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Wind-generated waves in thin liquid films with soluble contaminant

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Craik (1968) has previously examined the stability of horizontal liquid films when an air stream flows over the liquid surface and when the surface is contaminated by an insoluble surface-active agent. The present theoretical work extends this investigation to examine the role of soluble surface-active agents for cases where the liquid Reynolds number is small. This role is found to be a rather complex one which, under suitable conditions, may be either stabilizing or destabilizing.

Related experimental work is described which yields results in qualitative agreement with the theoretical analysis.

1. Introduction

Experimental and theoretical investigations by Craik (1966) of wave generation by wind on thin horizontal liquid films revealed a previously unknown type of instability which arises when the film thickness is sufficiently small. Later, the same author (Craik 1968) performed two theoretical analyses to examine the influence of insoluble surface-active agents on the conditions for wave generation by wind in liquid films at moderately large and at small Reynolds numbers respectively. In these analyses, as in earlier work by Benjamin (1963), the properties of the contaminated surface are identified with those of a visco-elastic membrane: thus, deformation of the surface produces quasi-elastic and quasi-viscous forces which are attributable to a surface elasticity and surface viscosity respectively.

The analysis at large liquid Reynolds numbers showed that surface contamination enhances stability owing to increased dissipation in the viscous layer just within the liquid surface. Similar results have been obtained by Levich (1962), Dorrestein (1951), Miles (1967) and others in the absence of a primary shear flow in the liquid, and this mechanism is now well understood. The analyses at low Reynolds number by Benjamin (1963) and Whitaker (1964) reveal that surface elasticity also exerts a stabilizing influence on falling liquid films: but the physical mechanism operating in this case differs from that just described for large Reynolds numbers. On the other hand, Craik's analysis at small liquid Reynolds numbers indicates that the presence of surface elasticity may promote instability, and the present work originated as an attempt to discover whether this is indeed so.

Many surface-active agents are somewhat soluble in water. Also, in thin films at low Reynolds numbers, waves travel very slowly (with velocities of the same order as that of the liquid surface) in comparison with waves in films at larger Reynolds numbers. Accordingly, the time available during one wave period for the transfer of material between the adsorbed surface layer and the bulk solution is correspondingly greater for the former than for the latter. Because of this, the influence of solubility of the surface-active agent is more likely to be felt in the thinner films, and it was thought necessary to include such effects in the present analysis. On the other hand, it was not considered worthwhile to investigate the effects of solubility on the stability of films at larger Reynolds numbers: the comparatively short periods of waves in the latter case are likely to ensure that, as far as stability considerations are concerned, most surface-active agents will behave as if they are virtually insoluble.

The effect of soluble surface-active agents on the damping of waves in deep water has been considered by van den Tempel & van de Riet (1965), Levich (1962), Miles (1967) and Lucassen & Hansen (1967). Also, Whitaker (1964) has shown that diffusion of solute may decrease the stabilizing action of surface contamination on falling liquid films at low Reynolds numbers. The present formulation of the equations and boundary conditions satisfied by the surface-active material is similar to that of those authors; but, in most other respects, the formulation of the stability problem follows that of Craik (1968).

To avoid possible confusion, the concentration of surface-active material in the bulk solution (in, say, moles cm^{-3}) will hereafter be called the 'solute concentration' while the surface concentration of adsorbed surface-active material (in, say, moles cm^{-2}) will be designated the 'surfactant adsorption'. The distribution of solute concentration is determined by the processes of convection and molecular diffusion, and the surfactant adsorption is directly related to the solute concentration just within the surface. Also, since matter is necessarily conserved during the transfer of material between the solution and the adsorbed surface layer, molecular diffusion normal to the surface along a gradient in solute concentration must result in a corresponding change in the amount of adsorbed material on the surface. In addition, local extension or contraction of the surface will bring about a respective deficit or excess both of surfactant adsorption and of solute concentration just within the surface.

Since the surface tension of the liquid is a function of the surfactant adsorption, local changes in surfactant adsorption produce corresponding variations in surface tension, and these contribute to the distribution of tangential stress at the liquid surface. This stress distribution in turn affects the motion of the liquid.

Thus, the dynamical influence of soluble surface-active material depends on four separate factors: the mean concentration of such material present, the functional dependence of surfactant adsorption on solute concentration and of surface tension on surfactant adsorption, and the molecular diffusivity of the solute.

A further factor, which is neglected in the present work, is surface diffusion of the adsorbed material. Even when the surface-active material is virtually insoluble and no significant molecular diffusion takes place in the bulk liquid, diffusion of adsorbed material along the surface may occur. Indeed, this process may readily be identified with the 'surface viscosity' of insoluble monolayers. However, with soluble material and, particularly, for the thin liquid films investigated here, surface diffusion is likely to remain unimportant in comparison with the transfer of material between the adsorbed layer and the solution.

The present investigation concerns waves in thin films at low Reynolds numbers when the influence of viscosity is felt throughout the depth of the liquid. This is in contrast to the situation at larger Reynolds numbers when the viscous effects are significant only in two thin layers, one close to the liquid surface and the other adjacent to the bottom boundary. Now, the diffusivity of solute is invariably small compared with the kinematic viscosity; and so, depending on circumstances, the influence of the former may either extend throughout the film or remain confined to thin layers near the boundaries of the film. To account for both possibilities two approximate analyses are developed. In the first of these, the equation governing the solute concentration is solved in the same approximate manner as are the equations of motion for long waves at low Reynolds numbers; while, in the second analysis, asymptotic approximations are used which are valid in the very thin boundary-layer regions where variations of solute concentration occur.

Further introductory remarks concerning other aspects of the present work, such as the formulation of the linearized stability problem and evaluation of the stresses exerted by the airflow on the perturbed liquid surface, are contained in the introductions to the papers of Craik (1966, 1968). For brevity, these have not been repeated here.

In § 2, some experimental work is described in which air is blown over contaminated liquid films and the conditions for onset of instability are determined. The equations governing the surface film and solute concentration are described in § 3 and the stability problem is formulated in § 4. The two separate analyses for large and small diffusion respectively are described in §§ 5 and 6, and a concluding discussion is given in § 7.

2. The experiment

2.1. *Apparatus and materials*

The apparatus was, in the main, that used by Craik (1966) in his investigations of uncontaminated liquid films, and reference may be made to that paper for descriptive details. An explanatory diagram is given in figure 1. The flow of air and water through the channel could be controlled independently, and the entry section was designed to allow the formation of very thin uniform liquid films. The airflow was measured by a movable Pitot-static arrangement of two parallel tubes of 1 mm bore attached to a 'Mercury' Greer manometer. The surface velocity and volume flux of the water film were measured directly and the film thickness was calculated in the manner described by Craik (1966, p. 373).

For a given airflow, the amount of water entering the apparatus could be finely adjusted until the critical conditions for wave formation were reached. In the present experiment the influence on these conditions of two different surface-active agents, Teepol and camphor, was examined.

Teepol is an industrial cleansing solution which is miscible with water and which has strong surface-active properties. It was first filtered to remove suspended matter and was used in two separate concentrations of 1 part Teepol to 2 parts and 4 parts respectively of water. This solution was allowed to drip from a thistle funnel of narrow bore onto the sponge-filled water reservoir at the entry section of the apparatus. The drip rate remained constant at 0·11 cm^3/min for the 1:2 solution and 0·15 cm^3/min for the 1:4 solution.

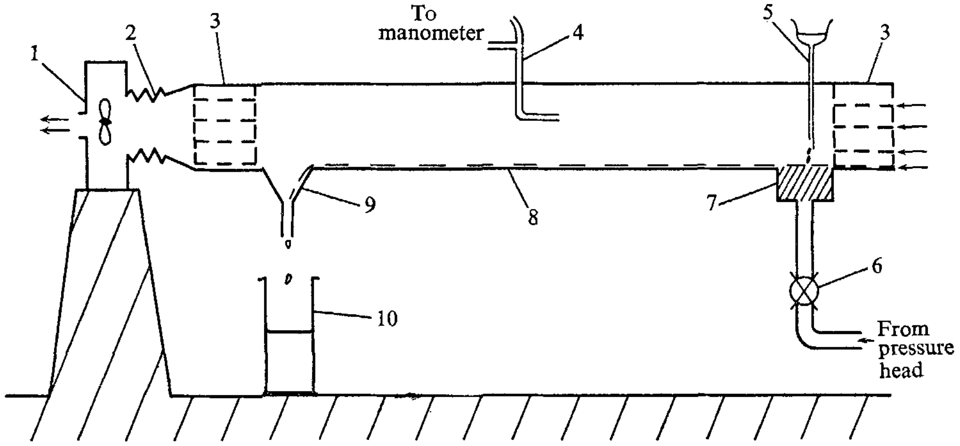

FIGURE 1. Diagram of apparatus (not to scale). 1, fan; 2, flexible ducting; 3, honeycomb grid; 4, Pitot-static tube, attached to manometer; 5, thistle funnel for application of Teepol; 6, needle valve controlling flow from head tank; 7, sponge-filled reservoir; 8, water film; 9, water exit; 10, measuring jar.

Camphor was introduced to the apparatus by the simple expedient of placing several solid pieces on the surface of the sponge-filled reservoir: the camphor then spread naturally over the liquid surface. Unfortunately, this method does not lend itself to a satisfactory determination of the amount of camphor present on the liquid film. Indeed, no attempt was made, for either contaminant, to measure the surface properties of the liquid. Such measurements, on a moving liquid film of thickness around 0·3 mm and in the presence of an air stream, are beyond the scope of the present authors' experimental talents, however desirable the results might be!

Very thin uniform films could be maintained in the presence of the airflow. When Teepol was added, such films were more easily maintained than for clean water. Initial difficulty was encountered when camphor was added, owing to the reluctance of the water film to leave the glass plate at the outlet end of the apparatus; but this was overcome by attaching several small pieces of foam rubber to the edge of the plate, which facilitated the flow over the edge.

2.2. *Observations*

(*a*) *Clean water*. With clean water, the results of Craik (1966) were confirmed. In particular, with constant airflow, a steady reduction in the film thickness produced the following sequence of events: (i) a 'pebbled' surface occurred for thick films; (ii) regular 'fast' waves travelling down the channel were obtained on decreasing the film thickness; (iii) these waves disappeared for still thinner films, leaving an essentially smooth surface; (iv) for very thin films, the surface again exhibited disturbances in the form of 'slow' waves; (v) with further decrease of the water flow, dry patches formed on the plate.

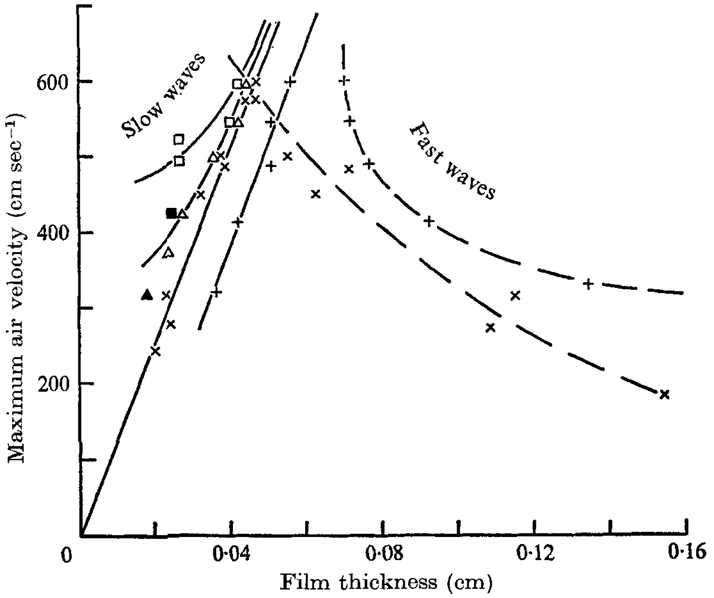

FIGURE 2. Maximum air velocity plotted against thickness of water film at transition from a stable film to 'slow' waves (——) and to 'fast' waves (- - -). ×, uncontaminated film; +, contamination by camphor; △, contamination by 1:4 Teepol solution; □, contamination by 1:2 Teepol solution. The points marked by ▲ and ■ denote observations of *stable* films with contamination by 1:4 and 1:2 Teepol solutions respectively.

(*b*) *Contamination by Teepol.* When a *single drop* of Teepol was allowed to fall onto the water reservoir, disturbances of type (i) and (ii) were immediately eliminated, to reappear after several seconds when the contaminant had been flushed out of the channel. When Teepol was continuously applied to the apparatus in the manner described above, disturbances of type (i) and (ii) could not be produced even at the maximum airflow available (i.e. a maximum velocity of just over 600 cm sec^{-1} in the centre of the channel). However, on reduction of the water flow, 'slow waves' of type (iv) were observed; but their onset occurred at film thicknesses *less* than the corresponding ones for clean water. Teepol therefore increased the range of stable film thicknesses by eliminating 'fast waves' and by restricting the occurrence of 'slow waves' to even thinner films than for clean water. This effect was greater with the stronger 1:2 solution of Teepol than with the weaker 1:4 solution.

Quantitative results showing the critical film thickness for onset of 'slow waves' against the maximum air velocity in the channel are given in figure 2 along with the corresponding results for clean water (cf. Craik 1966, figure 5). Results could not be obtained at film thicknesses less than about 0·02 cm, owing to drying of the film. However, two results are recorded of conditions where a very thin film remained *stable*, but where further reduction of the water flow rate caused the film to dry.

This drying process is worthy of mention. For uncontaminated films, small local dry patches first formed just ahead of the crests of slow waves (which had become horseshoe-shaped, concave in the downstream direction). These dry patches then grew in time, breaking up the film into separate wet streaks. However, when contaminated by Teepol, the film was found on several occasions to dry in a remarkably uniform manner. Indeed, once, when the water flow was inadvertently stopped, the authors attempted to observe the onset of 'slow waves' in a completely dry channel, so imperceptibly and uniformly had drying occurred!

A further feature occurred in these contaminated films which was absent in the uncontaminated case. On an otherwise stable film, a 'streak' or indentation would sometimes extend lengthwise for some distance down the channel. These originated at the entry section and, on occasion, extended right to the channel exit. Such streaks were best seen when the channel was illuminated from one side: the streak then cast a dark shadow on a sheet of white paper attached to the underside of the glass plate. A photograph of such a streak is shown in figure 3, plate 1. When a streak occurred, quantitative observations of onset of instability could not be made since the film was no longer uniform. It was found that the streaks could be eliminated by careful smoothing of the sponge-rubber in the entry section.

The explanation of these streaks is simple but interesting. An irregularity of the entry section causes an indentation of the film surface, where the film is locally thinner than elsewhere. With clean water, such an indentation is readily filled by flow under gravity from the adjacent regions where the film is thicker. However, when the liquid surface is contaminated, it resists extension and contraction, and the inflow to fill the indentation is inhibited. If the surface is sufficiently contaminated, it is virtually immobile, and the inflow under gravity is then a small fraction of that for a clean surface. Consequently, the initial indentation may persist for a considerable distance downstream.

(*c*) *Contamination by camphor.* With camphor, 'fast waves' of case (ii) are inhibited, but not eliminated as in (*b*) above. The onset of fast waves occurred at larger film thicknesses than for clean water, thereby extending the region of stability. However, the transition from a stable film to slow waves of type (iv) also occurred at larger film thicknesses than in the uncontaminated case, and this acts to decrease the region of stability. These results are shown in figure 2, where they may be compared with those for clean water and for contamination by Teepol.

A remarkable feature of the results is that, whereas Teepol restricted the appearance of slow waves to *thinner* films than for clean water, camphor has the opposite effect: it permits slow waves to occur in *thicker* films than with clean water.

Attempts to measure the velocities of propagation of slow waves were inconclusive. These velocities were always less than that of the liquid surface; but the dependence of propagation velocity on wave amplitude indicated that nonlinear effects were present whenever the waves were sufficiently visible to allow their speeds to be determined.

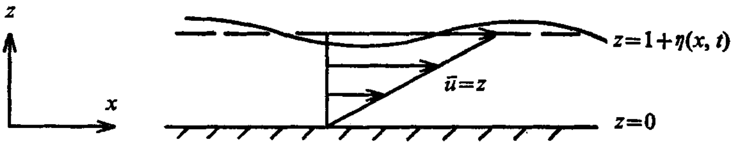

FIGURE 4. Sketch of shear flow and surface disturbance.

3. Surface-active agent

The primary flow configuration is shown in figure 4. In the ensuing analysis, all quantities are made dimensionless with respect to the surface velocity V of the liquid film, the film thickness h and the liquid density ρ. The liquid occupies the region between the rigid boundary $z = 0$ and the free surface $z = 1$, and motion is in the x direction with dimensionless primary velocity profile $\bar{\mathbf{u}} = [\bar{u}(z), 0, 0]$. The motion of the liquid derives from a constant mean tangential stress exerted on the undisturbed free surface by a co-current air stream. The pressure gradient in the direction of motion produces negligible curvature of the liquid velocity profile provided the depth of the air phase is large compared with that of the liquid. This condition is well satisfied, for example, in the experiments described in §2. Consequently, the primary liquid velocity profile may be taken to be linear, with $\bar{u}(z) = z$.

In the subsequent stability analysis, this primary flow is assumed to be perturbed by a small disturbance periodic in the x-direction. Such a disturbance causes periodic contractions and expansions of elements of the liquid surface, which produce corresponding periodic changes in the surfactant adsorption about its equilibrium value. These, in turn, are related to fluctuations of the (dimensionless) solute concentration C about its equilibrium value C_0.

The solute concentration C is governed by the linearized equation (cf. Miles 1967; van den Tempel & van de Riet 1965; Levich 1962)

$$\frac{DC}{Dt} \equiv \left(\frac{\partial}{\partial t}+\bar{u}\frac{\partial}{\partial x}\right) C = \Delta(\nabla^2 C), \tag{3.1}$$

where $\Delta \equiv \kappa/Vh$ is a dimensionless parameter proportional to the molecular diffusivity κ of solute. Also, since there is no diffusion of solute across the rigid boundary at $z = 0$,

$$\partial C/\partial z = 0 \quad (z = 0). \tag{3.2}$$

The appropriate boundary condition at the free surface is more complex, and requires some derivation. The amount of contaminant adsorbed on a material surface element of area A is ΓA, where Γ is the surfactant adsorption (both A and Γ being dimensionless). This amount ΓA may vary owing to diffusion of solute normal to the surface. Thus,

$$D(\Gamma A)/Dt = -\Delta A(\partial C/\partial n)_s,$$

where n denotes the direction normal to the surface and the subscript s denotes evaluation at the surface. Such a relationship was first proposed by Boussinesq (1913). Linearization yields

$$\frac{D\Gamma}{Dt} \equiv \left(\frac{\partial}{\partial t}+\bar{u}\frac{\partial}{\partial x}\right)\Gamma = -\frac{\Gamma}{A}\frac{DA}{Dt}-\Delta\left(\frac{\partial C}{\partial z}\right)_s.$$

Also, to linearized approximation, the rate of dilatation of a surface element is

$$\frac{1}{A}\frac{DA}{Dt} = \left(\frac{\partial u}{\partial x}\right)_s,$$

where u is the velocity component in the x direction. Therefore,

$$\frac{D\Gamma}{Dt} = -\left(\Gamma\frac{\partial u}{\partial x}+\Delta\frac{\partial C}{\partial z}\right)_s.$$

But the solute concentration C just inside the surface and surfactant adsorption Γ are directly related by some function $\Gamma(C)$, and small deviations from their equilibrium (i.e. unperturbed) values C_0, Γ_0 must satisfy the relationship

$$\Gamma-\Gamma_0 = \lambda(C-C_0)_s, \tag{3.3}$$

where $\lambda \equiv (d\Gamma/dC)_0$ is evaluated at equilibrium conditions. Similar relationships are derived by Miles (1967) and Levich (1962). On eliminating Γ from the above two results, the surface boundary condition satisfied by C is found to be

$$\left[\frac{DC}{Dt}+\frac{\Gamma}{\lambda}\frac{\partial u}{\partial x}+\frac{\Delta}{\lambda}\frac{\partial C}{\partial z}\right]_s = 0. \tag{3.4}$$

4. The stability problem

The primary flow described above is considered to experience a small two-dimensional perturbation such that the vertical displacement of the liquid surface is

$$z-1 = \eta(x,t) = \delta\, e^{i\alpha(x-ct)}. \tag{4.1}$$

Here, α and c are the dimensionless wave-number and complex phase velocity of the disturbance. The corresponding perturbation velocity components $(\hat{u}, 0, \hat{w})$ are expressible in terms of a stream function $\psi(x,z,t) \equiv -\phi(z)\,\eta(x,t)$ as

$$\hat{u} = \partial\psi/\partial z = -\phi'\eta, \quad \hat{w} = -\partial\psi/\partial x = i\alpha\phi\eta, \tag{4.2}$$

where the prime denotes differentiation with respect to z. On taking the primary velocity profile to be $\bar{u}(z) = z$, the linearized equations of motion yield the Orr–Sommerfeld equation in the form

$$\phi^{\mathrm{iv}}-2\alpha^2\phi''+\alpha^4\phi = i\alpha R(z-c)(\phi''-\alpha^2\phi), \tag{4.3}$$

where $R \equiv Vh/\nu$ is the Reynolds number of the liquid film and ν the kinematic viscosity.

The boundary conditions governing the motion are, with one exception, the same as those used by Craik (1968). At the rigid boundary,

$$\phi(0) = \phi'(0) = 0, \tag{4.4a,b}$$

and the kinematic surface condition is

$$\phi(1) = 1-c. \tag{4.5}$$

As in Craik (1966, 1968), the dimensionless normal and tangential stress perturbations exerted by the air stream on the liquid surface are represented as

$$\sigma_{yy} = \Pi\eta(x,t), \quad \sigma_{xy} = \Sigma\eta(x,t),$$

respectively, where the parameters Π and Σ are complex. The normal stress condition at $z = 1$ is then (cf. Craik 1968, equation (2.11))

$$(1-c)\,\phi' - \phi - (i\alpha R)^{-1}(\phi''' - 3\alpha^2\phi') - (T_0\alpha^2 + G - \Pi)(1-c)^{-1}\phi = 0, \tag{4.6}$$

where $G \equiv gh/V^2$, $T_0 \equiv \gamma(\rho V^2 h)^{-1}$ are dimensionless gravity and surface tension respectively, g being gravitational acceleration and γ the mean value of the coefficient of surface tension. Note that this boundary condition is influenced by the presence of surface-active agents only through the reduction in mean surface tension from its value for clean surfaces.

However, in the tangential-stress boundary condition, allowance must be made for variations in surface tension, which produce additional periodic stresses at the contaminated surface. Also, the dimensionless surface-tension parameter T is a function of the surfactant adsorption; i.e. $T = T(\Gamma)$, where $T(\Gamma_0) = T_0$. The tangential stress component due to deformation of the contaminated surface is then, to linearized approximation,

$$\bar{\sigma}_{xz} = \frac{\partial T}{\partial x} = \left(\frac{dT}{d\Gamma}\right)_0 \frac{\partial \Gamma}{\partial x} = \left(\frac{dT}{d\Gamma}\right)_0 \lambda \frac{\partial C}{\partial x}, \tag{4.7}$$

where $(dT/d\Gamma)_0$ is evaluated at the equilibrium value Γ_0 of surfactant adsorption. The quantity

$$T_1 \equiv -\Gamma_0(dT/d\Gamma)_0$$

is readily identified with the dimensionless surface-elasticity parameter

$$T_1 = \gamma_1(\rho V^2 h)^{-1}$$

used by Benjamin (1963) and Craik (1968), where γ_1 is the sum of the elastic moduli of surface dilatation and shear.

At this stage, it is convenient to write the perturbation in solute concentration as

$$C - C_0 = f(z)\,\eta(x,t). \tag{4.8}$$

Equation (4.7) then becomes

$$\bar{\sigma}_{xz} = -\frac{T_1\lambda}{\Gamma_0}\frac{\partial C}{\partial x} = -\frac{T_1\lambda}{\Gamma_0} i\alpha f\eta(x,t),$$

and the linearized boundary condition expressing continuity of tangential stress at the surface (cf. Craik 1968, equation (2.13)) is readily found to be

$$\phi'' + [\alpha^2 + R\Sigma(1-c)^{-1}]\,\phi - (T_1\lambda/\Gamma_0)\,i\alpha R f = 0 \quad (z = 1). \tag{4.9}$$

Equation (4.3) and the boundary conditions (4.4*a, b*), (4.5), (4.6) and (4.9) do not yet constitute a complete set which determines the motion, since the boundary condition (4.9) contains the unknown quantity $f(1)$. The governing equation for the solute concentration is found from (3.1) and (4.8) to be

$$f''-[\alpha^2+i\alpha\Delta^{-1}(z-c)]f=0, \tag{4.10}$$

while the boundary condition (3.2) is

$$f'=0 \quad (z=0). \tag{4.11}$$

Recalling that, to linearized approximation, the horizontal velocity u of the liquid surface is $\hat{u}+\bar{u}'\eta$ evaluated at $z=1$, the remaining boundary condition (3.4) reduces to

$$(1-c)f+\Delta(i\alpha\lambda)^{-1}f'+(\Gamma_0/\lambda)(1-\phi')=0 \quad (z=1). \tag{4.12}$$

The addition of equation (4.10) and boundary conditions (4.11), (4.12) to those above completes the specification of the eigenvalue problem for the complex phase velocity c.

This set of equations will now be solved approximately for two different models. In § 5, we consider cases where the perturbations of solute concentration extend throughout the depth of the liquid; and, in § 6, we examine a model in which such perturbations are significant only in a very thin layer next to the liquid surface. It should perhaps be recalled that, for both models, the kinematic viscosity of the liquid is large compared with the molecular diffusivity of solute.

5. Diffusion throughout film

If $\alpha\Delta^{-1}$, $\alpha|c|\,\Delta^{-1}$ and α^2 are small compared with unity the function $f(z)$ may be expressed as a series in ascending powers of z,

$$f(z)=\sum_{n=0}^{\infty}B_n z^n,$$

and the constants B_n determined by substitution for f in (4.10). It is found that

$$f=B_0\{1+\tfrac{1}{2}(\alpha^2-i\alpha c\Delta^{-1})z^2+i\alpha\Delta^{-1}z^3+\tfrac{1}{24}(\alpha^2-i\alpha c\Delta^{-1})^2z^4+\ldots\}$$
$$+B_1\{z+\tfrac{1}{6}(\alpha^2-i\alpha c\Delta^{-1})z^3+\tfrac{1}{12}i\alpha\Delta^{-1}z^4+\ldots\}. \tag{5.1}$$

Also, (4.11) immediately yields the result $B_1=0$. (Note that, although equation (4.10) has an exact solution in terms of Airy functions, the present approximate methods are preferable for our purposes because of their relative simplicity.)

A series solution of equation (4.3) is found in a similar manner to be (cf. Craik 1966, equation (6.4))

$$\phi(z)=A_0+A_1z+A_2\{z^2+\tfrac{1}{12}\hat{p}z^4+\tfrac{1}{60}\hat{q}z^5\}+A_3\{z^3+\tfrac{1}{20}\hat{p}z^5+\tfrac{1}{60}\hat{q}z^6\}, \tag{5.2}$$
$$\hat{p}=i\alpha R(1-c)+2\alpha^2, \quad \hat{q}=i\alpha R,$$

where second- and higher-order terms in the small quantities $\hat{p}$, $\hat{q}$ have been omitted. Boundary conditions (4.4a,b) give $A_0=A_1=0$.

We now assume that αR, $\alpha R|c|$, α^2 are all sufficiently small compared with unity to be neglected; but, since $\Delta^{-1}\gg R$ (by virtue of the fact that $\kappa\ll\nu$), terms of order $\alpha\Delta^{-1}$, $\alpha\Delta^{-1}|c|$ will be retained to first order, and only their products neglected compared with unity. These assumptions restrict attention to films of fairly small Reynolds numbers in which the waves are long compared with the film thickness. Such conditions hold for the 'slow' waves described in § 2. On substituting expressions (5.1) and (5.2) (with $A_0 = A_1 = B_1 = 0$) into equations (4.6), (4.9) and (4.12), using result (4.5) to replace unity by $\phi(1)(1-c)^{-1}$ in (4.12), and neglecting small terms, we obtain

$$A_2[2+R\Sigma(1-c)^{-1}]+A_3[6+R\Sigma(1-c)^{-1}]$$

$$+B_0(T_1\lambda/\Gamma_0)\,i\alpha R[1+i\alpha\Delta^{-1}-\tfrac{1}{2}i\alpha c\Delta^{-1}] = 0, \quad (5.3)$$

$$A_2 i\alpha R[1+(T_0\alpha^2+G-\Pi)(1-c)^{-1}]$$

$$+A_3[6+i\alpha R\{1+(T_0\alpha^2+G-\Pi)(1-c)^{-1}\}] = 0, \quad (5.4)$$

$$A_2[2-(1-c)^{-1}]+A_3[3-(1-c)^{-1}]-B_0\Gamma_0^{-1}[3-c-i\alpha\Delta+\lambda(1-c)] = 0. \quad (5.5)$$

In equation (5.3), terms of order αR, α^2, $\alpha R^2|\Sigma|$, $\alpha^2 R|\Sigma|$ have been omitted from the coefficients of A_2 and A_3, and terms of order α^2, $\alpha^2\Delta^{-2}$ have been neglected from the expression in square brackets in the coefficient of B_0. In (5.4), terms of order α^2R^2, α^2, $\alpha^3R(T_0\alpha^2+G-\Pi)$, $\alpha^2R^2(T_0\alpha^2+G-\Pi)$ have been omitted from the coefficients of A_2 and A_3; while, in (5.5), terms of order α^2, αR are neglected from the coefficients of A_2 and A_3, and those of order α^2, $\alpha\Delta^{-1}$, $\alpha^3\Delta$, $\lambda\alpha^2$, $\lambda\alpha\Delta^{-1}$ from the expression in square brackets in the coefficient of B_0. (In estimating the orders of magnitude of these terms, it is assumed that $|c|$ is of order unity.)

Excluding the trivial case $A_2 = A_3 = B_0 = 0$, it is evident that these equations are consistent only when the determinant of the coefficients of A_2, A_3, B_0 is zero. In evaluating this determinant, small terms of the same order as those already neglected must of course be omitted. This equation of consistency is then

$$T_0\alpha^2+G-\Pi+\frac{3i\Sigma}{2\alpha}-\frac{3(1-c)}{i\alpha R}$$

$$= \frac{\tfrac{1}{4}T_1\lambda(i\alpha R)\,[1+i\alpha\Delta^{-1}(1-\tfrac{1}{2}c)]}{3-c-i\alpha\Delta+\lambda(1-c)}\left\{T_0\alpha^2+G-\Pi+\frac{6(2c-1)}{i\alpha R}\right\}. \quad (5.6)$$

To elucidate this result, we shall now examine three cases for which further approximations can be made.

Case (5i): $|1-c|\lambda \gg 1, \alpha\Delta;\ \alpha\Delta^{-1}|1-\tfrac{1}{2}c| \ll 1$

Examination of equation (3.3) reveals that λ (which is dimensionless) is proportional to h^{-1}, where h is the liquid film thickness. The first of the above inequalities therefore holds for sufficiently thin films. It will also hold in situations where a given change in surfactant adsorption produces only a small change in the underlying solute concentration; as, for example, when the surface-active material is only slightly soluble. The second inequality is satisfied whenever the characteristic time scale associated with the diffusion of solute is short compared with the period of the wave: this is likely to be so at typical wave-numbers for sufficiently thin films or when the (dimensional) molecular diffusivity is large.

When both these conditions are satisfied, equation (5.6) simplifies to

$$3(1-c)^2 - i\alpha R\mathscr{G}(1-c) + i\alpha R T_1\{\tfrac{3}{2} + \tfrac{1}{4} i\alpha R(T_0\alpha^2 + G - \Pi)\} = 0, \tag{5.7}$$

where

$$\mathscr{G} \equiv T_0\alpha^2 + G - \Pi + \tfrac{3}{2}(i\Sigma/\alpha) + 3T_1.$$

This is identical to the result obtained by Craik (1968, equation (8.9)) for insoluble surfactants whose properties are characterized by the dimensionless surface-elasticity parameter T_1. Proceeding from this equation, Craik finds solutions with c_r close to unity for which surface elasticity is *destabilizing.*

Case (5ii): $|1-c|\,\lambda \ll 1;\ \alpha\Delta^{-1}|1-\tfrac{1}{2}c| \ll 1;\ \alpha\Delta^{-1} \gg \alpha^2$

The first condition implies that fairly large changes in solute concentration produce only small changes in the surfactant adsorption, the second is as for case (5i) and the third restricts attention to waves sufficiently long that only *vertical* diffusion of solute need be considered. Result (5.6) now yields a quadratic equation for c, namely

$$c^2 - c\{4 - \tfrac{1}{3} i\alpha R(T_0\alpha^2 + G - \Pi) + \tfrac{1}{2}R\Sigma - i\alpha R\lambda T_1\}$$
$$+ 3 - i\alpha R(T_0\alpha^2 + G - \Pi) + \tfrac{3}{2}R\Sigma - \tfrac{1}{2} i\alpha R\lambda T_1 = 0. \tag{5.8}$$

On denoting the real and imaginary parts of c, Π and Σ by subscripts r and i, and ignoring terms in $\alpha R\lambda T_1$, $\tfrac{1}{3}\alpha R\,|\Pi_i|$, $\tfrac{1}{2}R\Sigma_r$ and αR compared with unity (cf. Craik 1968, § 8), the real part of this equation yields the result that

$$\textit{either} \quad c_r = 1 \quad \textit{or} \quad c_r = 3,$$

and the imaginary part gives

$$c_i = -\tfrac{5}{4}\alpha R\lambda T_1 \quad \text{for} \quad c_r = 3$$
$$= \tfrac{1}{4}\alpha R\lambda T_1 + \tfrac{1}{2}R\Sigma_i - \tfrac{1}{3}\alpha R(T_0\alpha^2 + G - \Pi_r) \quad \text{for} \quad c_r = 1.$$

Since c_i is negative when $c_r = 3$, such disturbances are *stable*; but a disturbance with $c_r = 1$ is *unstable* whenever

$$\Pi_r + \tfrac{3}{2}(\Sigma_i/\alpha) + \tfrac{3}{4}\alpha R\lambda T_1 > T_0\alpha^2 + G.$$

The latter result may be compared with the corresponding result for uncontaminated films, that $c_r \approx 1$ and such waves are unstable when $\Pi_r + \tfrac{3}{2}(\Sigma_i/\alpha) > T_0\alpha^2 + G$. Since $\alpha R\lambda T_1$ is positive, it is clear that the influence of surface contamination here reinforces the *destabilizing* action of the surface-stress components Π_r and Σ_i.

Case (5iii): *large surface-elasticity parameter*

When the parameter T_1 is sufficiently large—precise conditions, which depend on the magnitudes of α, R, λ and Δ, need not be given here—equation (5.6) may be approximated by equating the right-hand side to zero. This yields the solutions

$$c_r = \tfrac{1}{2} - \tfrac{1}{6}\alpha R\Pi_i,$$
$$c_i = \tfrac{1}{12}\alpha R(\Pi_r - T_0\alpha^2 - G).$$

(This solution may also be derived from the less general equations (5.7) or (5.8) on making suitable approximations.)

Since $\alpha R|\Pi_i|$ is generally small compared with unity, this solution corresponds to a wave travelling at about half the speed of the liquid surface, which is unstable whenever $\Pi_r > T_0\alpha^2+G$; that is, when the pressure component in phase with the wave elevation, which derives from the airflow, is sufficiently large to overcome the restoring forces of gravity and surface tension.

This is a much more stringent condition than that for instability of clean films; for the destabilizing role of the tangential-stress component Σ_i, which is dominant in very thin clean films, is here totally suppressed. Accordingly, the effect of a sufficiently large surface-elasticity parameter is strongly *stabilizing.*

6. Thin diffusion layers

Returning to equation (4.10), we now obtain two approximate solutions valid for large values of $\alpha\Delta^{-1}$. These are simply the asymptotic solutions of Airy's equation, and are (cf. Lin 1955, § 3.4)

$$f_{1,2} = (z-c)^{-\frac{1}{4}}\exp\left[\mp\tfrac{2}{3}(i\alpha\Delta^{-1})^{\frac{1}{2}}(z-c)^{\frac{3}{2}}\right]\{1+(\alpha\Delta^{-1})^{-\frac{1}{2}}g(z)+\ldots\}, \tag{6.1}$$

where $i^{\frac{1}{2}} = \exp(\frac{1}{4}i\pi)$ and, for nearly real c, $z-c = (c-z)\exp(-i\pi)$ when $z < c_r$. Both solutions oscillate rapidly, the amplitude of f_1 decreasing exponentially with distance from the solid boundary $z = 0$ and that of f_2 decreasing with distance below the surface $z = 1$. When $(\alpha\Delta^{-1})^{\frac{1}{2}}|1-c|^{\frac{3}{2}}$ and $(\alpha\Delta^{-1})^{\frac{1}{2}}|c|^{\frac{3}{2}}$ are both large compared with unity, the fluctuations in solute concentration, denoted by f, are confined to two very thin layers (i.e. thin compared to the film thickness which itself may be only about 0·3 mm), one close to the surface and the other next to the boundary $z = 0$.

The perturbation stream function will be represented as before by the series solution for $\phi(z)$ given in (5.2), which is valid when αR, $\alpha R|c|$ and α^2 are small. Proceeding as in § 5, but with $f(z)$ now given by linear combinations of the solutions (6.1), we obtain the three equations

$$\begin{gathered}
A_2[2+R\Sigma(1-c)^{-1}]+A_3[6+R\Sigma(1-c)^{-1}]+f(1)(T_1\lambda/\Gamma_0)i\alpha R = 0,\\
A_2 i\alpha R[1+(T_0\alpha^2+G-\Pi)(1-c)^{-1}]+A_3[6+i\alpha R\{1+(T_0\alpha^2+G-\Pi)(1-c)^{-1}\}] = 0,\\
A_2[2-(1-c)^{-1}]+A_3[3-(1-c)^{-1}]+\Gamma_0^{-1}[f'(1)\,i\Delta\alpha^{-1}-f(1)\,\lambda(1-c)] = 0,
\end{gathered}$$

from which may be derived the result corresponding to (5.6), namely

$$T_0\alpha^2+G-\Pi+\frac{3i\Sigma}{2\alpha}-\frac{3(1-c)}{i\alpha R} = \frac{\frac{1}{4}T_1\lambda(i\alpha R)\{T_0\alpha^2+G-\Pi+6(i\alpha R)^{-1}(2c-1)\}}{\{-i\Delta\alpha^{-1}[f'(1)/f(1)]+\lambda(1-c)\}}. \tag{6.2}$$

On writing $f = af_1+bf_2$, the boundary condition (4.11) requires that $af_1'(0)+bf_2'(0)$ is zero. Therefore, on neglecting terms which are exponentially small, $f = bf_2$ within the thin layer near the surface where diffusion of solute is significant. Consequently, from (6.1)

$$\frac{f'(1)}{f(1)} = \left(\frac{i\alpha}{\Delta}\right)^{\frac{1}{2}}(1-c)^{\frac{1}{2}}-\frac{1}{4(1-c)}+O\left\{\left(\frac{\alpha}{\Delta}\right)^{-\frac{1}{2}}\right\}. \tag{6.3}$$

Substitution of this in (6.2) yields the eigenvalue relationship for c.

As in § 5, we now examine several cases for which further approximations can be made.

Case (6i): $\Delta = 0$

On setting Δ equal to zero, we obtain the result for the case where no diffusion of solute takes place. One might expect that this should correspond to the case of insoluble contaminant, and this is indeed so. The result obtained is precisely equation (5.7) which is identical to a result obtained by Craik (1968) for insoluble contaminant. It is interesting to compare the physical mechanisms by which the present case and case (5i) yield the identical equation. Here, the (dimensionless) molecular diffusivity is taken to be so small that no significant diffusion of solute occurs; whereas, in the previous case, the diffusivity of solute may be large, but such diffusion is unimportant since changes in surfactant adsorption produce only small changes in the underlying solute concentration.

Case (6ii): *large surface-elasticity parameter*

When T_1 is sufficiently large, equation (6.2) yields the same approximate solution as that given in case (5iii). The stabilizing role of the contaminant in these cases is clearly independent of diffusion of solute, for the same results hold whether Δ/α is large or small.

Case (6iii): $\lambda \ll (\alpha\Delta^{-1}|1-c|)^{-\frac{1}{2}}$

In this case, the term in Δ dominates the denominator of the right-hand side of equation (6.2). In physical terms, this occurs when the diffusive transfer of material between the adsorbed surface and the bulk solution is sufficiently rapid to maintain the surfactant adsorption nearly—but not quite—constant, despite the periodic extension and contraction of the surface by a passing wave. Then, equation (6.2) becomes approximately

$$c(1+\Omega)-(1+\tfrac{1}{2}\Omega)+\tfrac{1}{3}i\alpha R(T_0\alpha^2+G-\Pi)(1+\tfrac{1}{4}\Omega)-\tfrac{1}{2}R\Sigma = 0, \tag{6.4}$$

where

$$\Omega \equiv -\left\{\frac{i\alpha}{\Delta(1-c)}\right\}^{\frac{1}{2}} T_1\lambda(i\alpha R). \tag{6.5}$$

When $|\Omega|$ is small compared with unity but possibly of the same order as $\alpha R|T_0\alpha^2+G-\Pi|$ and $R|\Sigma|$, further approximation yields the results

$$c_r = 1-\tfrac{1}{2}\Omega_r-\tfrac{1}{3}\alpha R\Pi_i+\tfrac{1}{2}R\Sigma_r,$$
$$c_i = -\tfrac{1}{2}\Omega_i-\tfrac{1}{3}\alpha R(T_0\alpha^2+G-\Pi_r)+\tfrac{1}{2}R\Sigma_i,$$

where the subscripts r and i denote real and imaginary parts respectively. If, further, we consider the wave to be neutrally stable, $c_i = 0$ and $1-c$ is real. But, when $1-c$ is real and positive, the above expression for Ω reveals that $\Omega_r = -\Omega_i$ and that Ω_r is positive; while, if $1-c$ is negative, Ω_r and Ω_i are seen to be equal and positive [on recalling that $1-c = (c-1)\exp(-i\pi)$]. But, in the above result for c_i, the term in Ω_i is stabilizing or destabilizing according as Ω_i is positive or negative. So, for the neutral case $c_i = 0$, the contribution of this term is stabilizing or destabilizing according as Ω_r is greater or less than $R\Sigma_r-\tfrac{2}{3}\alpha R\Pi_i$. However, since c is here close to unity, the assumption that $|\Omega| \ll 1$ is rather restrictive in view of its dependence on $(1-c)^{-\frac{1}{2}}$.

If $|\Omega|$ is large compared with unity, a first approximation to equation (6.4) is $c = \frac{1}{2}$. A better approximation might then be developed to obtain the same result as for case (6ii). Alternatively, if $|\Omega|$ is large but $|\alpha R\Omega(T_0\alpha^2 + G - \Pi)|$ remains small, result (6.4) yields the next approximation as $c = \frac{1}{2}(1+\Omega^{-1})$. Further, on setting $1-c = \frac{1}{2}$ in the expression (6.5) for Ω, the argument of Ω^{-1} is readily shown to be $\frac{1}{4}\pi$. Consequently, the imaginary part of Ω^{-1} is positive, and the disturbance is unstable.

The condition for neutral stability may also be determined for intermediate values of $|\Omega|$. Assuming that $1-c$ is then positive, we may write

$$\Omega_r = -\Omega_i = 2^{-\frac{1}{2}}|\Omega|$$

to find from (6.4) that

$$c_r = \frac{1+\frac{3}{2}2^{-\frac{1}{2}}|\Omega|+\frac{1}{2}|\Omega|^2}{|1+\Omega|^2} + O\{\alpha R|T_0\alpha^2+G-\Pi|, R|\Sigma|\},$$

confirming that c_r lies between $\frac{1}{2}$ and 1; and, since $c_i = 0$,

$$T_0\alpha^2+G-\Pi_r = \tfrac{3}{2}\alpha^{-1}[\Sigma_i + 2^{-\frac{1}{2}}(\Sigma_i+\Sigma_r)|\Omega| + 2^{-\frac{1}{2}}R^{-1}|\Omega|] \\ \times[1+\tfrac{5}{4}2^{-\frac{1}{2}}|\Omega|+\tfrac{1}{4}|\Omega|^2]^{-1} + O(|\Pi_i|). \qquad (6.6)$$

This last equation represents a balance between the restoring forces of gravity and surface tension and the other destabilizing forces. When $|\Omega|$ is zero, the result for uncontaminated films is obtained; and when $|\Omega|$ is sufficiently large the right-hand side of (6.6) may be taken as zero to retrieve the result of case (6ii).

The destabilizing role of the complex shear-stress parameter Σ is modified by the diffusion of adsorbed material. For small values of $|\Omega|$ this role may be somewhat enhanced (since Σ_r is probably greater than $\frac{1}{4}\Sigma_i$); but, as $|\Omega|$ increases, the influence of the Σ terms diminishes until, when $|\Omega| \gg 1$, it vanishes altogether and case (6ii) is recovered. Also, there is an additional destabilizing term which is represented on the right-hand side of (6.6) as proportional to R^{-1}. This term has a maximum at $|\Omega| = 2$ but it, too, decreases to zero as $|\Omega|$ becomes large. (This term is somewhat reminiscent of that in $\alpha R\lambda T_1$ which occurs in the stability criterion for case (5ii).) Equation (6.6) admirably illustrates the operation of conflicting stabilizing and destabilizing contributions which arise from the presence of contamination. The net effect may be stabilizing or destabilizing, depending on the relative importance of these contributions.

7. Discussion

The various cases examined in §§ 5 and 6 reveal that the role of soluble surface-active agents is a complex one, which may be either stabilizing or destabilizing. Cases (5iii) and (6ii) show that sufficiently large surface elasticity is strongly stabilizing owing to the effective suppression of the destabilizing action of the periodic tangential stress $\Sigma\eta$ exerted by the airflow; and case (6iii) demonstrates how the role of $\Sigma\eta$ progressively diminishes as the surface elasticity increases. On the other hand, case (5ii) provides an example of the destabilizing role of the surfactant; and a somewhat similar destabilizing term also arises in the stability criterion for case (6iii). Cases (5i) and (6i) both yield results identical to those for insoluble contaminants, for which Craik (1968, §8) has shown that surface elasticity may be destabilizing.

Cases (5i) and (6i) are especially instructive since they help to define conditions for which solubility and diffusion of solute may be neglected. In particular, these cases require, respectively, that $|1-c|\,\lambda \gg 1$ and $(\alpha/\Delta)^{\frac{1}{2}}\,|1-c|^{\frac{3}{2}} \gg 1$: but, on the basis of equation (5.7), Craik found solutions for which c is close to unity. Clearly, the range of validity of these solutions must be restricted either to very insoluble materials or to those with small molecular diffusivity. This is so because, when c is near to unity, the period of the wave *in a reference frame moving with the liquid surface* is very large; and, consequently, a long time is available for transfer of material between the adsorbed layer and the solution.

It can be shown that the waves under discussion are examples of the 'kinematic waves' discussed by Lighthill & Whitham (1955)—see also Craik & Smith (1968). Since the wavelength is large compared with the film thickness, the surface of the liquid is raised or lowered according as the x derivative of the net horizontal volume flux Q is negative or positive. If Q is measured relative to a frame of reference moving with the wave velocity c_r, the wave is neutrally stable if $\partial Q/\partial x$ is zero. If the periodic tangential stress exerted by the adsorbed surface layer is represented as $\Xi\eta$, where Ξ is complex, the (dimensionless) horizontal velocity distribution in such a reference frame is, to first order in $|\eta|$,

$$u(x,y) = y-c_r+R(\Sigma+\Xi)\,\eta y-i\alpha R(T_0\alpha^2+G-\Pi)\,\eta y(1-\tfrac{1}{2}y),$$

where the last term derives from the (hydrostatic) pressure gradient in the x direction. But

$$\frac{\partial Q}{\partial x} = \frac{\partial}{\partial x}\int_0^{1+\eta(x,t)} u\,dy = i\alpha\eta[1-c_r+\tfrac{1}{2}R(\Sigma+\Xi)-\tfrac{1}{3}i\alpha R(T_0\alpha^2+G-\Pi)],$$

and this is zero for neutral stability. Therefore

$$c_r = 1+\tfrac{1}{2}R(\Sigma_r+\Xi_r)-\tfrac{1}{3}\alpha R\Pi_i$$

and

$$T_0\alpha^2+G = \Pi_r+\tfrac{3}{2}\alpha^{-1}(\Sigma_i+\Xi_i),$$

the latter being the criterion for neutral stability.

The complexities which became apparent in §§5 and 6 are attributable to the dependence of Ξ on the (linearized) velocity $u_s(x, 1+\eta)$ at the liquid surface and on the transfer of contaminant between surface layer and solution. These complexities are best illustrated with reference to one particular case, and, for this purpose, we shall consider case (6iii).

For this case, the diffusive transfer of material between surface and solution is sufficiently large to maintain the surfactant adsorption *nearly* constant despite the periodic stretching and contraction of the surface: that is (cf. equation (3.4)) $\Gamma_0(\partial u/\partial x)_s = -\Delta(\partial C/\partial z)_s$ at the surface. Also, since (6.3) shows that $C-C_0$ and $\partial C/\partial z$ differ in phase by 45° at the surface, the surface stress $\Xi\eta$ owing to the x gradient of the corresponding surfactant adsorption must also differ in phase from $(\partial^2u/\partial x^2)_s$ by 45°. Further, since $-(\partial^2u/\partial x^2)_s$ is approximately in phase with the wave elevation η when $R\,|\Sigma+\Xi|$ and $\alpha R\,|T_0\alpha^2+G-\Pi|$ are sufficiently small, it follows that $\Xi\eta$ and $-\eta$ are about 45° out of phase. Comparison of the above results with those of case (6iii) show that Ξ may be identified with $-R^{-1}\Omega$ when $|\Omega|$ is small; and the expression (6.5) for Ω confirms this 45° phase difference. The sign of Ω_i then determines whether the tangential stress component $\Xi_i\eta$ is stabilizing or destabilizing. However, when $|\Omega|$ is larger, the dependence of Ξ on the wave velocity c and the other parameters of the problem gives rise to greater complexity. For example, the fact that the stress $\Xi\eta$ depends on $(\partial^2 u/\partial x^2)_s$, and that $u(x, 1+\eta)$ itself depends upon Ξ and Σ, accounts for the occurrence of terms like $|\Omega|^2$ and $\Sigma|\Omega|$ in the analysis.

The rather subtle role of surface contamination which is revealed by the theoretical results of §§ 5 and 6 is supported qualitatively by the experiments described in § 2. There, with Teepol as contaminant, the onset of 'slow waves' occurred at smaller film thicknesses than for clean water. This increased *stability* is consistent with the reduction in effectiveness of the shear-stress component $\Sigma_i\eta$ which is demonstrated in case (6iii) when $|\Omega|$ is $O(1)$. However, since instability eventually occurred on making the film thickness sufficiently small, the influence of this stress component cannot be entirely absent, as in cases (5iii) and (6ii); for then the (dimensional) stability criterion does not depend explicitly on the film thickness.

When contaminated by camphor, slow waves manifest themselves in thicker films than for clean water. The greater *instability* in this case may correspond to the situation of case (5ii), or to that of case (6iii) when the net effect is destabilizing. In view of the restrictive conditions under which cases (5i) and (6i) give rise to instability of the kind discussed by Craik (1968), it seems somewhat less likely that these cases might apply.

The experimental observations of slow waves indicated that their velocities of propagation were less than the velocity of the liquid surface. This is consistent with the results of the various theoretical models; but, owing to the presence of finite-amplitude effects for the observed waves, the measurement of these velocities does not constitute a valid criterion for determining which of these models is the most appropriate.

Unfortunately, it is impossible to proceed beyond this qualitative comparison of theory and experiment. A quantitative test of the theory must await experiments which incorporate measurements of all the relevant properties of the contaminated surface and of the solute. Nevertheless, the present experiment convincingly supports the theoretical conclusion that the effect of soluble surface-active agents can be stabilizing or destabilizing.

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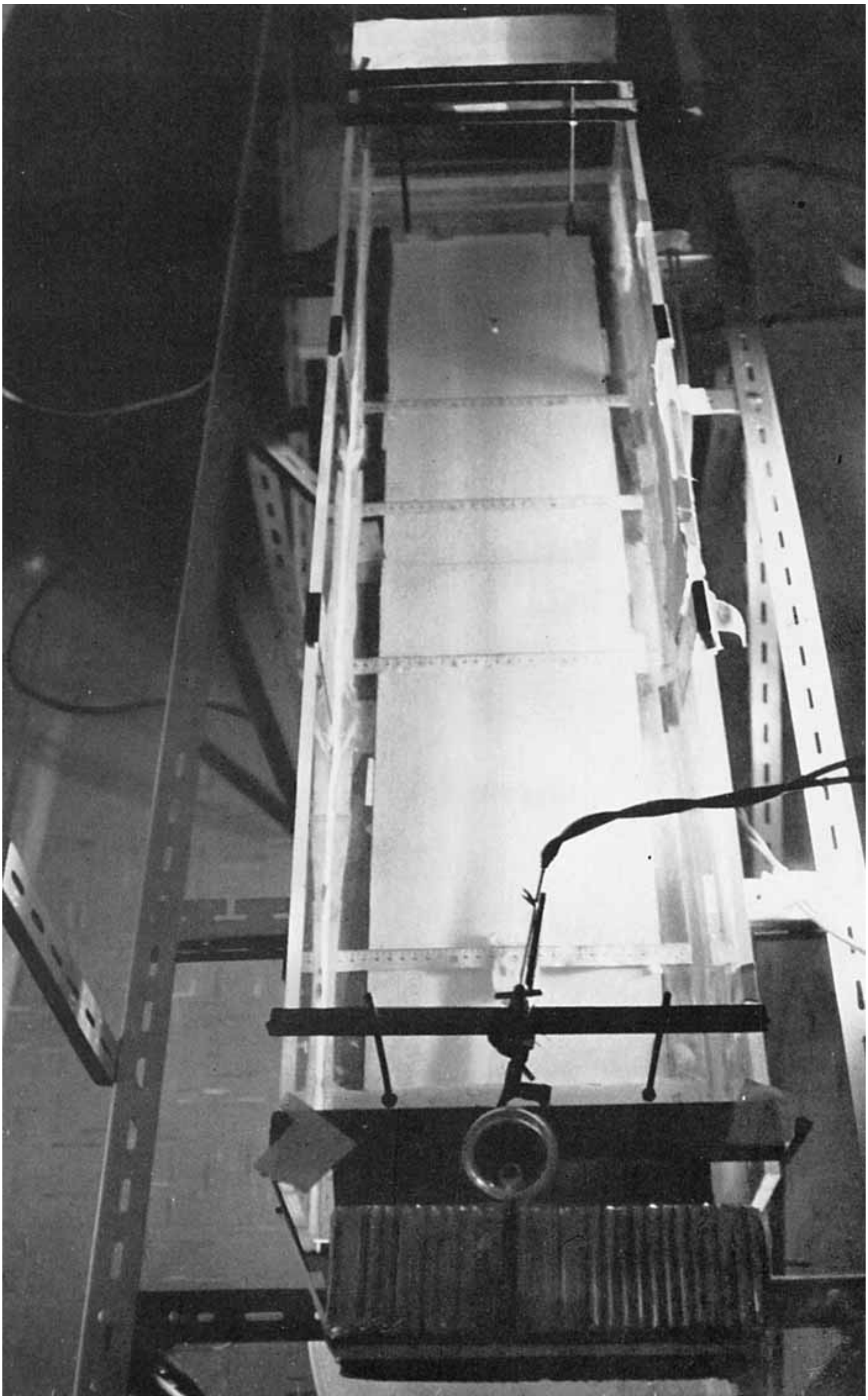

FIGURE 3. Photograph of typical streak.