Stabilizing Effects of Surface-Active Agents on a Film Flow

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The effects of surface-active agents on the stability of a liquid film is reinvestigated. The present analysis differs from the previous works in the treatment of the surface boundary conditions. The well-known damping and stabilizing effects of surface-active agents are shown to be due to the redistribution of surface material caused by wave motions and diffusion. The equations of neutral stability for both cases of soluble and insoluble surface-active agents are obtained.

The instability of a liquid film contaminated by insoluble surface-active agents has been studied by Benjamin (*1*). The surface was assumed to be a thin layer of Voigt body material characterized by so-called *surface elasticities* and *surface viscosities*. His results indicate that surface viscosities do not have a direct effect on stability. The stabilizing effect was shown to be due to the variation of overall surface tension caused by the nonuniform straining of the surface film. The same problem was examined again recently by Whitaker and Jones (*10*). The surface was modeled with a Newtonian fluid, and both cases of soluble and insoluble surface-active agents were treated. Unfortunately, their free surface boundary conditions are not exact, since the dependence of the wave profile on the wave speed was not fully taken into account. The apparent agreement between their results and Benjamin's results for the case of insoluble surface-active agents will be explained in the following sections. In order to gain a deeper physical insight of the roles of surface-active agents, it seems worthwhile to investigate the same problem from a different point of view. Levitch's (*3*) theory will be used to show that the wave motion as well as the adsorption and desorption between the surface-active substances and the bulk of the liquid tend to collect the surface-active agents around the wave trough. This variation in concentration along the surface causes a surface tension variation which tends to lift the wave trough back to the undisturbed position, since it is known in statistical mechanics (*8*) that a larger concentration implies a lower surface tension.

THE FORMULATION OF THE PROBLEM

The primary flow consists of a layer of liquid covered with a microscopically thin film of a surface-active agent flowing down an inclined plane (see Figure 1). Using the depth of the liquid layer d and the average velocity U_a as units, and assuming the inclined plane is infinitely long, one can express the velocity distribution in the liquid layer in a dimensionless form as

$$U = \frac{3}{2}(1 - y^2) \tag{1}$$

where U is the velocity and y the distance measured perpendicularly from the free surface into the liquid film. The above equation is true even when the surface-active agent is soluble, since it is assumed that in the primary flow the surface-active agents and the main flow are in equilibrium.

The governing differential equation of the instability of the parallel flow is the well-known Orr-Sommerfeld equation (*5*)

$$\phi^{iv} - 2\alpha^2\phi'' + \alpha^4\phi = i\alpha N_{Re}\left[(U - c)(\phi'' - \alpha^2\phi) - U''\phi\right] \tag{2}$$

where ϕ is related to infinitesimal velocity disturbances u' and v' in the x and y directions by

$$\begin{aligned} u' &= \phi'(y)\exp\left[i\alpha(x - ct)\right] \\ v' &= -i\alpha\phi(y)\exp\left[i\alpha(x - ct)\right] \end{aligned} \tag{3}$$

In (2) and (3), we have put $t = \tau U_a/d$, where α is defined by $2\pi d/\lambda$ and $c = c_r + ic_i$ is the complex wave speed. As can be seen from (3), the disturbances will grow or decay exponentially with respect to time t depending on whether $c_i > 0$ or $c_i < 0$. If $c_i = 0$, there will be a sustained oscillation.

The boundary conditions at the bottom surface are the nonslip conditions

$$\phi(1) = 0 \tag{4}$$

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

The shear stress acting at the inner side of the free surface must be equal to the tangential force P_t' induced by the variation of the surface tension due to the redistribution of the surface-active agents caused by the wave motion; that is

$$\frac{U_a\mu}{d}\left[\frac{\partial(U + u')}{\partial y} + \frac{\partial v'}{\partial x}\right] = P_t' = P_t U_a^2\rho \tag{6}$$

Clearly

$$P_t' = -\text{grad. }\sigma = \frac{-\partial\sigma}{\partial\gamma_1}\text{grad. }\gamma_1 \tag{7}$$

where γ_1 is the concentration of the surface-active agents defined as the amount of the surface-active agents in mass per unit area. The concentration depends on the motion of the fluids as well as on the properties of the agents. Therefore, one will expect to have different expressions of P_t' for soluble and insoluble surface-active agents. First consider the case of insoluble agents. The law of conservation of mass enables one to write

$$\frac{\partial\gamma_1}{\partial\tau} + \text{div}(j_s + j_d) = 0$$

where $j_s = \gamma_1 \, U_a \, (U + u')$ is a convective flux of the surface-active agents along the liquid surface and $j_d = - D_{s1}$ grad. γ_1, D_{s1} being the surface diffusion coefficient is the diffusional mass flux arising on the surface. Thus, in terms of velocities, diffusion coefficient, and concentration, the above equation can be written in a dimensionless form as

$$\frac{\partial \gamma}{\partial t} + \frac{\partial}{\partial x} (U + u')\gamma = D_s \frac{\partial^2 \gamma}{\partial x^2}$$

where $D_s = D_{s1}/dU_a = 1/N_{Pe}$ and $\gamma = \gamma_1/\rho_s d$, ρ_s being the density of the surface material is the dimensionless concentration. Assuming the concentration can be written as $\gamma = \gamma_0 + \gamma'$, where γ_0 is the constant concentration on the undeformed surface and γ' is a small perturbation which is of the same order as the velocity perturbations, one can write in place of the above equation

$$\frac{\partial \gamma'}{\partial t} + U \frac{\partial \gamma'}{\partial x} + \gamma_0 \frac{\partial u'}{\partial x} = D_s \frac{\partial^2 \gamma'}{\partial x^2}$$

The solution of the preceding equation is readily obtained as

$$\gamma' = \frac{- i \, \gamma_0 \phi'(0)}{D_s \alpha - ic'} \exp{[i\alpha(x - ct)]}$$

where $c' = c - 3/2$.

Substitution of the above expression into the dimensionless form of Equation (7) gives

$$P_t = \frac{-\partial S}{\partial \gamma} \frac{\alpha \gamma_0 \phi'(0)}{D_s \alpha - ic'} \exp{[i\alpha(x - ct)]}$$

where $S = \sigma/\rho U_a^2 \, d$ is a dimensionless surface tension parameter.

With P_t given by the above equation, the surface condition (6) is to be evaluated at the deformed surface $y = \eta$ instead of $y = 0$, since the gradient of the shear stress is not zero at $y = 0$. On the other hand, η is related to v' by the kinematic condition at the free surface, that is, $v' = \partial\eta/\partial t + U \, \partial\eta/\partial x$ and is readily found to be $\eta = [\phi(0)/(c - 3/2)] \cdot \exp[i\alpha(x - ct)]$. With the expressions for P_t and η known, the free surface condition (6) can be written as

$$\phi''(0) + (\alpha^2 - 3/c')\phi(0) + \frac{i\alpha N_{Re}\Sigma}{c'} \phi'(0) = 0 \quad (8)$$

where $c' = c - 3/2$, $\Sigma = \gamma_0 \, (\partial S/\partial\gamma)$. In obtaining Equation (8), $D_s\alpha$ is neglected compared with $|ic|$, since the influence of the diffusion on the concentration distribution is insignificant compared with the influence due to convection. This point will be verified later.

The other boundary condition at the free surface, namely the balance of normal stress and the normal force induced by the surface tension, is the same for both contaminated and clean surface. The reason is that in this analysis, the surface deformation and thus the concentration variation are assumed to be infinitesimal. Therefore, the effects of surface variation in the normal direction is of second order. Hence, the normal boundary condition at the free surface is given by (*11*)

$$[\alpha(3 \cot\beta + \alpha^2 S N_{Re})/c']\phi(0) + \alpha(N_{Re}c' + 3\alpha i)\phi'(0) - i\phi'''(0) = 0 \quad (9)$$

Next, consider the case of soluble surface-active agents. When the equilibrium between the surface and the bulk of the liquid is destroyed by waves of period $1/\alpha c_r$, two limiting cases are possible. In the first, the relaxation time for the re-establishment of equilibrium between the surface and the bulk of liquid is large compared with the period of the wave motion. In the second, this relaxation time is so short that the surface and the bulk of the liquid are continually in a state of equilibrium. In the first case, the surface-active substance is essentially insoluble, and the solution of the problem for this limiting case should approach the results for the case of insoluble surface-active agents. The second limiting case differs significantly from the first case and deserves to be examined further. To obtain the boundary condition corresponding to (8) for this case, one considers the conservation of matter on the surface film. Again, neglecting the diffusion along the surface, one has

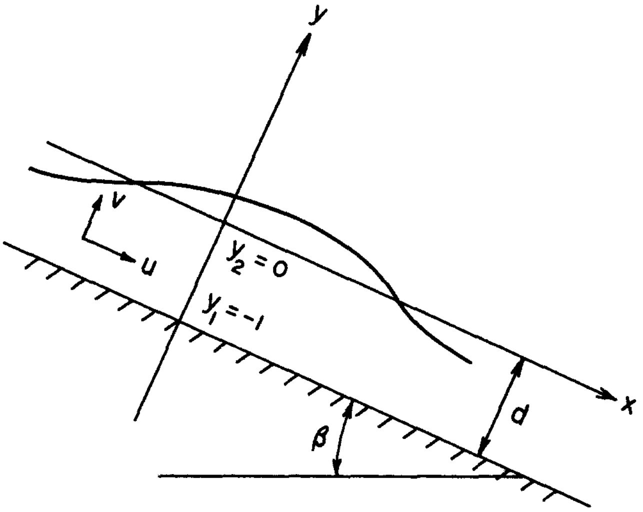

Fig. 1. Definition sketch.

$$\frac{\partial \gamma'}{\partial t} + U \frac{\partial \gamma'}{\partial x} + \gamma_0 \frac{\partial u'}{\partial x} = - \frac{D}{U_a d} \left(\frac{\partial s'}{\partial y} \right)_{y=0} \quad (10)$$

where γ' and s' are the concentration deviation from the equilibrium value on the surface and in the bulk of the liquid, respectively. The right side of Equation (10) gives the diffusion flow from the bulk.

The perturbations s' and γ' in the above equation are not, however, independent of each other. They are related by an equilibrium condition between the surface and the bulk of the solution (6); thus $\mu_n(\gamma_0 + \gamma') = \mu_p(s_0 + s')$. To the first-order in perturbations, one has

$$\gamma' = \frac{\left(\frac{\partial \mu_p}{\partial s} \right)_0}{\left(\frac{\partial \mu_n}{\partial \gamma} \right)_0} s'$$

where μ_p and μ_n are the chemical potentials of the bulk solution and of the solution on the surface, respectively. For a weak solution, one has (6)

$$\mu_p = kT \, \ln \, s + g \, (p, T)$$

The above two equations together give

$$\gamma' = \frac{kT}{s_0} \frac{1}{\left(\frac{\partial \mu_n}{\partial \gamma} \right)_0} s'$$

Substituting the above expression into Equation (10), one obtains

$$\frac{1}{s_0}\,\frac{kT}{\left(\dfrac{\partial \mu_n}{\partial \gamma}\right)_0}\left(\frac{\partial s'}{\partial t}+U\frac{\partial s'}{\partial x}\right)=$$

$$-\,i\gamma_0 c'\alpha\phi'(0)\exp\left[i\alpha(x-ct\right]+\frac{1}{N_{Pe}}\left(\frac{\partial s'}{\partial y}\right)_{y=0} \qquad (11)$$

where $N_{Pe} = U_a d/D$.

The above equation is the boundary condition at free surface to be satisfied by s'. On the other hand, s' is given with an accuracy to the first-order infinitesimals by the diffusion equation

$$\frac{\partial s'}{\partial t}+(U+u')\frac{\partial s'}{\partial x}=\frac{1}{N_{Pe}}\,\frac{\partial^2 s'}{\partial y^2}$$

The boundary-layer solution of the above equation, which satisfies Equation (11) and the boundary condition

$$s' = 0 \quad \text{at} \quad y = \infty \qquad (12)$$

is

$$s'=\frac{i\,\gamma_0\alpha\phi'(0)\exp\left[i\alpha(x-ct)\right]}{i\alpha c'\,\dfrac{kT}{s_0}\,\dfrac{1}{\left(\dfrac{\partial \mu_n}{\partial \gamma}\right)_0}+\left[\dfrac{-\,i\alpha c'}{N_{Pe}}\right]^{1/2}}\exp\cdot(-y)$$

The above expression and the relation between γ' and s' gives the concentration variation on the surface as

$$\gamma'=\frac{\gamma_0\phi'(0)\exp\left[i\alpha(x-ct)\right]}{c'+\dfrac{s_0}{kT}\left(\dfrac{\partial \mu_n}{\partial \gamma}\right)_0\left[i\dfrac{c'}{N_{Pe}}\right]^{1/2}}$$

For the boundary condition, Equation (12) is used rather than $s' = 0$ at $y = 1$, because of the fact that the diffusion-layer thickness is very small compared with the film thickness d.

With γ' given by the above expression, P_t induced by soluble surface-active agents is given by

$$P_t=\frac{-\,i\alpha\Sigma\phi'(0)\exp\left[i\alpha(x-ct)\right]}{c'\left[1+\dfrac{s_0}{kT}\left(\dfrac{\partial \mu_n}{\partial \gamma}\right)_0\dfrac{1}{c'}\left(i\dfrac{c'}{N_{Pe}\,\alpha}\right)^{1/2}\right]}$$

Substitution of the above equation into (6) yields the tangential boundary condition at the free surface covered with soluble agents, that is

$$\phi''(0)+\left(\alpha^2-\frac{3}{c'}\right)\phi(0)+\frac{i\alpha N_{Re}\Sigma'}{c'}\phi'(0)=0 \qquad (13)$$

where

$$\Sigma'=\frac{\Sigma}{1+\dfrac{s_0}{kT\,c'}\left(\dfrac{\partial \mu_n}{\partial \gamma}\right)_0\left(\dfrac{ic'}{N_{Pe}\,\alpha}\right)^{1/2}}$$

The normal boundary condition at the free surface covered with soluble agents is still given by Equation (9) for the reason that the additional normal force induced by the surface tension variation is of second-order in perturbations.

SOLUTION OF THE STABILITY PROBLEM

The Orr-Sommerfeld Equation (2) together with the boundary conditions (4), (5), (8), and (9) constitute an eigenvalue problem. The solution of this under the condition $c_i = 0$ gives the criterion of neutral stability for a liquid film covered with insoluble surface-active agents flowing down an inclined plane. A similar criterion for the same flow with soluble surface-active substance is obtained by solving another eigenvalue problem which consists of Equations (2), (4), (5), (13), and (9).

First, consider the case of insoluble surface agents. It is observed that the instability of a film covered with surface-active agents occurs at large wavelengths. For long wavelength, the wave number α is small, and the differential system (2), (4), (5), (8), and (9) can be solved by ordinary perturbation technique. For the first-order approximation, α can be set equal to zero, and Equation (2) becomes simply

$$\phi^{iv} = 0$$

The boundary conditions for this approximation are

$$\phi(1)=0,\quad \phi'(1)=0,\quad \phi''(0)-\frac{3}{c'}\phi(0)=0,$$
$$\text{and}\quad \phi'''(0)=0$$

The solution of the above system is found to be

$$\phi(y) = (1-y)^2, \qquad c = 3$$

The above results indicate that, to the first-order of approximation, the axis $\alpha = 0$ is part of the neutral stability curve for any value of β, S, and R as long as αR remains small. The next step is to find how the eigenvalue c is affected when α is increased from zero.

For the second approximation, Equation (2) becomes

$$\phi^{iv} = i\alpha N_{Re}\left[(U-c_0)\phi_0''-U''\phi_0\right]=-\,6i\alpha N_{Re}\,y \qquad (14)$$

The solution of Equation (14) can be written as

$$\phi = \phi_0 + \phi_1 \qquad (15)$$

where $\phi_1 = -i\alpha N_{Re}y^5/20 + \Delta By + \Delta Cy^2 + \Delta Dy^3$. The first term on the right-hand side of Equation (15) is the particular solution, and the rest is the complementary solution of (14). In the complementary solution, a constant term is omitted because the eigenfunction of a homogeneous linear system is determined only up to a constant multiplier. This constant was chosen to be 1 in the first approximation.

The corresponding boundary conditions for the second approximation are

$$\phi(1)=0,\quad \phi'(1)=0$$

$$\phi_1''(0)-\frac{3}{c_0'}\phi_1(0)+\left[3\Delta c'/(c_0')^2\right]\phi_0(0)$$
$$+\,i\Sigma\alpha N_{Re}\frac{\phi_0'(0)}{c_0'}=0,$$

$$\left[\alpha(3\cot\beta+\alpha^2 SN_{Re})/c_0'\right]\phi_0(0)$$
$$+\,\alpha N_{Re}\,c_0'\phi_0'(0)-i\phi'''(0)=0$$

where the subscript 0 denotes the results obtained in the first approximation, and $\Delta c'/(c_0')^2$ is the second term in the Taylor's series expansion of $1/c'$ around c_0. Substitution of (15) into the boundary conditions gives

$$\Delta B+\Delta C+\Delta D=i\alpha N_{Re}/20,$$

$$\Delta B+2\Delta C+3\Delta D=i\alpha N_{Re}/4,$$

$$\Delta C=-\frac{2}{3}\Delta c'+i\frac{2\Sigma\alpha N_{Re}}{3}$$

$$\Delta D=\frac{1}{2}\,i\alpha N_{Re}-\frac{i\alpha}{9}\left(3\cot\beta+\alpha^2 SN_{Re}\right)$$

The solution of the above system yields

$$\Delta c' = \Delta c_r + i\Delta c_i$$

where

$$\Delta c_i = i\alpha \left[\Sigma N_{Re} + \frac{6}{5} N_{Re} - \frac{1}{3}(3 \cot \beta + \alpha^2 S N_{Re}) \right] \tag{16}$$

and

$$\Delta c_r = 0 \tag{17}$$

Equation (16) shows that $c_i = 0$ at $\alpha = 0$ and will increase or decrease when α is increased from zero accordingly as

$$N_{Re} \gtrless \frac{5}{6} \left(1 + \frac{5\Sigma}{6}\right)^{-1} \cot\beta$$

That is to say, the neutral-stability curve has a bifurcation point at $\alpha = 0$, $N_{Re} = 5/6(1 + 5\Sigma/6)^{-1} \cot\beta$. The neutral-stability curve is obtained simply by letting $\Delta c_i = 0$ in Equation (16).

Since an increase in the surface concentration implies lowering of the surface tension, it is seen from the definition of Σ that Σ is a quantity of negative value. The case $\Sigma = 0$ is possible only when the surface is clean. Since Σ is negative, (16) shows that the insoluble surface-active substance is stabilizing, and it raises the critical Reynolds number for any given α from

$$N_{Re_1} = \frac{5}{6} (\cot\beta + \alpha^2 S N_{Re}/3) \tag{18}$$

to

$$N_{Re} = \frac{5}{6} \left(1 + \frac{5\Sigma}{6}\right)^{-1} (\cot\beta + \alpha^2 S N_{Re}/3) \tag{19}$$

These results can be used to obtain experimentally the change of surface tension with respect to the concentration of surface-active agents. First, one measures the critical Reynolds number and the wavelength for a given equilibrium concentration γ_0 and angle of inclination β. Second, compute the value of Σ from $N_{Re} = 5/6\ (1 + 5\Sigma/6)^{-1}$ $(\cot\beta = \alpha^2 S N_{Re}/3)$. Then obtain $\partial\sigma/\partial\gamma_1$ from the definition of Σ. Thus, the variation of surface tension with respect to the surface concentration can be determined with a single measurement. Equation (16) indicates that insoluble surface-active agents have stronger damping effects on shorter waves at high Reynolds number. It is seen from (17) that the surface active agents do not have a first-order effect on the wave speed. The effects of the surface active agent on the wave speed will have to be obtained from a higher approximation. Since the stabilizing effects of the surface active agents is the main concern in this paper and the analysis is based on a linearized theory, it does not appear worthwhile to carry out a higher order approximation for Δc_r. It is certainly more meaningful to find the effects of the surface-active agents on the wave speed from the point of view of nonlinear theory (9). The results of this analysis also verify the assumption $D_s\alpha << |ic|$ used in obtaining the tangential boundary condition at the free surface, since it has been found that $c = 3$ and the instability indeed occurs at small α. This assumption amounts to ignoring the diffusion of the surface-active agents along the surface.

A comparison of Δc_i given in this work and c_i given by equation (5.7) in Benjamin's work (*1*) indicates that the neutral stability curves obtained by two different approaches are identical if

$$T_1 = -\Sigma$$

In Benjamin's work, $T_1 = T' + T''$, where T' and T'' are the elastic moduli of surface dilatation and shear, respectively. However, the above relation is merely a formal one. T_1 and Σ represent totally different physical quantities as can be seen easily from their definitions. If one substitutes Benjamin's first-order solutions of the present eigenvalue problem into his free surface boundary conditions and properly identifies the material coefficients, one obtains Whitaker and Jones' (*10*) free surface boundary conditions. Whitaker and Jones obtained the imaginary part of the wave speed in their first approximation and the real part of the wave speed in the second-order approximation. This explains why the imaginary part but not the real part of their wave speeds agrees with Benjamin's result, since their boundary conditions are correct only for the first-order approximation.

The solution of the eigenvalue problem for the case of soluble surface-active agents can be put down immediately by noticing the fact that the governing differential system of this problem is identical to that of the previous problem if one puts $\Sigma = \Sigma'$ in the boundary condition (8). Substituting the expression of Σ' into Equations (16) and (17) for Σ (this step will not introduce an error in the approximation since Σ' is of order at most Σ), one has

$$\Delta c_i = \alpha \left\{ \frac{6}{5} N_{Re} - \frac{1}{3}(3 \cot\beta + \alpha^2 S N_{Re}) + \frac{3}{2} \Sigma\alpha N_{Re} \frac{3P_e\alpha\left(1 + \frac{1}{E\sqrt{2}}\right) - \frac{\sqrt{\alpha}}{2E\sqrt{3}N_{Pe}}\left[\frac{7N_{Re}}{120} - \frac{1}{54}(3\cot\beta + \alpha^2 S N_{Re})\right]}{6N_{Pe}\alpha\left(1 + \frac{1}{E\sqrt{2}}\right)^2 + 1/2E^2} \right\} \tag{20}$$

$$\Delta c_r = 0 \tag{21}$$

where

$$E = kT/s_0 \left(\frac{\partial \mu_n}{\partial \gamma}\right)_0$$

If the concentration in the bulk of the liquid (that is, s_0) is zero, then $1/E$ vanishes and Equations (20) and (21) are reduced to (16) and (17) as expected, since $s_0 = 0$ implies insolubility of the surface material. For finite solubility, it is seen from (20) that all neutral curves $c_i = \Delta c_i = 0$ pass through $\alpha = 0$, $N_{Re} = 5 \cot\beta/6$. Moreover, if the Peclet number is large, but the solubility is small, then (20) can be reduced to

$$\Delta c_i = \alpha \left\{ \frac{\frac{3}{2}\Sigma N_{Re}}{2\left(1 + \frac{1}{\sqrt{2}E}\right)} + \frac{6}{5} N_{Re} - \frac{1}{3} (3 \cot\beta + \alpha^2 S N_{Re}) \right\} \tag{22}$$

$$\Delta c_r = 0$$

and the neutral stability curve is given by

$$N_{Re} = \left[1 + \frac{15\Sigma}{24\left(1 + \frac{1}{E\sqrt{2}}\right)} \right]^{-1} \frac{5}{6} (\cot\beta + \alpha^2 S N_{Re}/3) \quad (23)$$

A comparison of Equation (23) with (18) and (19) indicates [note $E > 0$ and $\Sigma < 0$ (*6*)] that the neutral stability curve for the flow of a film covered with a slightly soluble surface-active material of small diffusion coefficient lies to the right of the neutral-stability curve of the same flow with a clean surface and to the left of the neutral-stability curve of a film covered with an insoluble surface-active agent. On the other hand, if the solubility is very high and the diffusion coefficient is very large (that is, N_{Pe} small but s_0 large), then in the limit, as can be seen from (20), the neutral-stability curve for the case of clean surface is recovered. Thus, the diffusion of the liquid from the bulk lowers the stabilizing effects of the surface-active agents. This reduction is especially prominent when the wavelength is large.

In general, the stabilizing effect of soluble surface-active substance depends not only on the elastic property Σ, the diffusion coefficient D, and the concentration s_0, but also on the wavelength. This is the main difference between soluble and insoluble surface-active agents. An experimental method of determining $\partial\sigma/\partial\gamma$ and $(\partial\mu_n/\partial\gamma)_0$ follows immediately from Equations (20) and (21). No direct comparison between the present results and the results of Whitaker and Jones is possible, because their results for the case of soluble surface-active agents were obtained as a fourth-order perturbation solution to an eigenvalue problem in which two of the boundary conditions are correct only up to the first-order approximation.

A physical explanation of the stabilizing effects of both soluble and insoluble surface-active substances is as follows. From the expression of the wave profile η, the concentration variation γ', and the eigenfunctions obtained in this analysis, it is easily seen that the surface wave motion and the mass transfer between the surface and the bulk of the liquid interacts in such a way that surface-active agents tend to accumulate around wave troughs. Thus, the surface tension around the trough is lowered, while that around the crest is raised. The consequent local surface tension gradients tend to bring the disturbed surface back to its original position. For the case of soluble active agents, this effect is smaller because the concentration around the trough is weakened by the diffusion of surface-active agents into the bulk of the film.

CONCLUSION

The equations of the neutral-stability curves for the flow of a film covered with soluble or insoluble surface-active agents are obtained. Both soluble and insoluble surface-active agents are found to have stabilizing effects. The effects of soluble surface-active agents are found to be weaker, owing to the diffusion of the solute from the bulk of the liquid into the surface. This reduction in the stabilizing effects is shown to depend on the wavelength as well as on the properties of the soluble active substances. The reduction is very prominent when the wavelength is large. A simple experimental method of measurement of surface tension reduction as a function of the concentration of surface-active agents is suggested. It should be pointed out that the foregoing analysis is only for the instability due to the long surface waves. The stabilizing effect of the surface-active agent may be so great that while the surface instability is completely suppressed, the film becomes unstable owing to Tollimen-Schlichting waves (7).

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NOTATION

c = complex wave speed
d = film thickness
D = bulk phase diffusion coefficient
D_{s1} = surface diffusion coefficient
g = gravitational acceleration
k = Boltzman's constant
N_{Re} = Reynolds number
N_{Pe} = Peclet number
P_t' = tangential force induced by the variations of the surface tension
P = pressure
s_0 = equilibrium bulk concentration
s' = deviation of the bulk concentration from the equilibrium value
t = dimensionless time
T = absolute temperature
U = mean velocity
u' = velocity perturbation in the direction of the flow
v' = velocity perturbation in the direction normal to the flow
x, y = spatial coordinates

Greek Letters

α = wave number
β = angle of inclination of liquid film
γ = surface concentration
η = surface wave profile
λ = dimensionless wavelength with d as unit
μ = dynamic viscosity
μ_p = chemical potential of the bulk solution
μ_n = chemical potential of the surface solution
ρ = density of the film liquid
σ = surface tension
Σ = a coefficient of variation of surface tension
τ = dimensional time
ϕ = velocity potential

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