh \Omega - \Omega \sinh \alpha}\right] \sinh \Omega\eta - \left[\frac{1/(\Omega^2 - \lambda^2)}{\cosh \Omega - \cosh \alpha}\right] \cosh \Omega\eta - \left[\frac{\Omega/(\alpha^2 - \lambda^2)}{\alpha \sinh \Omega - \Omega \sinh \alpha}\right] \sinh \alpha\eta + \left[\frac{1/(\alpha^2 - \lambda^2)}{\cosh \Omega - \cosh \alpha}\right] \cosh \alpha\eta \tag{10}$$

The constants c_1 and c_2 are determined by the boundary condition at the free surface

$$-\,g'(1) = [L + \alpha^2 \mathcal{S} + p\mathcal{G}]\; g(1) + \mathcal{A}\, f'(1) \tag{11}$$

and by the boundary condition at the bottom wall, which takes the form of Equation (12) or Equation (13) for the conducting or the insulating case, as described in references (*1, 2*).

$$g(0) = 0 \tag{12}$$

$$g'(0) = 0 \tag{13}$$

For the conducting case, the result is

$$c_2 = \frac{1/(\Omega^2 - \lambda^2) - 1/(\alpha^2 - \lambda^2)}{\cosh \Omega - \cosh \alpha} \tag{14}$$

$$c_1 = -\frac{c_2\,\lambda\sinh\lambda + \Phi'(1) + \dfrac{\mathcal{R}\,f'(1)}{a} + (L + \alpha^2\mathcal{S} + \mathcal{G}p)\,[c_2\cosh\lambda + \Phi(1)]}{\lambda\cosh\lambda + (L + \alpha^2\mathcal{S} + \mathcal{G}p)\sinh\lambda} \qquad (15)$$

For the insulating case, the corresponding result is

$$c_1 = \left(\frac{\alpha\Omega}{\lambda}\right)\left[\frac{1/(\alpha^2-\lambda^2) - 1/(\Omega^2-\lambda^2)}{\alpha\sinh\Omega - \Omega\sinh\alpha}\right] \qquad (16)$$

$$c_2 = -\frac{c_1\,[\lambda\cosh\lambda + (L + \alpha^2\mathcal{S} + \mathcal{G}p)\sinh\lambda] + \Phi'(1) + \dfrac{\mathcal{R}\,f'(1)}{a} + (L + \alpha^2\mathcal{S} + \mathcal{G}p)\,\Phi(1)}{(L + \alpha^2\mathcal{S} + \mathcal{G}p)\cosh\lambda + \lambda\sinh\lambda} \qquad (17)$$

Finally, the tangential stress condition at the free surface

$$B = \frac{f''(1)}{\alpha^2\,g(1)} \qquad (18)$$

is used to determine the Maranoni number B. In seeking values of B corresponding to neutral stability, the real part of the growth rate constant p is taken to be zero, and therefore

$$p = i\,\omega \qquad (19)$$

With ω equal to zero, the state of neutral stability is a stationary one. But with nonzero values of ω, the time function in Equations (1) and (2) is an oscillation of steady amplitude.

The parameter L represents the gas phase mass transfer coefficient divided by the conductance of the liquid layer. The parameters $\mathcal{R}$, $\mathcal{S}$, and $\mathcal{G}$ represent convection, diffusion, and accumulation of solute within the Gibbs adsorption layer, as discussed in (*1*). For fixed values of these parameters, the value of B corresponding to neutral stability can be computed at various values of the wave number α and the oscillation frequency ω by use of Equation (18). This requires that the functions f, f', f'', Φ, Φ', and g all be evaluated at $\eta = 1$. This task is simplified enormously by the availability of complex algebra FORTRAN programming, which was employed in the digital computations for the results presented here.

RESULTS

For values of p which are imaginary, according to Equation (19), the calculations will generally result in complex values of the Marangoni number B

$$B = B_R + i\,B_I \qquad (20)$$

Only when B is real does the result have physical significance, and therefore the state of neutral stability corresponds to the points where B_I vanishes.

Figure 1 shows a plot of B_I versus B_R as ω varies from 0 to 2,100, for the conducting case with a Schmidt number of 500 and with values of $\mathcal{R}$, $\mathcal{S}$ and L equal to 0.04, 0.004, and 0.1, respectively. The curve for $\alpha = 1$ also shows results for negative values of ω which confirm the obvious requirement that conjugate values of p must produce the complex conjugate values of B. This test was met by all of the computations, but the results are shown only for the curve for $\alpha = 1$.

With $\omega = 0$, $B_I = 0$ and $B_R = 1{,}300$, corresponding to a stationary mode of instability in agreement with the results of reference *1*. As ω takes on positive values, the polar plot moves counterclockwise into the second quadrant and then crosses over into the third quadrant and remains there, with both B_I and B_R taking on increasingly negative values as ω is increased. B_I is seen to vanish at $\omega = 16$, $B_R = -625$. This corresponds to an oscillatory mode of instability, which however is not physically realizable because in a real system the product of $\mathcal{R}$ and B must be positive, as discussed in reference *1*. It is seen therefore that the only value of B in the neutrally stable state corresponding to physical reality is the stationary mode at $\omega = 0$, the result obtained in reference *1*.

The result for $\alpha = 1$ is characteristic of the results obtained for all values of α between 0 and approximately 1.4. For larger values of α, B_R corresponding to the stationary mode is negative, and the result is similar to the curve for $\alpha = 2$, shown in Figure 1. With $\omega = 0$, $B_I = 0$ and $B_R = -410$. At $\omega = 13$, $B_I = 0$ and $B_R = -202$. The first is a stationary mode and the second an oscillatory mode, but they both correspond to the unrealistic case of positive $\mathcal{R}$ and negative B. At larger values of ω, the curve moves into the third quadrant with both B_I and B_R becoming increasingly negative as ω increases.

Figure 2 shows results for other values of $\mathcal{R}$. The upper curve is for $\mathcal{R}$, $\mathcal{S}$, and $\mathcal{G}$ equal to zero, and therefore this corresponds to the problem analyzed by Vidal and Acrivos (*3*). Confirming their result, it is seen that the stationary mode is the only one for which B_I vanishes, the curve re-

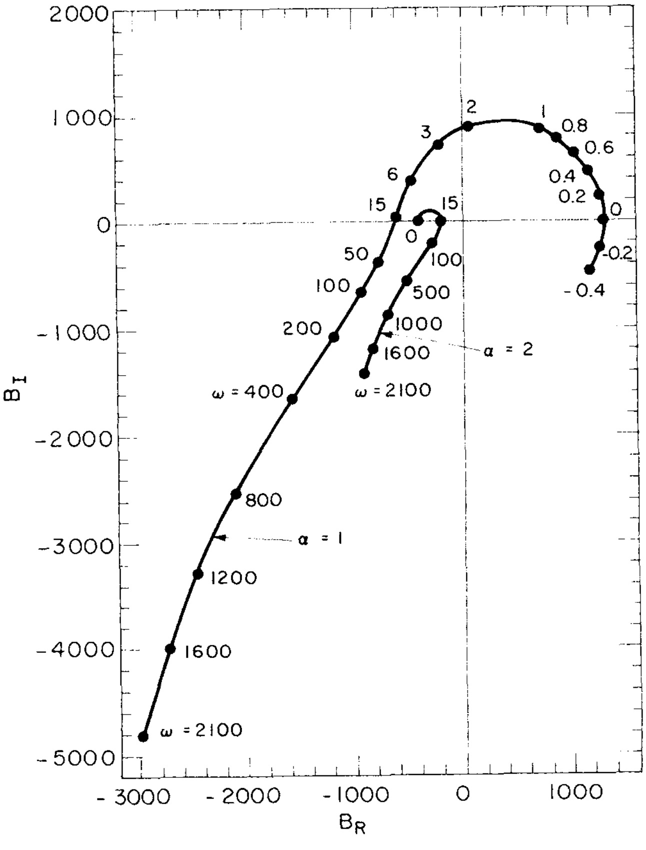

Fig. 1. Neutral stability results $\mathcal{R} = 0.04$, $L = 0.1$, $\mathcal{S} = \mathcal{G} = 0.004$, $N_{Sc} = 500$.

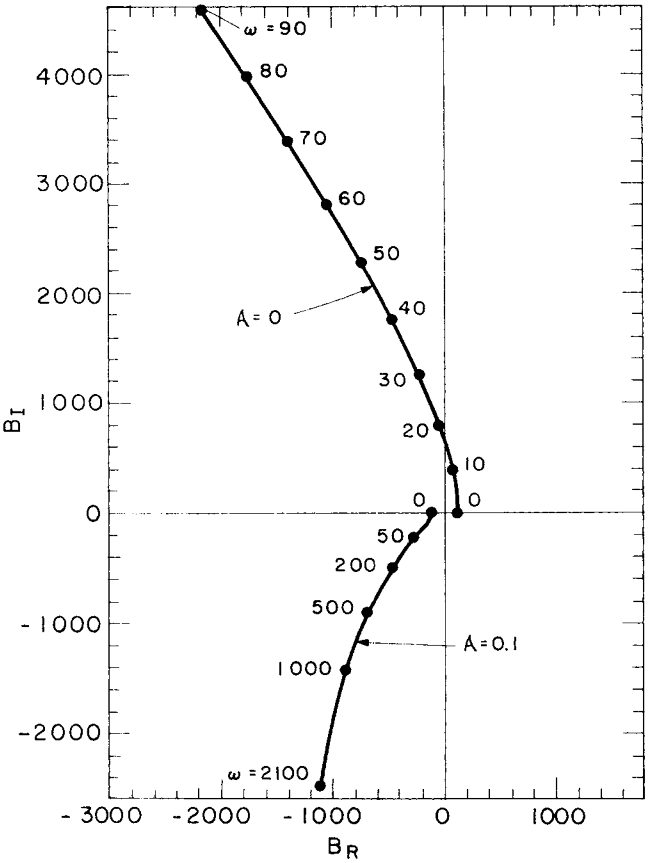

Fig. 2. Neutral stability results $L = 0.1$, $\mathcal{S} = \mathcal{G} = \mathfrak{A}L$, $N_{Sc} = 500$, $\alpha = 1$.

maining in the second quadrant as ω takes on increasingly large values. The bottom curve is for $\mathfrak{A} = 0.1$, which is greater than the critical value of $\mathfrak{A}$ as determined in reference *1*. The stationary mode corresponds to the unrealistic case of a negative value of B_R, and the curve then moves into the third quadrant and remains there. Both of the curves in Figure 2 are for $\alpha = 1$ but are characteristic of all values of α for the respective values of $\mathfrak{A}$ shown.

A great many computations of this type were performed, corresponding to Schmidt numbers of 5, 250, 500, and 1,000 and also corresponding to negative values of $\mathfrak{A}$ as well as positive values and to the insulating as well as the conducting case. The only oscillatory modes found corresponded to negative values of the product of $\mathfrak{A}$ and B_R which is physically unrealizable. It is therefore concluded that no oscillatory modes of instability exist, confirming the assumption upon which the analysis in (*1*) was based.

ACKNOWLEDGMENT

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NOTATION

$\mathfrak{A}$ = $\Gamma_0/\beta d^2$, the adsorption number, represents surface convection
a = arbitrary constant in Equations (6) and (8)
B = $\sigma\beta d^2/\mu\mathcal{D}$, the Marangoni number
C = small perturbation in the solute concentration in liquid phase, g.-mole/cu.cm.
c_1, c_2 = adjustable constants, determined by Equations (15) and (14) for the conducting case and by Equations (16) and (17) for the insulating case
D = $d/d\eta$
$\mathcal{D}$ = diffusion coefficient for solute in liquid phase, sq.cm./sec.
$\mathcal{D}_s$ = surface diffusion coefficient for solute in adsorbed layer, sq.cm./sec.
d = depth of liquid layer, cm.
$F(\xi, \zeta)$ = function representing the variation of the perturbations with x and z, as in Equations (1) and (2)
$f(\eta)$ = function representing the variation of v with y, Equation (1); given by Equation (6)
$f'(\eta)$ and $f''(\eta)$ = first and second derivatives of $f(\eta)$ with respect to η
$\mathcal{G}$ = δ/d; represents accumulation in the surface
$g(\eta)$ = function representing the variation of C with y, Equation (2); given by Equation (8)
$g'(\eta)$ and $g''(\eta)$ = first and second derivatives of $g(\eta)$ with respect to η
i = $\sqrt{-1}$
L = $Hk_G d/\mathcal{D}$, the liquid-to-gas phase resistance ratio
N_{Sc} = Schmidt number
p = growth rate constant for the disturbances, Equations (1) and (2)
R = ideal gas law constant, 8.314×10^7 erg/(g.-mole)(°K.)
$\mathcal{S}$ = $(\mathcal{D}\delta)/(\mathcal{D}_s d)$; represents surface diffusion
T = absolute temperature, °K.
t = time, sec.
u, v, w = small velocity components in the x, y, and z directions, respectively
x, z = position coordinates in the horizontal plane, cm.
y = coordinate in vertical direction, measured upward, cm.

Greek Letters

α = wave number for periodic variation of $F(\xi, \zeta)$
β = negative of the slope of the linear variation of the unperturbed concentration with respect to y
Γ_0 = surface concentration of solute in Gibbs adsorption layer in the unperturbed state, g.-moles/sq.cm.
δ = σ/RT, the Gibbs depth, cm.
ζ = z/d
λ = $\sqrt{\alpha^2 + p}$
η = y/d
μ = liquid viscosity, poise
ξ = x/d
σ = negative of the slope of the curve of surface tension versus solute concentration, (dyne)(sq.cm.)/g.-mole
τ = $t\mathcal{D}/d^2$
$\Phi(\eta)$ = function defined by Equation (10)
$\Phi'(\eta)$ = derivative of $\Phi(\eta)$ with respect to η
Ω = $\sqrt{\alpha^2 + p/N_{Sc}}$
ω = imaginary part of p

Subscripts

I = imaginary part
R = real part

LITERATURE CITED

1. Brian, P. L. T., *AIChE J.*, 17, 765 (1971).
2. Pearson, J. R. A., *J. Fluid Mech.*, 4, 489 (1958).
3. Vidal, A., and Andreas Acrivos, *Phys. Fluids*, 9, 615 (1966).