J. Fluid Mech. (1972), *vol.* 51, *part* 2, *pp.* 385–402
Printed in Great Britain

Hydrodynamic stability of surfactant solutions heated from below

By HARVEY J. PALMER AND JOHN C. BERG
Department of Chemical Engineering, University of Washington

(Received 22 January 1971 and in revised form 9 September 1971)

The interfacial hydrodynamics of pools of dilute binary solutions heated from below is examined using linear stability analysis. Results show that the stabilizing effect of the solute can vary greatly with its interfacial properties, its concentration, and the rate and mechanism of its transfer between the bulk phase and the surface.

1. Introduction

The linear hydrodynamic stability analysis of shallow liquid pools heated from below can be used as a tool for investigating the surface behaviour of dilute binary solutions in which the solute is surface active.

The stability of pure liquid pools heated from below, and subject to surface tension variations, was analysed first by Pearson (1958), while Nield (1964) first considered the stability of such a pool subject to both surface tension variations and adverse density stratification. The predicted stability criteria of Nield's linear analysis have recently been observed experimentally by Palmer & Berg (1971) using a modification of the Schmidt–Milverton technique (Schmidt & Milverton 1935), in which the maximum supportable temperature gradient is identified by the sudden change of slope in the plot of heat flux versus temperature drop across the pool.

Berg & Acrivos (1965) extended Pearson's analysis to consider the effect of insoluble surfactants, and predicted that even trace amounts of such materials would exert an extreme stabilizing influence on the system. The stabilization depends primarily upon the slowness with which monolayer concentration variations can be diminished by surface diffusion, and only secondarily upon surface viscosity. The sustained non-uniformities in surface monolayer concentration maintain surface tension gradients opposing the disturbing forces.

The stability analysis presented here, of pools containing small amounts of dissolved surfactant, involves not only the rheological and transport properties of the monolayer itself, but also the rate and mechanism (adsorption–desorption) of interchange of surfactant between the surface and the adjacent bulk phases. All of this is necessary because, as described in more detail below, surface concentration following a disturbance may be restored to uniformity not only through surface transport, but also through interchange with the adjacent bulk phases. The analysis delineates the relative importance of the system properties in stabilizing the system, and embraces the insoluble monolayer analysis as a limiting case. It also reveals some coupling effects between the different properties determining the system's stability.

Stability analysis is advantageous in the study of the nature of fluid interfaces for two reasons. First, it provides a situation which can be described in terms of linearized equations and boundary conditions. Second, the results of the analysis are amenable to experimental examination using the adaptation of the Schmidt–Milverton technique, which has already proved successful in the quantitative verification of the predicted stability criteria for pure liquid pools heated from below. Subcritical instabilities (i.e. convection induced by finite amplitude disturbances) thus appear to have been eliminated in the proposed experimental technique.

The object of the present paper is to perform the linear hydrodynamic stability analysis of a shallow liquid pool heated from below and consisting of a dilute non-volatile solution of a surface active solute. The analysis is developed first for the case in which only surface tension variations lead to instability (valid for very shallow pools), and second for the case in which both surface tension and buoyancy effects are operative. A later paper will present experimental results for a number of cases suggested by this analysis.

2. Quiescent system

The system analysed is a binary solution pool infinite in lateral extent and bounded on the bottom by a flat solid surface and on the top by an inviscid gas. The upper surface is assumed to remain flat, as in the analyses of Pearson (1958) and Nield (1964). This assumption was relaxed in similar studies by Scriven & Sternling (1964) and Smith (1966), whose results indicate that the effects of the surface deformability on system stability are generally confined to disturbances of very large wavelength.

The pool is heated from below and cooled from above to maintain a steady one-dimensional heat flux through the fluid. The solution is dilute and non-volatile, and all its physical properties except density and surface tension are assumed constant. Density, as it appears in the gravity term of the momentum equation, varies linearly with temperature, and surface tension varies with both temperature and solute concentration.

Prior to the onset of convection, the concentration of the surface active solute is uniform throughout the depth of the pool. Its equilibrium concentration at the free surface, however, is greater (possibly much greater) than it is in the bulk liquid. The surface concentration of the solute is usually expressed in terms of its 'relative adsorption' $\Gamma_{2,1}$ with units of moles area^{-1}, and defined as

$$\Gamma_{2,1} \equiv \Gamma_2 - \Gamma_1 \frac{c_2^g - c_2^l}{c_1^g - c_1^l},$$

where c_1^g, c_2^g, c_1^l, c_2^l are molar concentrations of solvent 1 and solute 2 in the bulk gas and liquid phases, and Γ_2 and Γ_1 are the 'surface excesses' of solute and solvent, respectively (cf. Defay *et al.* 1966, p. 26). The surface excesses are reckoned by comparing the actual system with the model in which the phases are assumed uniform in composition up to an arbitrarily located 'dividing surface' representative of the true interface. While the magnitude of the individual surface excesses depends on the location of the dividing surface, the relative adsorptions are invariant with respect to its location. For dilute, non-volatile solutions, $\Gamma_{2,1}$ is well approximated by Γ_2, and the actual concentration of solute in the surface layer (of thickness δ) is given (dropping the subscript) by

$$c_s = c + \Gamma/\delta,$$

where c is the bulk concentration of solute. δ is known, from optical measurements, to be of the order of a few molecular diameters. Thus, even for rather weak surface active agents, $c \ll \Gamma/\delta$, so that $c_s \sim \Gamma/\delta$. The surface concentration of solute may then be expressed in terms of Γ for the type of system under study here. For highly concentrated surfactant solutions, more general expressions for surface concentration would be required, while, for non-surface active solutes, the situation reduces to the one analysed by Pearson (1958) or Nield (1964).

3. Stabilizing mechanism: three special cases

When the system, as described above, is perturbed, it responds according to the equations of motion, energy and diffusion. Depending on the system properties, this response may carry it still further from the original unperturbed state. A disturbance in the form of a local surface dilation, for example, will bring liquid from the interior of the pool to the point of local dilation, increasing the surface temperature, and hence reducing the surface tension at that point. The surface tension gradient so generated tends to increase the original surface dilation, so that the disturbance is self-amplifying. The presence of an adsorbed solute, however, may greatly inhibit the auto-amplification of such disturbances. Local surface dilation will locally decrease the surface solute concentration Γ, and thus will establish a surface tension gradient opposite in sign to that produced by the upward flow of warm liquid to the surface. The effectiveness of the solute in stabilizing the system depends on the magnitude of Γ, the sensitivity of surface tension to Γ, and the ability of the surface concentration gradient to sustain itself against erosion by surface diffusion and bulk phase transport. One may define three special cases based upon the controlling mechanism for the diminution of surface concentration gradients: (i) bulk diffusion controlled, (ii) adsorption–desorption rate controlled, and (iii) surface diffusion controlled. In cases (i) and (ii) above, surface migration is accomplished primarily through transport in the bulk phases, while in case (iii) it is accomplished by surface diffusion of a monolayer, which is either insoluble in the substrate or kinetically blocked from entering it. In addition to the effectiveness and mechanism of surface solute redistribution, the stability of the system also depends on the rheological properties of the surface.

4. Mathematical formulation

The linear stability is analysed in the usual manner by imparting to the quiescent system a small disturbance, exponential in time and periodic in the plan form spatial variables, but of arbitrary wavelength. The disturbance is made to obey the conservation equations of momentum and energy, as in the analysis of Nield (1964) and others, and, in addition, it must satisfy the equation of mass conservation for the solute.

The heart of the present analysis lies in the specification of the boundary conditions for the upper free surface of the pool. To describe the spatial distribution of the surface excess of the solute Γ, a surface material balance is needed:

$$\frac{\partial \Gamma}{\partial t}+\nabla_{\mathrm{II}}\cdot(\Gamma \mathbf{u}_s - D_s \nabla_{\mathrm{II}}\Gamma) = j \quad \text{at} \quad z = d, \tag{1a}$$

where $\nabla_{\mathrm{II}} \equiv \mathbf{i}\frac{\partial}{\partial x}+\mathbf{j}\frac{\partial}{\partial y}$, x and y are the horizontal co-ordinates, z the vertical co-ordinate, d the pool depth, t the time, $\mathbf{u}_s$ the surface velocity, D_s the surface diffusion coefficient, and j the mass flux from the adjacent bulk phases to the interface. Since the solute is assumed to be non-volatile, j is just the net rate of solute transfer from the liquid subphase, and in general

$$j = -D_b\,\partial c/\partial z \quad \text{at} \quad z = d,$$

where D_b is the diffusivity of solute in the bulk liquid phase. Mass transfer between subphase and surface, as stated earlier (§§1, 3), may also be expressed as an adsorption–desorption process, yielding a second boundary condition. For highly dilute solutions, solute–solute interactions are negligible, and the adsorption and desorption rates are given by first-order expressions. Thus,

$$j = -D_b\,\partial c/\partial z = k_1 c - k_{-1}\Gamma \quad \text{at} \quad z = d, \tag{2a}$$

where k_1 and k_{-1} are the rate constants for adsorption and desorption.

In the bulk diffusion controlled case, the adsorption and desorption rates are large with respect to the diffusion term, and the surface excess of solute is essentially in local equilibrium with the solute in the adjacent subphase, i.e.

$$\frac{k_1}{k_{-1}}c - \Gamma \sim 0 \quad \text{at} \quad z = d,$$

where the ratio k_1/k_{-1} is the distribution equilibrium constant between surface and subphase. In the adsorption–desorption rate controlled case, the rates of adsorption and desorption are small and unequal, so that the surface excess of solute is not in equilibrium with the adjacent subphase solute concentration.

In the surface diffusion controlled case, the solute is either insoluble, so that c and $\partial c/\partial z$ are zero, or it is kinetically blocked from entering or leaving the surface, so that k_1 and k_{-1} are essentially zero. In either case (2a) simplifies to $j = 0$, indicating that no mass transfer takes place between the surface and the subphase.

A third boundary condition derives from a balance of the tangential forces at the free surface. The surface divergence of the shear stress balance is

$$\mu\frac{\partial}{\partial z}(\nabla_{\mathrm{II}}\cdot\mathbf{u}_s)+\mu_s\nabla^2_{\mathrm{II}}\frac{\partial w}{\partial z} = \left(\frac{\partial \sigma}{\partial \Gamma}\right)_T \nabla^2_{\mathrm{II}}\Gamma + \left(\frac{\partial \sigma}{\partial T}\right)_\Gamma \nabla^2_{\mathrm{II}} T \quad \text{at} \quad z = d, \tag{3a}$$

where w is the vertical component of velocity, T is the temperature, and μ, μ_s and σ are the bulk viscosity, surface shear viscosity and surface tension of the solution, respectively. Among the various rheological properties that might be formally assigned to the interface, only surface shear viscosity is considered in the present analysis.

The thermal boundary condition at the free surface is

$$-k\,\partial T/\partial z = h(T-T_a) \quad \text{at} \quad z = d, \tag{4a}$$

where k is the thermal conductivity of the liquid, h the heat transfer coefficient in the air near the surface, and T_a the constant ambient temperature.

Finally, the assumption of a flat upper surface requires that the vertical component of velocity be zero:

$$w = 0 \quad \text{at} \quad z = d. \tag{5a}$$

At the solid bottom boundary there is no slip, no vertical component of velocity, and no solute mass transfer. Thus,

$$\frac{\partial w}{\partial z} = w = \frac{\partial c}{\partial z} = 0 \quad \text{at} \quad z = 0. \tag{6a}$$

Assuming that the bottom surface is a perfect heat conductor,

$$T = \text{const.} \quad \text{at} \quad z = 0. \tag{7a}$$

The momentum, energy and diffusion equations together with boundary conditions (1a)–(7a) completely specify the behaviour of the system and are first solved for the quiescent state. The system variables are then displaced infinitesimally in the usual way by perturbations of the form

$$P(x,y,z,t) = P^*\{\lambda\hat{t}\}f(\hat{x},\hat{y})\,\hat{P}(\hat{z}),$$

where λ is the time growth constant, P^* is a scale factor, and $\hat{P}(\hat{z})$ is the non-dimensionalized z dependent factor of the disturbance. Since Γ is a function of x, y and t only, its z dependent factor is just unity.

After separation of variables, non-dimensionalization and linearization, the equations of momentum, energy and diffusion are

$$\lambda(D^2-\alpha^2)\,\hat{w} = (D^2-\alpha^2)^2\,\hat{w}+\alpha^2R\hat{T}, \tag{8}$$

$$\lambda Pr\hat{T} = (D^2-\alpha^2)\,\hat{T}-\hat{w}. \tag{9}$$

$$\lambda Sc\hat{c} = (D^2-\alpha^2)\,\hat{c}, \tag{10}$$

where $D \equiv d/d\hat{z}, \hat{w}, \hat{T}$ and $\hat{c}$ are the z dependent factors of the non-dimensionalized vertical velocity component, temperature, and bulk solute concentration perturbations, respectively, and α is the wavenumber. The variables z, w, c, t, T and Γ are non-dimensionalized by dividing them by d, $D_b(\partial c/\partial\Gamma)_0$, $\Gamma_0(\partial c/\partial\Gamma)_0$, $d^2\nu^{-1}$, $-\Delta T\,dD_b(\partial c/\partial\Gamma)_0\,\kappa^{-1}$ and $-\Gamma_0$, respectively, where ν and κ are the kinematic viscosity and thermal diffusivity of the fluid, ΔT is the steady-state temperature difference between the bottom and top surfaces, and the zero subscript indicates quiescent state values of the physical parameters.

Similarly, the boundary conditions are rewritten as follows. At $\hat{z} = 1$,

$$\lambda N_{SS} + D\hat{w} + \alpha^2 N_{SD} = D\hat{c}, \tag{1b}$$

$$-N_{AD} D\hat{c} = \hat{c} + 1, \tag{2b}$$

$$D^2\hat{w} + \alpha^2 N_V D\hat{w} - \alpha^2 Ma \hat{T} - \alpha^2 N_{EL} = 0, \tag{3b}$$

$$D\hat{T} + Bi\hat{T} = 0, \tag{4b}$$

$$\hat{w} = 0, \tag{5b}$$

and, at $\hat{z} = 0$,

$$D\hat{w} = \hat{w} = D\hat{c} = \hat{T} = 0. \tag{6b, 7b}$$

The dimensionless groups in the above equations are defined below:

Marangoni number	$Ma \equiv -\left(\frac{\partial\sigma}{\partial T}\right)_0 \frac{(\Delta T)\,d}{\kappa\mu}$,
Rayleigh number	$R \equiv \frac{\bar{\alpha} g(\Delta T) d^3}{\kappa\nu}$,
Elasticity number	$N_{EL} \equiv -\left(\frac{\partial\sigma}{\partial c}\right)_0 \frac{\Gamma_0}{\mu D_b}$,
Adsorption number	$N_{AD} \equiv \frac{D_b}{k_1 d}$,
Surface diffusion number	$N_{SD} \equiv \left(\frac{\partial\Gamma}{\partial c}\right)_0 \frac{D_s}{D_b d}$,
Surface viscosity number	$N_V \equiv \mu_s/\mu d$,
Biot number	$Bi \equiv hd/k$,
Prandtl number	$Pr \equiv \nu/\kappa$,
Schmidt number	$Sc \equiv \nu/D_b$,
Surface Schmidt number	$N_{SS} \equiv \left(\frac{\partial\Gamma}{\partial c}\right)_0 \frac{\nu}{D_b d}$,

where $\bar{\alpha}$ is the coefficient of thermal expansion of the fluid, and g is the gravitational acceleration. In the above equations, k_{-1} has been replaced by its equivalent, $k_1(\partial\Gamma/\partial c)_0^{-1}$.

The condition of marginal stability is sought, and it requires that the real part of the time growth constant λ be zero. Equations (8)–(10) are first solved for the special case of pure surface tension driven instability, and secondly for the more general case in which both surface tension and buoyancy forces are present to induce convection.

5. Solution for surface tension driven instability

To consider instability induced by surface forces alone, the Rayleigh number is set equal to zero. The general solution to (8)–(10) may then be written down immediately, and the coefficients evaluated from (1b), (2b), (4b)–(7b). Substitution of the solution into (3*b*) then yields the characteristic equation relating Ma to α, $\operatorname{Im}\lambda$ (the imaginary part of the growth constant), and the other dimensionless groups at the condition of marginal stability. This characteristic equation for the Marangoni number in the absence of buoyancy effects (Ma^*) is

$$Ma^* = (q\cosh q + Bi\sinh q)\,(i\operatorname{Im}\lambda D_1 + D_2 f_s)/D_3 \quad (\operatorname{Im}\lambda \neq 0); \tag{11a}$$

$$Ma^* = 4\alpha^2\left[\frac{\alpha\cosh\alpha + Bi\sinh\alpha}{\alpha^3\cosh\alpha - \sinh^3\alpha}\right]\left[2 - \frac{1}{\alpha}\sinh 2a + (\alpha^2 - \sinh^2\alpha)\,F_s\right] \quad (\operatorname{Im}\lambda = 0); \tag{11b}$$

with
$$\begin{aligned}
f_s &= N_V + N_{EL}/[\alpha^2 N_{SD} + \operatorname{Im} i\lambda N_{SS} + s/(\coth s + sN_{AD})],\\
F_s &= N_V + N_{EL}/[\alpha^2 N_{SD} + \alpha/(\coth\alpha + \alpha N_{AD})],\\
D_1 &= (\alpha\sinh\eta\cosh\alpha - \eta\sinh\alpha\cosh\eta)/a^2,\\
D_2 &= 2\eta\alpha(\cosh\eta\cosh\alpha - 1) - (\eta^2+\alpha^2)(\sinh\eta\sinh\alpha),\\
D_3 &= \eta\alpha(2Pr-1)\sinh q\,(\cosh\eta\cosh\alpha - 1) - [Pr\,(\eta^2+\alpha^2) - \alpha^2]\\
&\qquad \times (\sinh\eta\sinh q\sinh\alpha) + q(\alpha s\sinh\eta - \eta\sinh\alpha)\\
&\qquad + q\cosh q(\eta\sinh\alpha\cosh\eta - \alpha\sinh\eta\cosh\alpha),
\end{aligned}$$

where

$$\eta = (\alpha^2 + i\operatorname{Im}\lambda)^{\frac{1}{2}}, \quad q = (\alpha^2 + i\operatorname{Im}\lambda\,Pr)^{\frac{1}{2}}, \quad \text{and} \quad s = (\alpha^2 + i\operatorname{Im}\lambda\,Sc)^{\frac{1}{2}}.$$

Equation (11*a*) can be written simply as

$$Ma^*(\alpha, \operatorname{Im}\lambda, N_j) = \operatorname{Re} Ma^* + i\operatorname{Im} Ma^*,$$

where N_j represents all the dimensionless groups describing the system. Physically, of course, the Marangoni number must be a real number so that the only admissible values of $\operatorname{Im}\lambda$ are those for which the imaginary part of the Marangoni number, $\operatorname{Im} Ma^*$, equals zero. When only the value $\operatorname{Im}\lambda = 0$ makes $\operatorname{Im} Ma^*$ vanish, the principle of exchange of stabilities is said to hold, and oscillatory instability will not occur. Such is the case for the pure liquid pool heated from below (Vidal & Acrivos 1966), but in the more general case treated here, non-zero values of $\operatorname{Im}\lambda$ do exist for which $\operatorname{Im} Ma^*$ equals zero. For a given binary solution system, there is one non-zero value of $\operatorname{Im}\lambda$, at each wavenumber α, for which $\operatorname{Im} Ma^*$ equals zero. At these values of $\operatorname{Im}\lambda$ and α, $\operatorname{Re} Ma^*$ can be calculated and is equal to the oscillatory critical Marangoni number for the system at the wavenumber α. Thus, a single curve of Ma^* versus α can be generated representing the neutral oscillatory stability limit for the system.

Similarly, the curve of Ma^* versus α for $\operatorname{Im}\lambda = 0$ can be generated representing the locus of all neutral stationary states of the system. Each curve has a minimum value of Ma^*. The smaller of the two minima is the actual stability limit for the system. If it is the value of Ma^* corresponding to a non-zero value of $\operatorname{Im}\lambda$, then convection will be initiated through an oscillatory mode characterized by a period growth and decay of the disturbances in the fluid.

The oscillatory critical Marangoni number decreases as the Prandtl number and Biot number decrease and as the Schmidt number and N_{SS} increase. Increasing adsorption barrier, however, reduces the possibility of oscillatory instability, because it masks the effect of the Schmidt number, as can be deduced from the expression for f_s in (11*a*).

The degree of stability imparted to the system by the solute depends on the magnitude of f_S, which embodies in it all the dimensionless groups pertaining to the solute. In general, however, N_V may be neglected since, from calculations using reasonable values for the physical properties, its effect on Ma^* is of secondary importance compared to the other dimensionless groups in the analysis.

Therefore, the most important dimensionless groups to consider are N_{EL}, N_{SD}, N_{AD} and, in the case of oscillatory modes of instability, N_{SS}, Pr and Sc. The elasticity number N_{EL} represents the effectiveness of the solute in generating surface restoring forces. The surface diffusion number N_{SD} relates the importance of surface diffusion to bulk diffusion as a mechanism for lateral mass transfer. The adsorption number N_{AD} is the ratio of the effectiveness of bulk diffusion to adsorption in transferring mass to the surface. It can be viewed as a measure of the adsorption barrier; the larger the value of N_{AD}, the greater is the adsorption barrier.

6. Special cases in surface tension driven instability

6.1. *Bulk diffusion control*

The most common special case of the general solution is the situation where there is no adsorption barrier to mass transfer between the surface and the subsurface layer (i.e. $N_{AD} \to 0$). This means that the surface concentration of the solute is always in equilibrium with the solute concentration just below the surface. Thus, the rate of mass transfer into the surface is controlled by the rate at which the solute can diffuse from the bulk to the subsurface layer.

For low Prandtl number fluids, like water solutions, the mode of instability is always oscillatory, and the critical oscillatory Marangoni number is a weak function of N_{SS} and Sc. For fluids whose Prandtl number is of the order of 10^3 or greater, however, the stationary mode of instability predominates. Regardless of Prandtl number, surface diffusion cannot effect a significant change in the critical Marangoni number unless D_S is at least 100 times as large as the bulk diffusion coefficient. This is not likely to be the case (cf. Sakata & Berg 1969). Therefore, for a given Prandtl number, the critical Marangoni number for the bulk diffusion controlled system is a function of the elasticity number N_{EL} only.

Curves (*a*) and (*b*) in figure 1 illustrate the large increase in the critical Marangoni number with increasing elasticity number for the diffusion controlled system. Curve (*a*) represents the oscillatory stability limit for a solution whose Prandtl number is 10 ($Sc = 10^3$ and $N_{SS} = 0{\cdot}1$), while curve (*b*) represents the stationary stability limit that is the true stability limit for fluids whose Prandtl number is of the order of 10^3 or larger. Since N_{EL} is proportional to both Γ_0 and $(\partial\sigma/\partial c)_0$, an increase in either solute concentration or $(\partial\sigma/\partial c)_0$, by a change of solute, will increase the stability limit for the system. For instance, from curve (*a*) we find that a 3×10^{-5} molar solution of *n*-butanol in water ($\partial\sigma/\partial c = 5 \times 10^6$ dyne cm^2 mole^{-1}), or a 10^{-8} molar solution of decanol in water ($\partial\sigma/\partial c = 3 \times 10^8$ dyne cm^2 mole^{-1}), will have a stability limit which is an order of magnitude higher than the stability limit for pure water.

6.2. *Adsorption–desorption rate control*

Several cases have been reported in which adsorption or desorption of surface active solutes at fluid interfaces is very slow (cf. England & Berg 1971). Thus, the adsorption rate may be the controlling factor in the transfer of solute between the surface and the bulk phase. Increasing the adsorption barrier will reduce the rate at which surface concentration gradients can be diminished and therefore will increase the stability limit of the system. Curves (*c*) and (*d*) of figure 1 illustrate the increase in the stationary stability limit with increasing N_{AD} at constant values of N_{EL}.

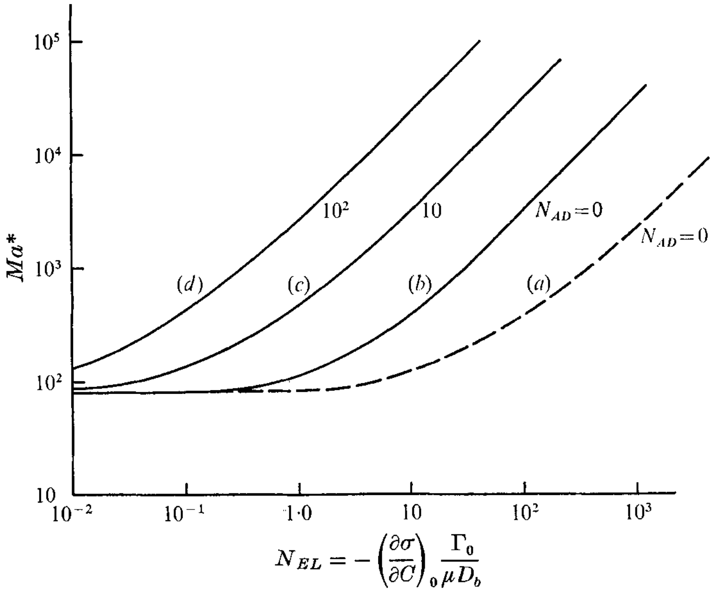

FIGURE 1. Representative stability limits of surfactant solutions in which buoyancy forces are absent. Surface diffusion and Biot numbers are zero. (*a*) Oscillatory stability limit for a system in which $Pr = 10$, $Sc = 10^3$, $N_{SS} = 0{\cdot}1$, and $N_{AD} = 0$. (*b*), (*c*), (*d*) Stationary stability limits for systems in which $N_{AD} = 0$, 10, and 100, respectively.

The adsorption rate begins to have a significant effect on the stability of the system when N_{AD} is greater than 0·01, corresponding to an adsorption rate constant less than 10^{-3} cm sec^{-1}. This means that the stabilizing effect of the adsorption barrier in a system such as 1, 5 pentanediol in water (for which $k_1 \sim 10^{-5}$ cm sec^{-1}) should be easily detected experimentally. When N_{AD} is greater than 100, mass transfer is entirely adsorption controlled; the solute concentration in the bulk is effectively uniform throughout the pool, and bulk diffusion is no longer important in the stabilizing mechanism.

As in the special case of the bulk diffusion controlled system, high Prandtl number fluids do not exhibit oscillatory instability for physically reasonable values of N_{SS}. However, for the low Prandtl number fluids, prediction of the mode of instability is more complicated for the adsorption controlled system than it is for the diffusion controlled system. Increasing the adsorption number reduces the possibility of oscillatory instability, because it minimizes the effect of the Schmidt number. However, increasing N_{AD} enhances the effect of N_{SD} and N_{SS} on the critical Marangoni number.

While in the diffusion controlled system N_{SD} and N_{SS} have little effect on the mode of instability or the stability limit, the combination of N_{SD} and N_{SS} for a given value of N_{AD} in the adsorption controlled system is significant for determining whether the instability will be oscillatory or stationary and, thus, what the critical Marangoni number will be. Figure 2 illustrates the combinations of N_{AD}, N_{SD} and N_{SS} for which the stationary mode of instability is preferred for a fluid whose Prandtl number is 10 and Schmidt number is 10^3. For a given value of N_{SS}, for instance, all combinations of N_{AD} and N_{SD} to the right of the N_{SS} curve will give stationary instability, and, to the left, oscillatory instability. For example, if $N_{SS} = 0{\cdot}6$ and $N_{AD} = 100$, all values of $N_{SD} > 0{\cdot}1$ will yield stationary stability limits, and all values of $N_{SD} < 0{\cdot}1$ will yield oscillatory stability limits.

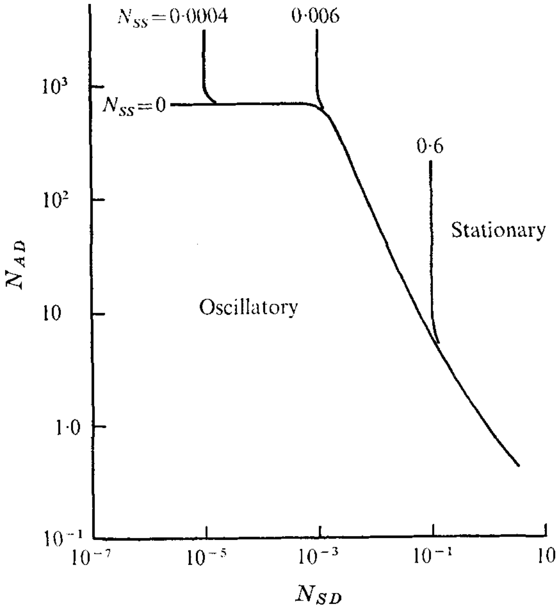

FIGURE 2. The boundary between the regions of oscillatory and stationary instability as a function of N_{AD}, N_{SD} and N_{SS} for a system with $P = 10$, $Sc = 10^3$ and $Bi = 0$.

In the cases where stationary instability predominates, N_{SS} plays no role in determining the stability criteria. The relative importance of surface diffusion to adsorption in determining the stationary stability limit is readily seen in figure 3, in which the critical stationary Marangoni number for $N_{EL} = 100$ is plotted versus the adsorption number for three different values of N_{SD}. There is a marked increase in Ma^* with increasing adsorption barrier, until surface diffusion takes over as the dominant factor in diminishing surface concentration gradients. Because of the coefficients of surface diffusion and bulk diffusion are usually about the same order of magnitude, we have $N_{SD} \sim (1/d)\,(\partial\Gamma/\partial c)_0$. This means that a highly surface active substance like decanol, for which

$$(\partial\Gamma/\partial c)_0 = 0{\cdot}0125\,\text{cm}$$

at low concentrations, would have to exhibit an abnormally large adsorption barrier (i.e. $k_1 \sim 10^{-7}\,\text{cm sec}^{-1}$), if surface diffusion is to have a significant effect on the criteria for stability.

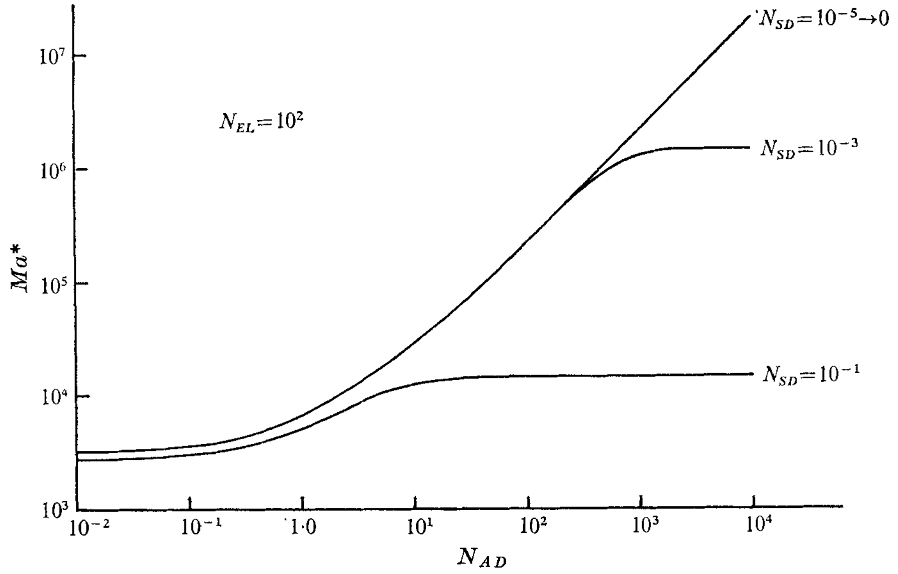

FIGURE 3. Graph illustrating the effect of adsorption barrier and surface diffusion on the stationary stability limit in the absence of buoyancy forces at $N_{EL} = 100$ and $Bi = 0$.

N_{AD}	N_{SD}	N_{SS}	Ma^* at $N_{EL} = 100$
10	10^{-3}	10^{-2}	22 300
10^2	10^{-5}	10^{-2}	22 300
	10^{-1}	1·0	8 920
		10	996
		10^3	89·3
	10^{-3}	10^{-2}	206 000
	10^{-5}	10^{-2}	206 000
10^4	10^{-1}	1·0	8 900
		10	995
		10^3	89·3
	10^{-3}	10^{-2}	866 000
		10^{-1}	86 800
		10	991
		10^3	89·2
	10^{-5}	10^{-2}	866 000
		10^{-1}	86 800
		10	991
		10^{-3}	89·2

TABLE 1. Values of the oscillatory critical Marangoni number for $N_{EL} = 100$ and various values of N_{AD}, N_{SD} and N_{SS}

In the cases where oscillatory instability dominates, N_{SS} as well as N_{SD}, N_{AD} and N_{EL} is important in determining the stability limit for the system. Table 1 is a brief list of the oscillatory critical Marangoni number at $N_{EL} = 100$ for various values of N_{AD}, N_{SD} and N_{SS}, and it illustrates the trend of decreasing Ma^* with increasing N_{SS} and N_{AD} as well as the unimportance of N_{SD} and N_{AD} for comparatively large values of N_{SS}.

6.3. *Surface diffusion control*

As the adsorption barrier becomes infinite, or as the solubility of the solute becomes negligibly small, the general solution (11) reduces to the case for the insoluble surfactant spread on a liquid pool. The special solution for $\operatorname{Im}\lambda = 0$ is identical to that of Berg & Acrivos (1965). It is the solution for $\operatorname{Im}\lambda \neq 0$ that is new, and of particular interest. The present results show that oscillatory instability does indeed exist in the insoluble surfactant case.

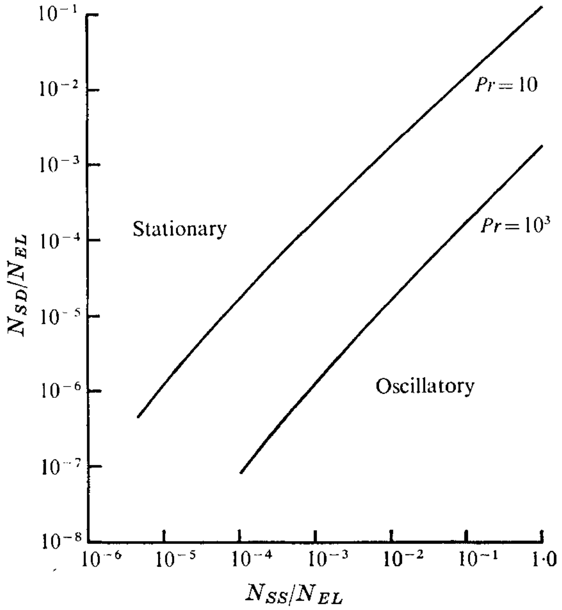

FIGURE 4. The boundary between the regions of oscillatory and stationary instability for a liquid pool with an insoluble surfactant spread on the surface. $Bi = 0$.

As N_{AD} approaches infinity, the number of pertinent dimensionless groups required to describe the system is reduced to three: Pr, N_{SD}/N_{EL} and N_{SS}/N_{EL}. Thus, the boundary between oscillatory and stationary states can be represented graphically, as shown in figure 4. All combinations of N_{SD}/N_{EL} and N_{SS}/N_{EL} that lie above the curve corresponding to the Prandtl number for the liquid represent system configurations for which the stationary mode of instability will dominate, and all combinations below the appropriate curve represent configurations for which oscillatory instability, will be initiated.

If the mode of instability is stationary, the stability limit for the liquid pool with an insoluble surfactant on its surface depends solely on the value of

N_{SD}/N_{EL}, as shown by Berg & Acrivos. When oscillatory modes of instability dominate in the insoluble surfactant case, however, the effect of surface diffusion on the stability limit becomes negligible, because, in the relatively short period of oscillation, surface diffusion does not have time to alter the surface concentration gradient. The important parameter in this case is N_{SS}/N_{EL}. Figure 5 shows the stability limit Ma^* versus the modified surface diffusion number N_{SD}/N_{EL}. The solid line is the stationary stability limit presented by Berg & Acrivos, while the dashed curves are the oscillatory stability limits for three values of N_{SS}/N_{EL} for a liquid pool whose Prandtl number is 10.

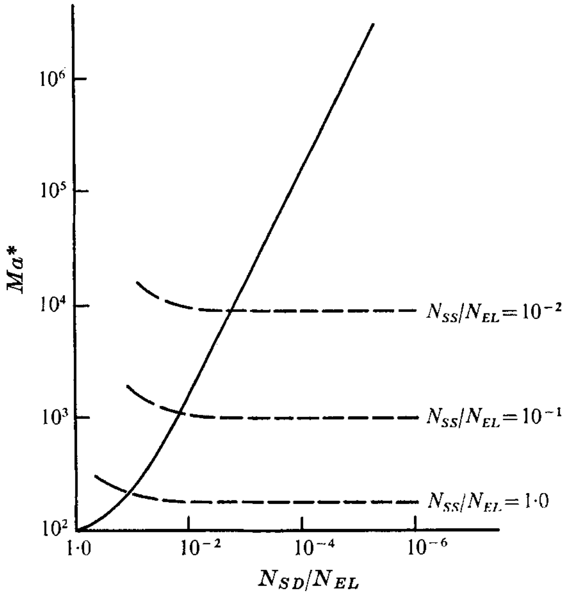

FIGURE 5. The stability limit of insoluble surfactant systems with buoyancy forces absent. ———, stationary stability limit; – – – –, oscillatory limits for specific values of N_{SS}/N_{EL}, with $Pr = 10$. $Bi = 0$ for all curves.

For most physically realizable insoluble surfactant systems, the preferred mode of instability will be oscillatory. Consider, for example, a 'liquid expanded' monolayer of oleic acid on a 1 mm deep pool of water at 20 °C. For this system, $(\partial\sigma/\partial\Gamma)_0 = -5{\cdot}5\times10^{10}$ dynes cm mole^{-1} at $\Gamma = 3{\cdot}7\times10^{-10}$ moles cm^{-2}. Therefore, $N_{SD}/N_{EL} \sim 5\times10^{-8}$ and $N_{SS}/N_{EL} = 5\times10^{-5}$. From figure 4, it is evident that this system will exhibit oscillatory instability. From figure 5 it is seen, by extrapolation, that, although the stationary stability limit yields a value of Ma^* of nearly 3×10^8, the actual minimum stability limit (due to oscillatory instability) puts Ma^* at 2×10^6.

Whether or not such instability is observed experimentally, however, will depend on the period of oscillation of the disturbance associated with the critical Marangoni number. If the period of oscillation is extremely long, for instance, it may never be observed during the course of an experiment. The period of oscillation τ is given by the value of $\operatorname{Im}\lambda$ associated with the critical oscillatory Marangoni number for the system: $\tau = 2\pi d^2/\operatorname{Im}\lambda\nu$.

For the insoluble surfactant case, the modified surface diffusion number N_{SD}/N_{EL} has little effect on τ in the region where oscillatory instability dominates. Rather τ, like the oscillatory stability limit, is a strong function of N_{SS}/N_{EL} only. For a 1 mm deep pool of a 1 cs. fluid, τ varies from 6 to 30 sec as N_{SS}/N_{EL} varies from 10^{-4} to 10. Thus, as a monolayer becomes more condensed (i.e. more highly concentrated), the initial period of oscillation becomes shorter.

In particular, for oleic acid spread on water at a concentration of $\Gamma = 3{\cdot}7 \times 10^{-10}$ moles cm^{-2}, the initial period of the oscillatory disturbance is predicted to be 10 sec. This is the period of the infinitesimal disturbance at the point of neutral stability, and may not be the period observed experimentally after the disturbance has grown to a detectable amplitude.

7. General solution including buoyancy effects

The addition of the destabilizing buoyancy force to the problem would not appear to add any additional potential for oscillatory instability in the system because of the comparatively weak dependence of the buoyancy stability limit on the upper surface boundary condition and because the destabilizing forces of buoyancy and surface tension are so tightly coupled in the pure liquid pool (Nield 1964). Thus, it is expected that the true stability limit will be the stationary stability limit for larger Prandtl number fluids even when both surface forces and density stratification act in concert to initiate convection in the binary solution pool.

The solution of (8)–(10) for an arbitrary R is substantially simpler if we assume that $\mathrm{Im}\,\lambda$ as well as $\mathrm{Re}\,\lambda$ equals zero. Therefore, we will limit ourselves to the consideration of large Prandtl number fluids for which $\mathrm{Im}\,\lambda = 0$ is expected to coincide with the true stability limit for the system.

The solution is obtained using Fourier series expansions in a technique paralleling Nield's analysis of the pure liquid pool. The solution for the critical stationary Marangoni number is

$$Ma = \left[\frac{1}{S_1S_4 - S_2S_5}\right]\left\{RS_2^2 + \frac{S_4}{2\alpha^2}[2\alpha^2S_3 + Bi + 1]\right.$$
$$\left. + F_s[2\alpha^2R(S_1^2S_4 + S_2^2S_4 - 2S_1S_2S_5) + (S_4^2 - S_5^2)(2\alpha^2S_3 + Bi + 1)]\right\}, \quad (12)$$

where
$$S_1 = \sum_{n=1}^{\infty}\frac{n^2\pi^2}{\beta^3 - \alpha^2R}, \quad S_2 = \sum_{n=1}^{\infty}\frac{n^2\pi^{12}(-1)^n}{\beta^3 - \alpha^2R},$$
$$S_3 = \sum_{n=1}^{\infty}\frac{\beta^2 - R}{\beta^3 - \alpha^2R}, \quad S_4 = \sum_{n=1}^{\infty}\frac{\beta n^2\pi^2}{\beta^3 - \alpha^2R},$$
$$S_5 = \sum_{n=1}^{\infty}\frac{\beta n^2\pi^2(-1)^n}{\beta^3 - \alpha^2R},$$
$$\beta = n^2\pi + \alpha^2,$$

and
$$F_s = N_V + N_{EL}/[\alpha^2N_{SD} + \alpha/\coth\alpha + \alpha N_{AD})].$$

The effect of the solute on the critical Rayleigh number in the absence of surface tension forces is determined by setting $Ma = 0$ in (12). Figure 6 illustrates the effect of elasticity number N_{EL} on the critical Rayleigh number for various values of the adsorption number N_{AD}. The transition of the upper surface from a hydrodynamically free surface ($R^* = 669$) to a hydrodynamically fixed surfact ($R^* = 1296$) with increasing elasticity number, and increasing adsorption barrier, is seen to be abrupt.

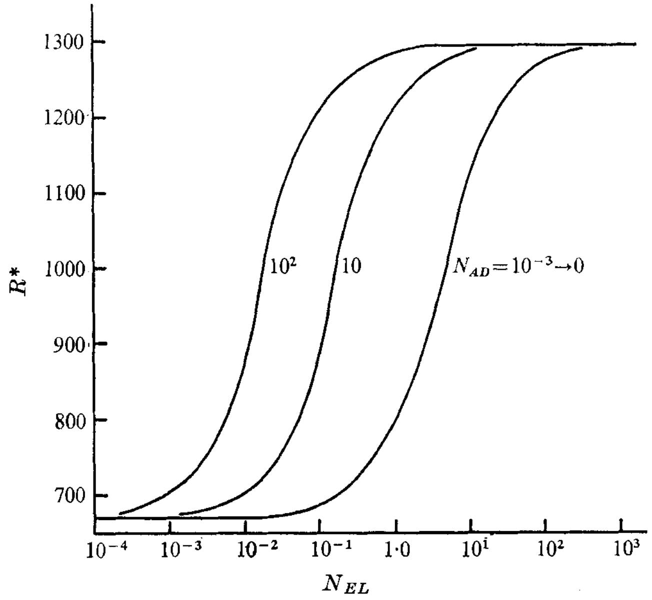

FIGURE 6. The boundary between stability and buoyancy induced convection for surfactant solution pools with N_{SD} and $Bi = 0$.

The results for pure buoyancy instability, together with those obtained from (11*b*) for Ma^*, are used to normalize the values of R and Ma in the presentation of the combined solution (12). Results are presented for the three special cases previously set forth: the bulk diffusion controlled system, the adsorption controlled system, and the surface diffusion controlled system. Regardless of which case obtains in a given situation, varying the Biot number between zero and infinity is found to have only a very small effect on the location of the stability curves. Results are thus shown only for the case of Bi equal to zero.

Figure 7 shows the normalized critical Marangoni number versus the normalized Rayleigh number for the full range of elasticity numbers for the system in which the rate of mass transfer into the surface is bulk diffusion controlled. There is strong coupling between the two destabilizing mechanisms (indicated by the almost 45° line) over the whole range of N_{EL} from zero to infinity. In this case, as in the pure liquid pool, the destabilizing surface forces and buoyancy forces almost completely reinforce one another to cause instability.

Imposition of an absorption barrier to mass transfer between the surface and the subsurface layer, however, tends to break down the tight coupling between mechanisms. Figure 8 illustrates, for the adsorption controlled system, that there is no longer tight coupling between surface tension and buoyancy effects over the full range of values of N_{EL}. This lack of interaction between the two destabilizing mechanisms coincides with a sizeable difference in preferred wavenumber α, for the case of pure surface tension driven and pure buoyancy driven instability in an adsorption controlled system. In the former case, the preferred wavenumber is of the order of 0·5, as compared with approximately 2·5 for the latter.

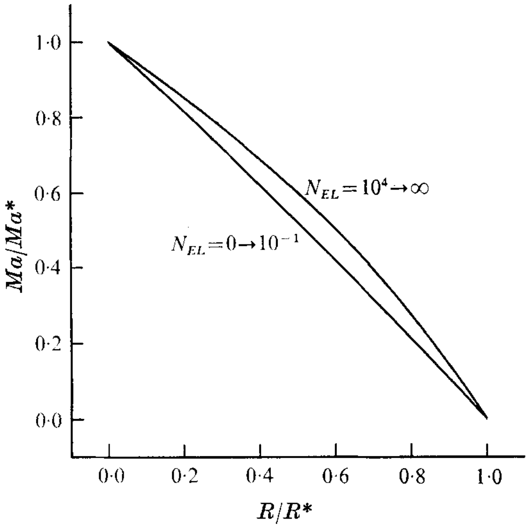

FIGURE 7. The normalized critical Marangoni number *vs.* the normalized critical Rayleigh number for the surfactant solution pool with no adsorption barrier to mass transfer into the surface. $Bi = 0$ and $N_{SD} = 10^{-3} \rightarrow 0$. At $N_{SD} = 10^{-1}$ the coupling is even tighter, i.e. the $N_{EL} = \infty$ curve is even closer to the $N_{EL} = 0$ curve.

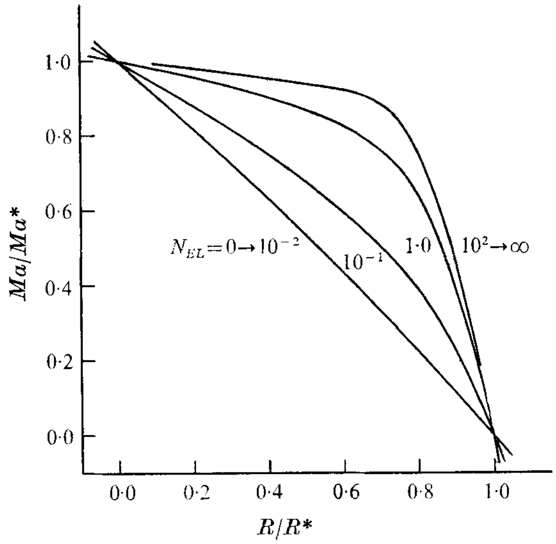

FIGURE 8. The normalized critical Marangoni number *vs.* the normalized critical Rayleigh number for the soluble surfactant system in which there is a noticeable absorption barrier to mass transfer into the surface. $N_{AD} = 100$, $Bi = N_{SD} = 0$.

The lack of interaction between mechanisms increases with increasing N_{AD} for a constant value of N_{EL} until mass transfer between the surface and the subsurface layer becomes so hindered that surface diffusion takes over as the dominant mechanism for diminishing surface concentration gradients. At this point, the tight coupling abruptly returns. The transition from tight coupling to loose coupling to tight coupling with increasing N_{AD} is illustrated in figure 9. Figure 10 illustrates that the tight coupling between mechanisms has again returned over the full range of elasticity numbers and surface diffusion numbers for the case of the insoluble surfactant.

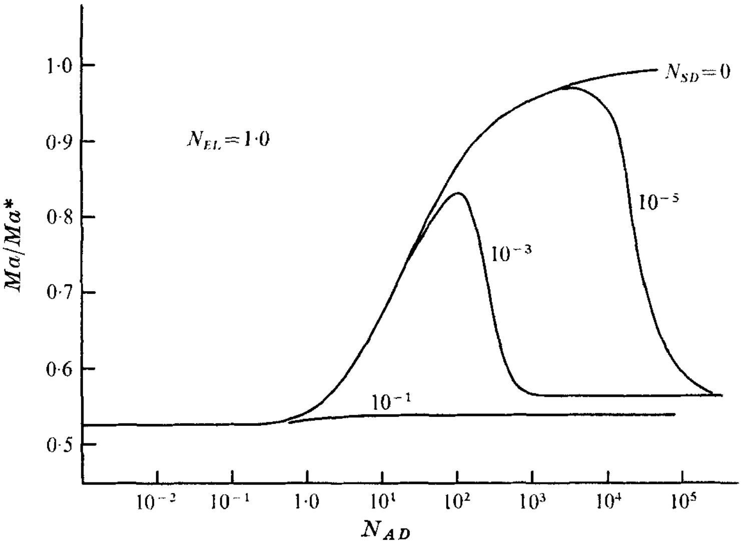

FIGURE 9. Illustration of how decoupling between the two destabilizing mechanisms occurs only when adsorption controls the rate of lateral mass transfer. $R/R^* = 0·5$, $N_{EL} = 1·0$ and $Bi = 0$.

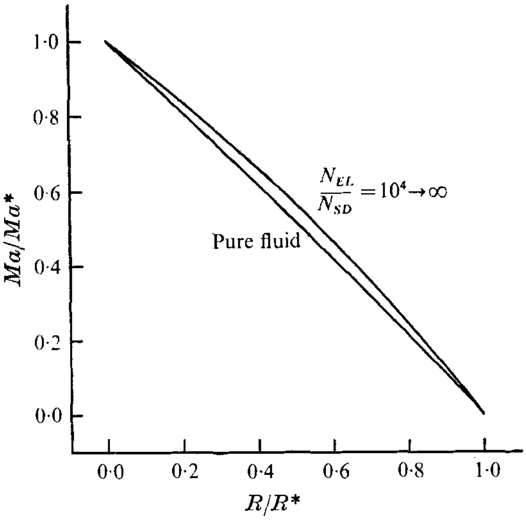

FIGURE 10. The normalized critical Marangoni number *vs.* the normalized critical Rayleigh number for the insoluble surfactant system. $Bi = 0$.

8. Conclusion

The present theoretical investigation of the stability of shallow pools of dilute surfactant solutions heated from below has demonstrated that such systems are apt tools for the experimental investigation of interfacial hydrodynamics. The calculated stability results have revealed that the solute in the liquid pool need be but slightly surface active to have a marked effect on the hydrodynamic behaviour of the system. The stability limit has been shown to be extremely sensitive not only to the amount of surface active material in the surface and to the magnitude of its effect on surface tension, but also to the rate and mechanism of its lateral transport. The more effectively the induced surface concentration gradients are sustained with time, the greater will be the stabilizing effect of the solute.

REFERENCES

Berg, J. C. & Acrivos, A. 1965 *Chem. Engng. Sci.* **20**, 737.

Defay, R., Prigogine, I., Bellemans, A. & Everett, D. H. 1966 *Surface Tension and Adsorption*. London: Longmans.

England, D. C. & Berg, J. C. 1971 *A. I. Ch. E. J.* **17**, 313.

Nield, D. A. 1964 *J. Fluid Mech.* **19**, 341.

Palmer, H. J. & Berg, J. C. 1971 *J. Fluid Mech.* **47**, 779.

Pearson, J. R. A. 1958 *J. Fluid Mech.* **4**, 489.

Sakata, E. K. & Berg, J. C. 1969 *Indust. Engng. Chem. Fundamentals*, **8**, 570.

Schmidt, R. J. & Milverton, S. W. 1935 *Proc. Roy. Soc.* A **152**, 586.

Scriven, L. E. & Sternling, C. V. 1964 *J. Fluid Mech.* **19**, 321.

Smith, K. A. 1966 *J. Fluid Mech.* **24**, 401.

Vidal, A. & Acrivos, A. 1966 *Phys. Fluids*, **9**, 615.