Effect of Gibbs Adsorption on Marangoni Instability

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SCOPE

In the transfer of mass from one fluid phase to another, solute concentration gradients or temperature gradients may produce surface tension gradients, resulting in cellular convection at the interface. In liquid-liquid extraction systems the convection may become so intense that it causes the break-up of the interface, resulting in "spontaneous emulsification." Often referred to as Marangoni instability, convection driven by surface tension gradients also occurs frequently in gas-liquid mass transfer systems and has been known to enhance the mass transfer rate more than tenfold.

A theoretical understanding of Marangoni instability should lead ultimately to the prediction of its occurrence and of its effect upon the mass transfer rate when it occurs, permitting this important phenomenon to be properly accounted for and perhaps even exploited in the design and development of processes involving interphase mass transfer.

Previous workers have made substantial progress toward defining the conditions under which the instability occurs, usually measured by the critical value of the Marangoni number. These workers have employed small disturbance hydrodynamic stability theory to predict the point of convective instability. Recent experimental measurements of the critical Marangoni number in desorbing surface tension-lowering solutes from water, however, were found to be several orders of magnitude greater than the theoretical predictions. One speculation offered to explain the discrepancy involved the Gibbs adsorption layer. Because previous theoretical work had not considered the effect of Gibbs adsorption, the present study was undertaken to evaluate the effect of Gibbs adsorption on the theoretically predicted critical Marangoni number.

SUMMARY

The influence of Gibbs adsorption has been incorporated into a small disturbance hydrodynamic stability analysis of Marangoni convection. The model used was the first and perhaps the simplest model studied by previous workers, the mass transfer analog of the problem studied by Pearson (9). In this model, the unperturbed state is a horizontal liquid layer at rest, from which a surface tension-lowering solute is desorbing into a gas phase above. The concentration gradient within the liquid layer is linear, and it is assumed that the planar gas-liquid interface is not deformed. The fluid mechanics of the gas phase are not considered, mass transfer in the gas phase being represented by a constant mass transfer coefficient which is unaffected by convection in the liquid phase. These simplifications appear to be adequate for gas-liquid systems, and in any event they are appropriate for this initial analysis of the effect of Gibbs adsorption.

The present theory, therefore, involves the incorporation of the effect of Gibbs adsorption into Pearson's hydrodynamic stability analysis. The influence of Gibbs adsorption enters the problem in the boundary condition which represents a solute material balance on a small element of the gas-liquid interface

$$- \mathcal{D} \left(\frac{\partial C}{\partial y} \right) = H k_G \, (C - C^*) + \frac{\partial \Gamma}{\partial t} - \mathcal{D}_s \left(\frac{\partial^2 \Gamma}{\partial x^2} + \frac{\partial^2 \Gamma}{\partial z^2} \right) + \frac{\partial (u \, \Gamma)}{\partial x} + \frac{\partial (w \, \Gamma)}{\partial z}$$

The term on the left-hand side of this equation represents diffusion of the solute to the surface from the liquid beneath, C representing solute concentration and y the vertical distance coordinate measured upward. The first term on the right-hand side of the equation represents the transfer of solute from the interface to the bulk gas. These first two terms correspond to the boundary condition employed by previous investigators the last four terms in the equation represent the effect of Gibbs adsorption.

The second term on the right-hand side of the equation represents solute accumulation within the Gibbs layer. The surface concentration Γ refers to the moles of solute per square centimeter adsorbed at the surface according to the Gibbs theory. This term is expected to influence the rate of growth of an unstable disturbance, but it will not affect the curve of neutral stability, which represents the condition in which a small disturbance neither grows nor

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decays. It will not, therefore, influence the critical value of the Marangoni number. The next term represents surface diffusion within the adsorbed layer. The last two terms represent surface convection of solute in the Gibbs layer, expressed as the product of Γ and the surface velocity components. This term is found to have a profound influence upon the critical Marangoni number.

In terms of the small perturbation quantities, this boundary condition becomes

$$-\mathcal{D}\left(\frac{\partial C'}{\partial y}\right) = Hk_G C' + \frac{\partial \Gamma'}{\partial t} - \mathcal{D}_s\left(\frac{\partial^2 \Gamma'}{\partial x^2} + \frac{\partial^2 \Gamma'}{\partial z^2}\right) + \Gamma_0\left(\frac{\partial u}{\partial x} + \frac{\partial w}{\partial z}\right)$$

In this equation C' and Γ' represent the infinitesimal perturbations in the solute concentration and in the surface concentration in the adsorbed layer, respectively. The velocity components u and w are likewise infinitesimal perturbation quantities, and second order terms involving the product of Γ' and the velocities have been neglected. The last term in the equation represents surface convection in the Gibbs layer, and in this form it can be seen to be the product of Γ_0, the unperturbed value of Γ, and the surface divergence of the surface velocity.

This latter quantity represents the rate of expansion of the surface at any point, and its product with Γ_0 is seen to be the rate at which solute must be added to the expanding surface to maintain the inventory in the Gibbs layer. At a point where the surface is expanding, this convective term results in the removal of solute, which tends to raise the surface tension at that point, opposing the expansion of the surface. Where the surface is contracting, the surface divergence of the surface velocity is negative, and the convection term results in an accumulation of solute in the Gibbs layer, lowering the surface tension and opposing the surface contraction.

The results obtained show that surface diffusion has little effect, producing a maximum increase of 7% in the critical Marangoni number. Surface convection, on the other hand, has a profound effect.

The magnitude of the surface convection is determined by the value of $\mathcal{A}$, an "adsorption number," which is defined as Γ_0 divided by the liquid layer depth and by the concentration difference across the liquid layer in the unperturbed state. Quite small values of $\mathcal{A}$ result in large increases in the critical Marangoni number. As $\mathcal{A}$ approaches a critical value, the critical Marangoni number approaches infinity, corresponding to the complete stabilization of the system. The critical values of $\mathcal{A}$ have been found to be 0.05 and 0.083 for the two cases considered here; it is expected that somewhat higher values will be found for other cases which are inherently somewhat less stable.

For a recent experimental study, in which the critical Marangoni number had been found to be several orders of magnitude greater than previously published theoretical predictions, the values of $\mathcal{A}$ range as high as 0.16. The present model is not directly applicable to those experiments, but it is seen that values of $\mathcal{A}$ to be expected in experimental situations are in the range where the results of this study show Gibbs adsorption to completely suppress the Marangoni convection. The incorporation of the effects of Gibbs adsorption into other models of Marangoni convection is expected to show a similar influence of $\mathcal{A}$ and hopefully will result in agreement between experimental results and theoretical predictions of the critical Marangoni number.

PREVIOUS WORK

Cellular convection driven by surface tension gradients frequently accompanies the transfer of mass from one fluid phase to another. The phenomenon, often called Marangoni instability, can result in convection so intense in liquid-liquid extraction systems that it may break up the interface, resulting in "spontaneous emulsification" (*11*). In gas-liquid systems, the convection generally does not produce effects visible to the eye, but it has been known to enhance the mass transfer rate more than tenfold. Schlieren techniques can be used to view the convection cells, and a number of researchers have reported optical studies to define the nature of the convection patterns established (*2, 8, 11, 14*).

The pioneering theoretical work on the problem, due to Pearson (*9*) and Sternling and Scriven (*13*), employed small disturbance hydrodynamic stability theory to determine whether or not the surface tension gradients produced by infinitesimally small cellular convective flows could result in surface forces sufficiently strong to amplify the convection currents. Subsequently, a number of other investigators performed similar analyses to modify and improve the theoretical models (4, 10, 12, 15).

The results were usually expressed in terms of the critical value of the Marangoni number, at which the system becomes unstable, resulting in the amplification of infinitesimally small convection currents of certain unstable wavelengths. These theoretical analyses define the conditions under which the system is unstable, but they do not determine the intensity of the convection when it occurs and therefore do not predict the effect of the cellular convection on the rate of interphase mass transfer. Experimental studies have been conducted to determine the enhancement in the mass transfer rate for some systems (*3, 5, 6, 7*).

In a recent experimental study (*6*), the observed values of the critical Marangoni number were found to be several orders of magnitude greater than the theoretical predictions. One speculation offered to explain the discrepancy involved the Gibbs adsorption layer, which represents a capacity for the gas-liquid interface to store solute molecules. Previous theoretical analyses of Marangoni instability have not considered Gibbs adsorption. It is therefore the purpose of this study to incorporate the effect of Gibbs adsorption into a small disturbance hydrodynamic stability analysis of Marangoni convection.

THEORY

The problem to be analyzed involves a horizontal liquid layer from which a surface tension-lowering solute is desorbing into a gas phase above the liquid. The fluid mechanics of the gas phase are not considered, mass transfer of the solute from the gas-liquid interface to the bulk gas phase being modelled by a constant gas phase mass transfer coefficient which is unaffected by convection in the liquid phase. Experimental evidence (*6*) suggests that this model is applicable to gas-liquid mass transfer, and in any event this simplification is appropriate in this initial analysis of the effect of Gibbs adsorption.

Similarly, deformation of the gas-liquid interface from its initial planar state is assumed to be negligible. In the unperturbed state, the liquid is at rest, and there is a linear concentration gradient of the solute species from a high concentration at the bottom of the liquid layer to a lower concentration at the gas-liquid interface. The solute component is steadily supplied at the wall bounding the liquid layer on the bottom and steadily diffuses through the liquid layer and desorbs into the gas phase.

This problem is the mass transfer analog of the heat transfer problem analyzed by Pearson (9) in his pioneering application of small disturbance hydrodynamic stability theory to cellular convection driven by surface tension gradients. The present objective is, therefore, to incorporate the effect of Gibbs adsorption into Pearson's analysis. The bulk of the analysis will remain unchanged; it will not be repeated here, and the reader is referred to Pearson's paper for the details of his analysis. To facilitate this reference, Pearson's coordinate system and his nomenclature will be employed in the present derivation.

The vertical coordinate is y, measured from the bottom of the liquid layer upward, and x and z are the coordinates in the plane of the gas-liquid interface. The liquid layer is bounded by the bottom wall at $y = 0$ and by the gas-liquid interface at $y = d$. The liquid is at rest in the unperturbed state, and the velocity components are all infinitesimal perturbation quantities. The concentration of the solute species is represented by the sum of the unperturbed value and an infinitesimal perturbation

$$C = C_o + C' \tag{1}$$

The unperturbed concentration C_o is a linear function of y with slope $-\beta$ but is invariant with x and z and with time. Using the dimensionless variables

$$(\xi, \eta, \zeta) \equiv \left(\frac{x}{d}, \frac{y}{d}, \frac{z}{d} \right); \quad \tau \equiv \frac{t\mathcal{D}}{d^2}$$

the velocity perturbation and the concentration perturbation are assumed to be of the form

$$v = -(\mathcal{D}/d)\, F(\xi, \zeta)\, f(\eta)\, e^{p\tau} \tag{2}$$

$$C' = (\beta d)\, F(\xi, \zeta)\, g(\eta)\, e^{p\tau} \tag{3}$$

which correspond to Pearson's Equations (12) and (13) but with his temperature perturbation replaced here by the concentration perturbation. The differential equations and the various boundary conditions all remain as given by Pearson except for the concentration boundary condition at the free surface, corresponding to Pearson's Equation (10).

The key to the present analysis is the incorporation of the effect of Gibbs adsorption into the boundary condition which represents a solute material balance on a small element of the gas-liquid interface

at $y = d$,

$$-\mathcal{D}\left(\frac{\partial C}{\partial y}\right) = Hk_G\,(C - C^*) + \frac{\partial \Gamma}{\partial t} - \mathcal{D}_s\left(\frac{\partial^2 \Gamma}{\partial x^2} + \frac{\partial^2 \Gamma}{\partial z^2}\right) + \frac{\partial (u\,\Gamma)}{\partial x} + \frac{\partial (w\,\Gamma)}{\partial z} \tag{4}$$

The term on the left-hand side of Equation (4) represents diffusion of the solute component to the interface from the liquid beneath. The first term on the right-hand side represents transfer from the gas-liquid interface to the bulk gas, which contains the solute component at a partial pressure corresponding to the liquid phase solubility C^*. The last four terms in Equation (4) result from the adsorption of solute molecules at the interface, with Γ representing the moles of solute adsorbed per unit of surface area.

The second term on the right-hand side represents the rate of change of the inventory of the solute in the Gibbs layer. The next term represents surface diffusion in the adsorbed layer. The last two terms reflect the fact that surface flow in an interface containing adsorbed molecules results in a convection of the absorbed species. The surface divergence of the product of Γ and the surface velocity represents the net flow of the solute species out of a surface element by surface convection, as given by the last two terms in Equation (4).

In the unperturbed state, the corresponding boundary condition is

at $y = d$,

$$-\mathcal{D}\left(\frac{\partial C_o}{\partial y}\right) \equiv \mathcal{D}\beta = Hk_G\,(C_o - C^*) \tag{5}$$

Subtracting Equation (5) from Equation (4) and using Equation (1) yields

$$-\mathcal{D}\left(\frac{\partial C'}{\partial y}\right) = Hk_G\,C' + \frac{\partial \Gamma}{\partial t} - \mathcal{D}_s\left(\frac{\partial^2 \Gamma}{\partial x^2} + \frac{\partial^2 \Gamma}{\partial z^2}\right) + \frac{\partial (u\,\Gamma)}{\partial x} + \frac{\partial (w\,\Gamma)}{\partial z} \tag{6}$$

The first two terms in Equation (6) correspond to Pearson's Equation (10). The last four terms represent the influence of Gibbs adsorption; they have not been included in previous theoretical analyses of Marangoni instability.

The surface concentration in the adsorbed layer is written as the sum of the unperturbed value and an infinitesimal perturbation

$$\Gamma = \Gamma_0 + \Gamma' \tag{7}$$

where Γ_0 is a constant and represents the surface concentration of solute molecules in the Gibbs layer in the unperturbed state. Using Equation (7), Equation (6) becomes

$$-\mathcal{D}\left(\frac{\partial C'}{\partial y}\right) = Hk_G\,C' + \frac{\partial \Gamma'}{\partial t} - \mathcal{D}_s\left(\frac{\partial^2 \Gamma'}{\partial x^2} + \frac{\partial^2 \Gamma'}{\partial z^2}\right) + \Gamma_0\left(\frac{\partial u}{\partial x} + \frac{\partial w}{\partial z}\right) \tag{8}$$

in which the terms involving the product of Γ' and the velocities u and w have been neglected as being of second order because they involve products of two infinitesimal perturbations.

In this form the last term in Equation (8) is seen to be Γ_0 multiplied by the local rate of expansion of the surface and therefore represents the rate at which solute must be added to the surface at that point in order to maintain the inventory in the Gibbs layer. The continuity equation

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0 \tag{9}$$

can be used to simplify the last term in Equation (8) to yield

$$-\mathcal{D}\left(\frac{\partial C'}{\partial y}\right) = Hk_G\,C' + \frac{\partial \Gamma'}{\partial t} - \mathcal{D}_s\left(\frac{\partial^2 \Gamma'}{\partial x^2} + \frac{\partial^2 \Gamma'}{\partial z^2}\right) - \Gamma_0\left(\frac{\partial v}{\partial y}\right) \tag{10}$$

The Gibbs equation (*1*) relates Γ to the negative of the slope of the curve of surface tension versus solute concentration. Following Pearson's nomenclature, $-\sigma$ will be used to denote the slope of the surface tension-concentration curve evaluated at the concentration at the gas-liquid interface in the unperturbed state. It is further assumed that the surface tension-concentration curve is linear in this region, and therefore σ is taken to be constant. This additional assumption does not affect the treatment of the surface convection term in Equation (10), the term of major importance, but it simplifies the treatment of the surface diffusion term and the accumulation term in what follows. Thus the Gibbs equation becomes

$$\Gamma = \left(\frac{\sigma}{RT}\right) C_i \equiv \delta\, C_i \qquad (11)$$

where δ, the "Gibbs depth," is taken to be constant. In an equilibrium system with no concentration gradient, δ may be interpreted as the depth of bulk liquid which contains the same quantity of solute as that adsorbed at the surface. Using Equations (1), (7), and (11), Equation (10) becomes

$$-\mathcal{D}\left(\frac{\partial C'}{\partial y}\right) = Hk_G\, C' + \delta \frac{\partial C'}{\partial t} - \delta \mathcal{D}_s \left(\frac{\partial^2 C'}{\partial x^2} + \frac{\partial^2 C'}{\partial z^2}\right) - \Gamma_0 \left(\frac{\partial v}{\partial y}\right) \qquad (12)$$

which is the boundary condition which will replace Pearson's Equation (10), the last three terms representing the influence of Gibbs adsorption.

Substitution of Equations (2) and (3) into Equation (12) yields, at $\eta = 1$

$$-g'(1) = L\, g(1) + p\, \mathcal{G}\, g(1) + \alpha^2\, \mathcal{S}\, g(1) + \mathcal{A}\, f'(1) \qquad (13)$$

In order to reduce the surface diffusion term to this form, it is necessary to employ Pearson's Equation (14):

$$\frac{\partial^2 F}{\partial \xi^2} + \frac{\partial^2 F}{\partial \zeta^2} + \alpha^2\, F = 0 \qquad (14)$$

Equation (13) contains four dimensionless groups which influence this problem

$$L \equiv \frac{Hk_G d}{\mathcal{D}} \qquad (15)$$

$$\mathcal{G} \equiv \frac{\delta}{d} \qquad (16)$$

$$\mathcal{A} \equiv \frac{\Gamma_0}{\beta d^2} \qquad (17)$$

$$\mathcal{S} \equiv \frac{\mathcal{D}_s\, \delta}{\mathcal{D}\, d} \qquad (18)$$

The first of these represents the ratio of the liquid phase mass transfer resistance to the gas phase resistance; it is analogous to the group defined in Pearson's Equation (19). The other three groups represent the effect of Gibbs adsorption. It will be seen, however, that the term containing $\mathcal{G}$ in Equation (13) will not affect the curve of neutral stability and thus the critical Marangoni number, although this group would be expected to influence the rate of growth of an unstable disturbance. The other important dimensionless group in this problem is the Marangoni number

$$B \equiv \frac{\sigma \beta d^2}{\mu \mathcal{D}} \qquad (19)$$

which enters the problem through the shear stress boundary condition at the surface, as developed by Pearson.

Equation (13) replaces the last of Pearson's boundary conditions in his Equation (17), which contains the first two terms in Equation (13) but not the last three. In seeking solutions for the case of neutral stability, in which the small disturbance neither grows nor decays, p is taken to be zero. As in the analyses of Pearson and others (*4*, *9*, *10*, *12*, and *15*), this corresponds to neglecting oscillatory modes of instability.* Equation (13) then becomes

$$-g'(1) = (L + \alpha^2 \mathcal{S})\, g(1) + \mathcal{A}\, f'(1) \qquad (20)$$

There remains now the problem of modifying Pearson's analysis by replacing the last condition of his Equation (17) with the present Equation (20).

The differential equation defining $g(\eta)$ is given as Pearson's Equation (23):

$$g''(\eta) - \alpha^2\, g(\eta) = f(\eta) \qquad (21)$$

The velocity function remains as presented in Pearson's Equation (24):

$$f(\eta) = a\left[\sinh \alpha\eta + \left(\frac{\alpha \cosh \alpha}{\sinh \alpha} - 1\right) \eta \sinh \alpha\eta - \alpha\eta \cosh \alpha\eta\right] \qquad (22)$$

where α represents the wave number for the periodic variation of the function $F(\xi, \zeta)$ as discussed by Pearson, and a is an arbitrary constant which represents the magnitude of the infinitesimal perturbation. Using Equation (22), the solution to Equation (21) is

$$g(\eta) = a[c_1 \sinh \alpha\eta + c_2 \cosh \alpha\eta + \Psi(\eta)] \qquad (23)$$

where the function $\Psi(\eta)$ is given by

$$\Psi(\eta) \equiv \left(\frac{1}{4\alpha^2}\right)\left(\frac{\alpha \cosh \alpha}{\sinh \alpha} - 1\right)(\alpha\eta^2 \cosh \alpha\eta - \eta \sinh \alpha\eta) + \left(\frac{3}{4\alpha}\right) \eta \cosh \alpha\eta - \left(\frac{1}{4}\right) \eta^2 \sinh \alpha\eta \qquad (24)$$

The adjustable constants, c_1 and c_2, are determined by the boundary condition represented by Equation (20) and by the boundary condition at the bottom wall. Pearson considers two limiting cases for the boundary condition at the bottom wall: a conducting case that corresponds to a constant concentration and an insulating case that corresponds to a constant concentration gradient at the bottom wall. The physical significance of these cases is discussed by Pearson in the context of the heat transfer problem.

In the present context, the continuous supply of the solute material at the bottom wall is perhaps difficult to visualize, but one could imagine the bottom wall to be a semipermeable membrane through which the solute diffuses from an intensely stirred solution beneath the membrane. In this case, if the permeability of the membrane were very high, the solute concentration just above the membrane would be in equilibrium with its concentration in the supply solution beneath the membrane; this would correspond to Pearson's conducting case. In the other extreme, if the permeation resistance of the membrane were quite high, a large concentration drop would occur owing to diffusion through the membrane. In the limiting case the flux through the membrane would be relatively un-

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* Note added in proof. It has now been established that no oscillatory modes exist. This will be documented in a subsequent publication.

affected by the concentration just above the membrane; this would correspond to Pearson's insulating case. The boundary condition at the bottom wall for the conducting case is

$$g(0) = 0 \tag{25}$$

For the insulating case, the boundary condition at the bottom wall is

$$g'(0) = 0 \tag{26}$$

These are identical to Pearson's Equations (20) and (21).

Using Equation (23), Equation (20) becomes

$$c_1\ (\alpha \cosh \alpha + M \sinh \alpha) + c_2\ (\alpha \sinh \alpha + M \cosh \alpha)$$
$$= -\left[M\Psi(1) + \Psi'(1) + \mathcal{A}\frac{f'(1)}{a} \right] \tag{27}$$

where M is used to represent $(L + \alpha^2\mathcal{S})$.

For the conducting case, Equation (25) applies, and it is clear from Equations (23) and (24) that

$$c_2 = 0 \tag{28}$$

Substitution of Equation (28) into Equation (27) yields

$$c_1 = \frac{-\left[M\Psi(1) + \Psi'(1) + \mathcal{A}\dfrac{f'(1)}{a} \right]}{\alpha \cosh \alpha + M \sinh \alpha} \tag{29}$$

For the insulating case, Equation (26) represents the boundary condition at the bottom wall. It then follows from the derivatives of Equations (23) and (24) that

$$c_1 = -\frac{3}{4\alpha^2} \tag{30}$$

Substitution of Equation (30) into Equation (27) yields

$$c_2 = \frac{\left(\dfrac{3}{4\alpha^2}\right)(\alpha \cosh \alpha + M \sinh \alpha) - \left[M\Psi(1) + \Psi'(1) + \mathcal{A}\dfrac{f'(1)}{a} \right]}{\alpha \sinh \alpha + M \cosh \alpha} \tag{31}$$

The value of the Marangoni number corresponding to neutral stability is obtained from the fourth condition of Pearson's Equation (17):

$$B = \frac{f''(1)}{\alpha^2\, g(1)} \tag{32}$$

The curve of neutral stability is a graph of the Marangoni number B versus the wave number α for fixed values of L, $\mathcal{S}$ and $\mathcal{A}$. It is obtained from these equations as follows:

For a selected value of α, c_1 and c_2 are given by Equations (29) and (28) for the conducting case and by Equations (30) and (31) for the insulating case. These values are then employed in Equation (23) with $\eta = 1$ to obtain $g(1)$. This value is then substituted into Equation (32) to obtain the Marangoni number B.

This procedure requires for each value of α the values of $\Psi(1)$, $\Psi'(1)$, $f'(1)$, and $f''(1)$. The function $\Psi'(\eta)$ is readily obtained by differentiating Equation (24) with respect to η. Similarly, Equation (22) is differentiated first once and then twice to produce the functions $f'(\eta)$ and $f''(\eta)$. This is quite straightforward, and the functions (which will not be written out here) are then all evaluated at $\eta = 1$ in Equations (29), (31), and (32). A digital computer program was written to accomplish these calculations for the neutral stability curves presented here.

RESULTS AND DISCUSSION

With $\mathcal{A} = \mathcal{S} = 0$, the present calculations reproduced the neutral stability curves given by Pearson in his Figures 1 and 2. In contrast to these are the curves obtained here for nonzero values of $\mathcal{A}$. Figure 1 presents an example of the neutral stability curves obtained, this example being for the "conducting case" with $L = \mathcal{S} = 0$. The solid curves are for $\mathcal{A} = 0.04$. For values of α between 0 and 1.43, the values of B are positive. The minimum value of B is found to be 1,170, occurring at $\alpha = 0.91$. This is the critical Marangoni number, below which the system is stable and above which the system is unstable to perturbations with wave numbers between the α values corresponding to the upper and lower branches of the curve. Remembering that Pearson obtained a critical Marangoni number of 80 for this case, it is seen that at $\mathcal{A} = 0.04$ surface convection in the Gibbs adsorption layer has stabilized the system to the point of raising the critical Marangoni number by a factor of 14.6.

For values of α greater than 1.43, it is seen in Figure 1 that the values of B are negative. At first it might be thought that surface convection could actually destabilize the system with negative Marangoni numbers because no negative branch exists when $\mathcal{A} = 0$. This is not the case because negative values of B and positive values of $\mathcal{A}$ do not correspond to a physically realizable system. Employing Equations (11) and (17), $\mathcal{A}$ can be expressed as

$$\mathcal{A} = \frac{\sigma\, C_{o_i}}{\beta\, RT\, d^2} \tag{33}$$

From Equations (19) and (33) it is seen that, if either σ or β is negative so as to make B negative, $\mathcal{A}$ will be negative also. Therefore, in Figure 1 the branch that corresponds to positive $\mathcal{A}$ and negative B has no physical significance.

For negative values of $\mathcal{A}$, neutral stability proved pos-

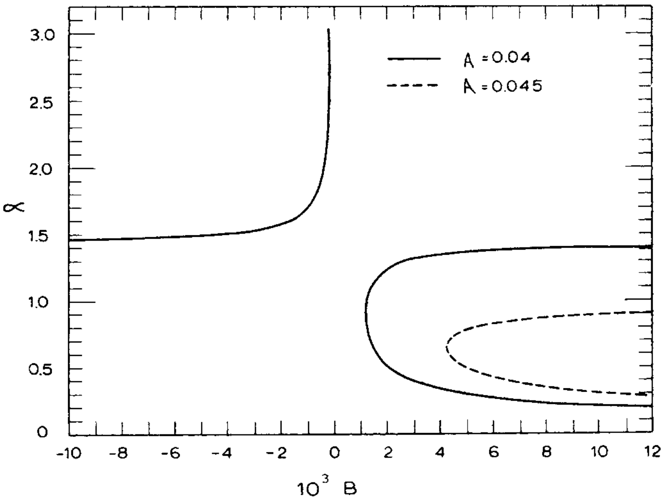

Fig. 1. Curve of neutral stability, conducting case, $L = S = 0$.

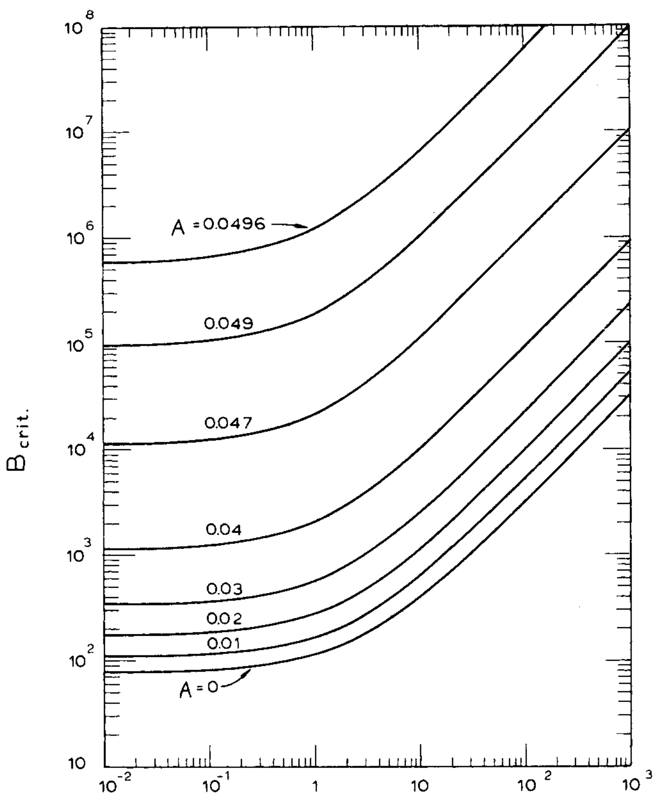

Fig. 2. Critical Marangoni number, conducting case, $S = 0$.

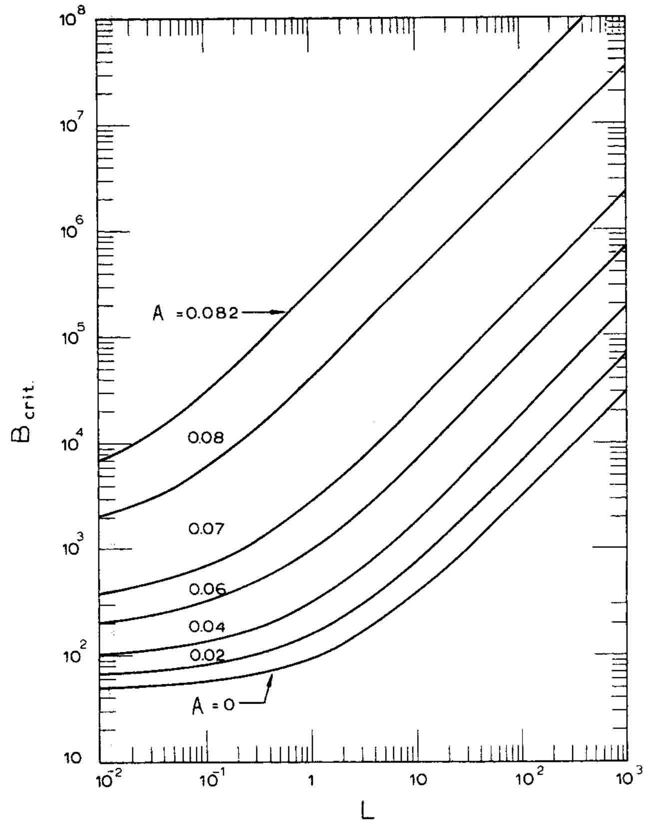

Fig. 4. Critical Marangoni number, insulating case, $S = 0$.

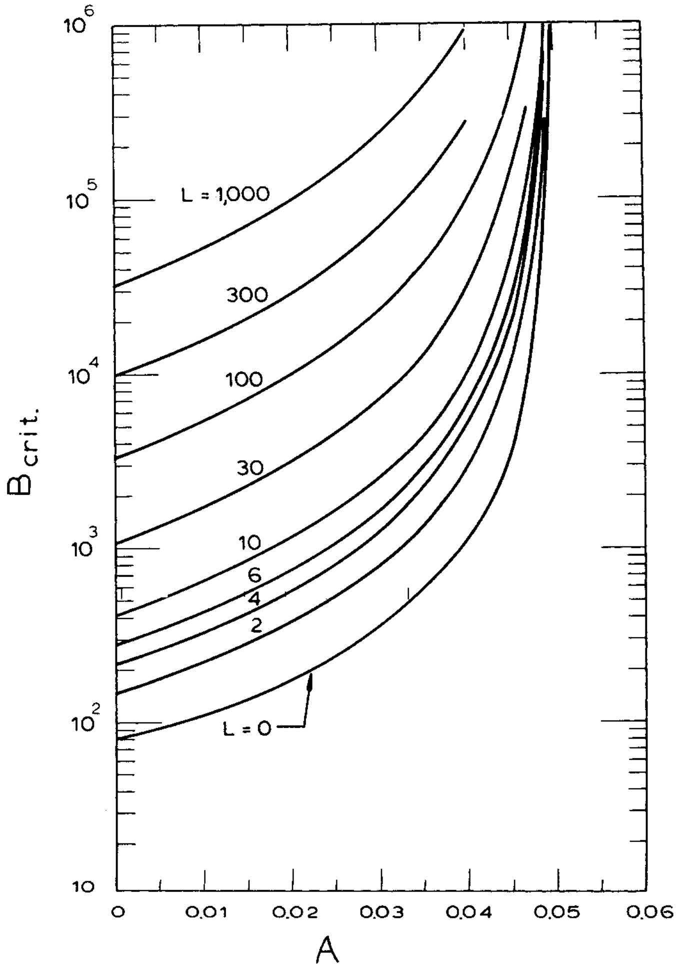

Fig. 3. Effect of A on $B_{crit.}$, conducting case, $S = 0$.

sible only with positive values of B, which also corresponds to a situation of no physical significance. The system is therefore always stable to transfer of the surface tension-lowering solute from the gas to the liquid phase ($\beta < 0$, $\sigma > 0$).

The dotted curve in Figure 1 shows the positive branch of the neutral stability curve for $\mathcal{A} = 0.045$. At this higher value of $\mathcal{A}$, the critical value of B has increased to 4,230, and the critical value of α has decreased to 0.64. The crossover from the positive branch to the negative branch occurs at $\alpha = 0.96$. As $\mathcal{A}$ increases further, this crossover value of α decreases toward zero and the critical value of B approaches infinity as $\mathcal{A}$ approaches 0.05.

Effect of Surface Convection

Anticipating that surface convection will be much more important than surface diffusion, consider first the case for which $\mathcal{S} = 0$. A number of additional neutral stability curves, such as those shown in Figure 1, were computed in order to determine the critical Marangoni number for a range of values of L and $\mathcal{A}$.

Figure 2 presents the results obtained for the conducting case, plotted as the critical value of B versus L at various values of $\mathcal{A}$. The lowest curve corresponds to $\mathcal{A} = 0$ and represents the solution obtained by Pearson. The upper curves correspond to the solution for increasing values of $\mathcal{A}$, and it is seen that $\mathcal{A}$ has a striking effect on the result. For $\mathcal{A} = 0.04$, the critical Marangoni number is increased fifteenfold at $L = 0$ and thirtyfold at $L = 1000$. Raising $\mathcal{A}$ to 0.049 raises the critical Marangoni number to a value approximately two thousand times the result with $\mathcal{A} = 0$. A very small further increase in $\mathcal{A}$ raises the critical Marangoni number to infinity.

Figure 3 is a cross-plot of the results in Figure 2, showing the critical Marangoni number plotted versus $\mathcal{A}$ at several values of L. Values of $\mathcal{A}$ less than 0.01 are seen to have relatively little influence upon the critical Mar-

TABLE 1. EXAMPLE OF TRIETHYLAMINE DESORPTION FROM WATER

Assumed values

$d = 10^{-3}$ cm
$\beta d = 0.7 \times 10^{-6}$ g.moles/cc.
$C^* = 0$
$\sigma = 1.2 \times 10^{6}$ (dyne) (sq. cm.)/g.mole
$\mu = 10^{-2}$ (dyne) (sec.)/sq. cm.
$\mathcal{D} = 0.8 \times 10^{-5}$ sq. cm./sec.
$T = 298$°K.
$L = 0.3$

Derived values

$C_{oi} = 0.23 \times 10^{-5}$ g.moles/cc.
$\delta = 0.485 \times 10^{-4}$ cm.
$\mathcal{A} = 0.16$
$B = 1.05 \times 10^{4}$

angoni number, but the curves rise rapidly and approach infinity at a critical value of $\mathcal{A}$, which is equal to 0.05, independent of the value of L. It is seen that surface convection in the Gibbs adsorption layer has a profound stabilizing influence on the system.

The stabilization of the system results from solute convection in the Gibbs layer, as represented by the last two terms in Equation (4) and the corresponding terms in Equations (6), (8), (10), and (12). At any point where the gas-liquid interface is expanding, convection in the Gibbs layer results in the removal of solute molecules, which tends to raise the surface tension at that point, opposing the expansion of the surface. Where the surface is contracting, convection in the Gibbs layer results in solute addition, lowering the surface tension and opposing the contraction.

Figures 4 and 5 present the corresponding results for the insulating case. With $\mathcal{A} = 0$, the critical Marangoni number is somewhat smaller for the insulating case than it is for the conducting case, reflecting the greater stability achieved when the concentration at the botom wall is held constant as in the conducting case. Figures 4 and 5 show that values of $\mathcal{A}$ required to stabilize the system are somewhat greater in the insulating case than they are in the conducting case. In Figure 5 the critical Marangoni number rises rapidly and approaches infinity at a critical value of $\mathcal{A}$ equal to 0.083, independent of the value of L. This value of $\mathcal{A}$ is greater than that observed in Figure 3 for the conducting case, again reflecting the poorer stability in the insulating case.

Effect of Surface Diffusion

Equation (5) may be put into the form

$$C_{oi} = \frac{\beta d}{L} + C^* \tag{34}$$

Combining Equations (18), (33), and (34) yields

$$\mathcal{S} = \left[\frac{\mathcal{D}_s/\mathcal{D}}{\frac{1}{L} + \frac{C^*}{\beta d}} \right] \mathcal{A} \tag{35}$$

For given values of $\mathcal{A}$ and L, $\mathcal{S}$ will be greatest when $C^* = 0$. Assuming that $\mathcal{D}_s \sim \mathcal{D}$, and considering the case with $C^* = 0$, Equation (35) becomes

$$\mathcal{S} = \mathcal{A}\, L \tag{36}$$

Such small values of $\mathcal{S}$ have very little effect on B_{crit}. This can be understood by referring to Equation (20) where the effect of surface diffusion adds to L the term $\alpha^2 \mathcal{S}$. For the conducting case with $\mathcal{A} = 0.04$, the critical value of α is 0.91 in Figure 1 and increases toward unity at larger values of L. With $\mathcal{S} = 0.04\ L$, the critical value of α shifts to slightly lower values but remains between 0.9 and unity. The effect of surface diffusion is, therefore, slightly less than that due to a 4% increase in L which, according to Figure 2, is less than a 4% increase in B_{crit}. With $\mathcal{A} = 0.02$, the effect is slightly greater. Here the critical value of α is approximately 1.9, and $\alpha^2 \mathcal{S}$ becomes 0.07 L, resulting in a 7% increase in $B_{\text{crit.}}$ at large values of L. This is the maximum effect observed for the conducting case.

For the insulating case the critical values of α are 1.68, 1.39, and 1.14 for $\mathcal{A} = 0.02$, 0.03, and 0.04, respectively. With $\mathcal{S} = \mathcal{A}L$, the maximum increase in $B_{\text{crit.}}$ is 6%, occurring at $\mathcal{A} = 0.025$.

It is seen that the effect of surface diffusion is not completely negligible but very much smaller than the effect of surface convection.

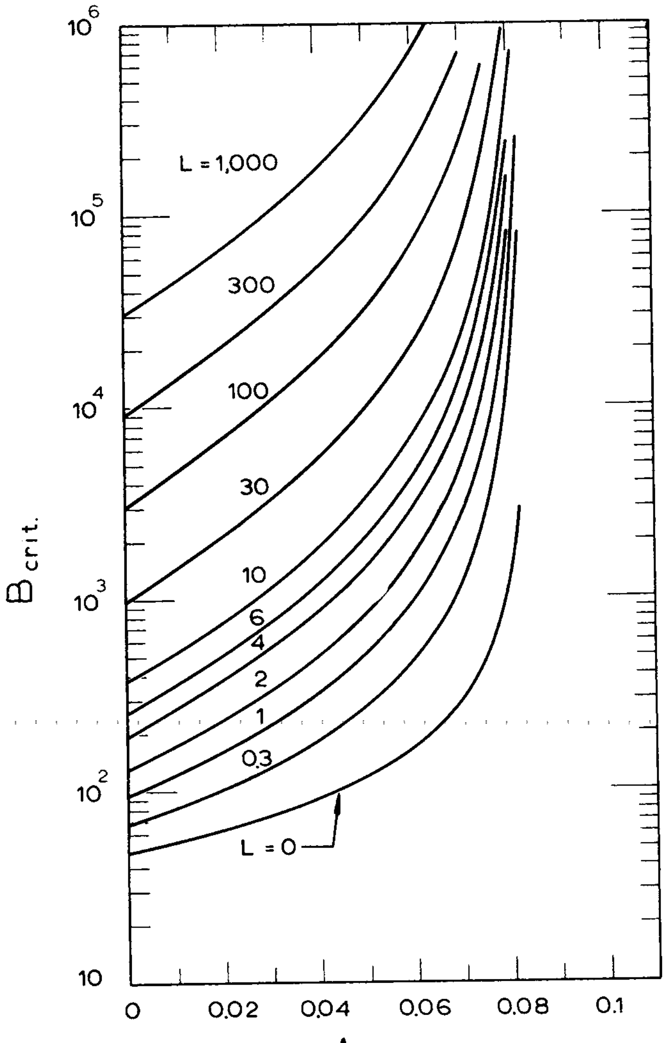

Fig. 5. Effect of A on $B_{\text{crit.}}$, insulating case, $S = 0$.

Significance

It remains to be shown that values of the adsorption number" $\mathcal{A}$ to be expected in laboratory experiments and in industrial processes might be in the range of 0.05 to 0.083 or greater. As an example, consider the desorption of triethylamine from water with a concentration at the bottom wall of 0.03 wt. % triethylamine and with a gas phase which is free of triethylamine. Assuming a liquid layer depth of 10^{-3} cm. and a value of L equal to 0.3, the parameters of the system are listed in Table 1.
The value of C_{o_i} is obtained from Equation (34). For this example, $B = 10^4$, which would cause instability if $\mathcal{A}$ were equal to zero. But $\mathcal{A} = 0.16$, large enough for complete stabilization in the insulating and conducting cases treated here.

This example corresponds approximately to the experimental critical Marangoni number for triethylamine determined in reference (*6*). The present analysis does not apply to that experimental system because there the mass transfer penetration depth was 10^{-3} cm. in a liquid layer 0.025 cm. deep. Vidal and Acrivos (*15*) analyzed the case in which the concentration gradient does not extend throughout the entire liquid layer depth, and their system is less stable than the cases treated by Pearson. When the effect of convection in the Gibbs layer is incorporated into their analysis, it may be expected that values of $\mathcal{A}$ somewhat higher than 0.083 will be required to stabilize the system. Hopefully, such further refinements of the theory will bring it into accord with the experimental data. For now, the example in Table 1 suffices to indicate that large values of $\mathcal{A}$ are encountered in the range where Figures 2 through 5 show a dominant influence of surface convection on the critical Marangoni number.

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NOTATION

$\mathcal{A}$ = $\Gamma_0/\beta d^2$, the adsorption number; represents surface convection
a = arbitrary constant in Equations (22), (23), (27), (29), and (31)
B = $\sigma\beta d^2/\mu\mathcal{D}$, the Marangoni number
C = solute concentration in liquid phase, g.-moles/cc.
C' = small perturbation in C
C^* = value of C in equilibrium with solute partial pressure in bulk gas
c_1, c_2 = adjustable constants, determined by Equations (29) and (28) for the conducting case and by Equations (30) and (31) for the insulating case
$\mathcal{D}$ = 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 (2) and (3)
$f(\eta)$ = function representing the variation of v with y, Equation (2); given by Equation (22)
$f'(\eta)$ 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 (3); given by Equation (23)
$g'(\eta)$ and $g''(\eta)$ = first and second derivatives of $g(\eta)$ with respect to η
H = Henry's law constant for solute, (atm.) (cc.)/ g.-mole
k_G = gas phase mass transfer coefficient, g.-moles/ (sec.) (sq.cm.) (atm.)
L = $Hk_Gd/\mathcal{D}$, liquid-to-gas phase resistance ratio
M = $L + \alpha^2\mathcal{S}$
p = growth rate constant for the disturbances, Equations (2) and (3).
R = ideal gas low 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 C_o with respect to y
Γ = surface concentration of solute in Gibbs adsorption layer, g.-moles/sq.cm.
Γ' = small perturbation in Γ
δ = σ/RT, Gibbs depth, cm.
ζ = z/d
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 = $t\mathcal{D}/d^2$
$\Psi(\eta)$ = function defined by Equation (24)
$\Psi'(\eta)$ = derivative of $\Psi(\eta)$ with respect to η

Subscripts

crit. = critical value
i = gas-liquid interface, $y = d$
o = unperturbed state

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