The Effect of Surfactants on the Stability of Fluid Interfaces during Phase Transformation

The influence of surface active solutes on the stability of fluids during phase transformation is examined both experimentally and theoretically. Experiments on the interfacial stability of triethanolamine as it steadily evaporates into a partial vacuum verifies that for high surface tension fluids, spontaneous convection induced by differential vapor recoil is stabilized by the addition of surfactants and that the degree of stability increases with the surface activity of the surfactant. The hydrodynamic stability of surfactant solutions undergoing phase transformation is then examined using linear stability analysis. Results reveal that surfactants have a marked stabilizing effect on the differential vapor recoil mechanism but have essentially no effect on the fluid inertia and moving boundary destabilizing mechanisms. Consequently, the maximum stabilizing effect of surface active solutes on liquids evaporating under vacuum is determined by the criterion for fluid inertia instability.

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SCOPE

The surface of a liquid evaporating at reduced pressure (<1 Torr) is potentially unstable to local variations in evaporation rate, local surface depressions being produced by the force exerted on the surface by the rapidly departing vapor and sustained liquid flows being driven by the resultant shear exerted on the liquid surface by the vapor. Hickman (1952, 1972) has shown experimentally that a tenfold increase in evaporation rate may be expected if the interface is disrupted by this differential vapor recoil mechanism. Furthermore, he demonstrated that chemical artifacts not only affect the criteria for vapor-recoil instability, but they also influence the nature of post critical convection patterns and introduce the potential for spasmodic fluctuations in pressure during vacuum distillations.

The mechanism of instability by differential vapor recoil has been confirmed theoretically by Palmer (1976) in a linear hydrodynamic stability analysis which predicts the criteria for vapor recoil instability and also identifies an additional fluid inertia destabilizing mechanism which dominates during both evaporation and condensation on steeply inclined surfaces. The objective of the present investigation is twofold: to demonstrate experimentally that surfactants stabilize the differential vapor recoil mechanism, and to determine theoretically the influence of nonvolatile surface active solutes on the stability of liquids evaporating at reduced pressure with the aid of linear stability analysis. Incorporated in the analysis is the effect of surfactants on the moving boundary destabilizing mechanism described by Miller (1973), which is applicable to certain secondary oil recovery techniques.

From a fundamental viewpoint, this investigation contributes to our understanding of interfacial flow phenomena and of the stability of interfaces during phase transformation. Of more immediate significance, the results will aid in the application of differential vapor recoil to increase substantially the efficiency of low pressure interphase transport processes and help guide process designs to avoid the control problems intrinsic to vapor recoil instability.

CONCLUSIONS AND SIGNIFICANCE

Experiments were conducted in which small amounts (<1 mg) of a specific surface active contaminant were introduced to the surface of a steadily evaporating, intensely turbulent surface of triethanolamine (TEA). Erucic acid, Igepal CO-210, Igepal CO-970, and α-tocopherol acid succinate were used as surfactants in the experiments. While the stabilizing effect of erucic acid and Igepal CO-210 was minimal and short-lived, the effect of Igepal CO-970 and α-tocopherol acid succinate was profound and permanent. Deposition of $\sim 10^{-8}$ mole/cm^2 of α-tocopherol acid succinate was sufficient to wipe out all vapor recoil instabilities on the liquid surface and to maintain fluid stability for many hours. Small amounts of Igepal CO-970 had equivalent effects. The steady evaporation rate was reduced by at least a factor of 3, and the degree of liquid superheat had to be increased sixfold before interfacial convection could be reinitiated.

The linear stability analysis presented in this paper predicts the conditions for neutral stationary instability in a liquid evaporating at reduced pressure and containing small amounts of a nonvolatile, surface active solute. The theoretical results reveal that surfactants have a profound stabilizing influence on convection induced by differential vapor recoil. Not only is the stability limit continuously increased, but also the range of evaporation rates over which vapor recoil instability can occur is reduced as the surface activity and concentration of the surfactant are increased. In contrast, surfactants have essentially no effect on the fluid inertia and moving boundary destabilizing mechanisms. This means that under most circumstances the practical upper limit of stability for the system is determined by the conditions necessary for fluid inertia instability.

When phase transformation is accompanied by a change in fluid density, a discontinuity in velocity and in the rate of momentum transport occurs at the interface. The result is a normal force on the interface (a dynamic pressure) which acts in the direction of the denser fluid. While this vapor recoil force is insignificant relative to atmospheric pressures, it can be a dominant force during evaporation and condensation under vacuum. In particular, for liquids evaporating at pressures below 1 Torr, local variations in this recoil force can produce intense interfacial turbulence which typically increases evaporation rates tenfold (Hickman, 1952, 1972). From a fundamental viewpoint, spontaneous convection is initiated because evaporation rate at reduced pressure depends on the local interfacial temperature (Hertz, 1882; Knudsen, 1915). Thus, any disturbance which increases local surface temperature will increase the local evaporation rate to produce a local increase in the normal force on the interface (vapor recoil). The result is a depression or crater in the surface with slanted walls which permits the departing vapor to shear the liquid surface and drag hot liquid up to the point of already higher temperature to amplify the original disturbance.

Of particular importance was Hickman's observation that the liquid surface often separates into two distinct regions of interfacial activity, with portions of the surface exhibiting rapid small scale movement and a substantially increased evaporation rate (which he called working) while the rest of the surface remained torpid and stable. The large difference in evaporation rate from the two adjacent regions was dramatically revealed by a difference in their surface elevations (~2 mm), caused by the difference in momentum transfer to the surface by the departing vapor. It is important to recognize that the spontaneous formation of a schizoid surface was observed on a wide variety of liquids of moderate to low surface tension, including silicone fluids. While it is possible that torpidity on high surface tension liquids is produced by surface active agents, the low surface tension fluids such as the silicones are highly resistant to surface active contaminants and their stabilizing effects (Palmer, 1971). Although Hickman was unable to uncover a specific additive which would induce torpidity on a working surface, he did demonstrate that the existence of the schizoid surface is due to the presence of a chemical artifact in the system. Whether it is a surface active substance or merely a less volatile constituent which concentrates at the interface during evaporation, this contaminant is continuously swept onto torpid areas through viscous drag by the rapidly departing vapor of the working areas (see Hickman, 1972). In fact, by carefully overflowing the interfacial layer of the torpid area to discard any interfacial contaminants, Hickman has shown that a schizoid surface can often be converted to one which is entirely working.

Descriptively satisfying, these observations call for quantitative interpretation and for identification of specific chemical relationships between artifacts and substrate liquids to provide a basis for predicting behavior in a diversity of experimental systems. Not only is the differential vapor recoil mechanism extremely effective at producing interfacial mixing and high interphase heat and mass transfer rates, but also it is often responsible for spasmodic fluctuations in pressure during vacuum distillations which can render the apparatus inoperative or ultimately result in loss of valuable product. Such control problems are intrinsic to the mechanism of instability. The presence of torpidogenic artifacts on the quiescent surface increases fluid stability above that for the clean interface. Thus, the bulk liquid temperature (sensible heat) must be increased substantially to guarantee sufficient heat conduction to the interface to maintain an adequate evaporation rate. Yet when the stability limit is exceeded locally, contaminants are swept away from the point of instability to expose a highly unstable, pristine surface which maintains an extremely high evaporation rate until all the excess sensible heat in the bulk liquid has been utilized. Evaporation then ceases, the torpidogenic material respreads over the liquid surface, and the sequence is repeated.

Recently, Palmer (1976) has demonstrated that the stability of a pure liquid undergoing steady evaporation at reduced pressure is amenable to theoretical investigation with the aid of linear stability analysis. His results show that horizontal evaporating surfaces are unstable to local variations in evaporation rate, local surface depressions being produced by the force exerted on the surface by the departing vapor (differential vapor recoil) and sustained liquid flow being driven by the resultant shear exerted on the liquid surface by the vapor. The criteria for instability is shown to be extremely sensitive to the density change on evaporation which, in turn, is directly related to the operating pressure; the lower the pressure, the greater the potential for instability via the differential vapor recoil mechanism.

Apart from this differential vapor recoil mechanism, Palmer's analysis reveals that a fluid interface may become unstable due to local variations in fluid inertia which obtain when the interface is deformed during phase transformation. This fluid inertia mechanism is operative even in the absence of local variations in evaporation rate and is the dominant destabilizing mechanism on steeply inclined surfaces for which gravitational stabilization is minimal. Furthermore, the fluid inertia mechanism is equally effective at producing instabilities during condensation as well as during evaporation.

The purpose of the present investigation is twofold. First, a model system of a pure liquid and a specific contaminant is devised which demonstrates experimentally that surface active contaminants may induce torpidity on high surface tension liquids evaporating at reduced pressures. Second, linear hydrodynamic stability analysis is used to explore the potential stabilizing effect of nonvolatile, surface active solutes on interfacial instabilities in liquids of high surface tension evaporating under vacuum. This is a prelude to future treatment of the more usual but interpretatively difficult case of schizogenic liquids of low surface tension.

EXPERIMENT

To gain insight into the nature and chemistry of torpidity and the schizoid surface, it is necessary to determine experimentally the conditions which promote formation of torpid regions on an otherwise unstable, rapidly evaporating liquid surface. While Hickman was able to create an entirely working surface by carefully overflowing torpid regions to discard interfacial contaminants, he could find no named additive which would induce torpidity on a working surface. This is hardly surprising, since the common industrial oils on which he had observed the phenomena were all of low surface tension, where a likely adsorbate of still lower tension was hard to come by. Temporarily begging this question, or as a forerunner to approaching it, this research selects a pure liquid of high surface tension and suitable volatility at convenient temperatures. Triethanolamine (TEA) meets the requirements for a test fluid because of its moderately high surface tension (47 dyne/cm at 25°C) and waterlike qualities. In addition, its vapor pressure is low enough ($\sim 10^{-3}$ Torr at 25°C) to

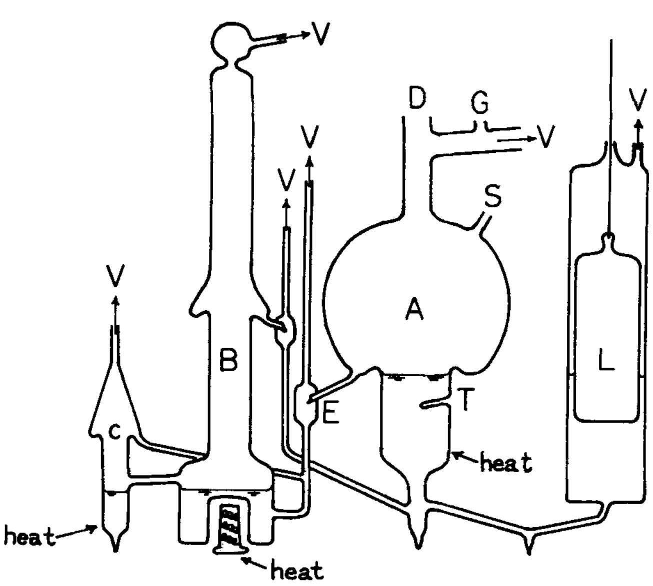

Fig. 1. Schematic diagram of the experimental apparatus used to determine the influence of specific surface active contaminants on the habits of the evaporating surface of triethanolamine under vacuum. Illustration shows the main observation flask (A), second and third boilers (B) and (C), dropper (E) for evaporation rate measurement, location of vacuum gauge (G), plumb for level control (L), port for surfactant addition (S), thermocouple well (T), and vacuum connections (V). A telescoping thermocouple probe may be attached at (D) Heat is supplied where indicated.

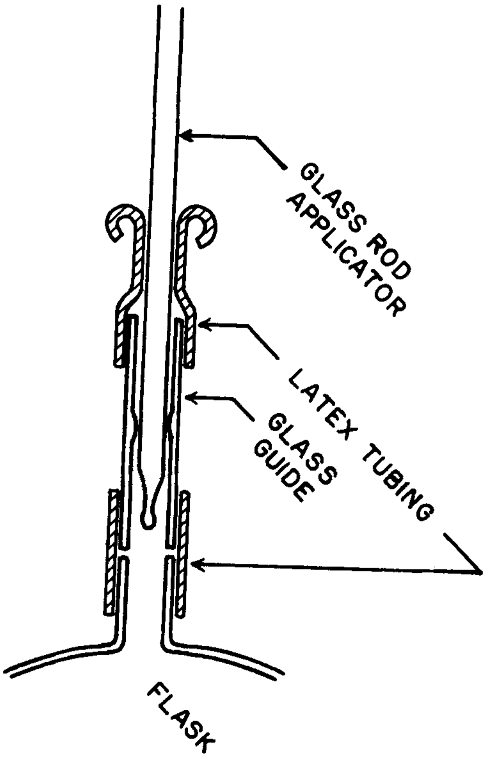

Fig. 2. Illustration of glass probe assembly for applying small quantities of surfactant to the working surface of triethanolamine under vacuum. All glass-to-latex seals are lubricated with TEA.

permit low pressure vaporization experiments to be conducted with a simple, air cooled condenser.

The all glass apparatus used in the experiments is similar to that used by Hickman (1972) and is illustrated schematically in Figure 1. The TEA in the main flask (A) is steadily vaporized and is condensed on the walls of the flask, where it drains through the dropper (E) and into the second boiler (B). The dropper (E) permits the measurement of evaporation rate, while the boiler (B) not only provides a purification step for the TEA but also lifts the fluid to an elevation sufficient to permit gravity return of the condensate to the main flask. Torpidogenic material may be successively concentrated from (A) to (B) to (C) by surface overflow using the level control (L) and by adjusting evaporation rates in each boiler. Heat is supplied continuously in the positions indicated with windings of nichrome wire. Cooling for condensation is supplied by jets of air directed on the condensing surfaces of (A), (B), and (C). Vacuum was produced with a mechanical pump and an oil diffusion pump in series connected at (V). Operating pressure was measured with both a thermocouple gauge and a Pirani gauge.

After the system was charged with TEA, it took approximately 10 days of continuous redistillation with surface overflow from flask (A) to (B) before interfacial contamination was removed from the TEA in the main flask to provide a working surface for several hours with overflow terminated before small areas of torpidity reappeared. Thus, a temporary clean surface of TEA could be obtained on which to test the stabilizing effect of various surface active contaminants on instability induced by differential vapor recoil.

All experiments were conducted at an operating pressure of 0.02 Torr and at an evaporation rate of 2×10^{-3} g/cm^2 s. With an entirely working surface present, thermocouple measurements indicated a bulk temperature of ~110°C and a degree of superheat of ~10°C.

Small amounts of surfactant are introduced to the working surface of TEA on the tip of a glass probe which is inserted through a decompression port at (S) and touched to the liquid surface. The design of the decompression port is shown in Figure 2. The decompression port virtually eliminates any disturbance of the operating pressure in the main flask during the introduction of surfactant to the system. Erucic acid, Igepal CO-210, Igepal CO-970, and α-tocopherol acid succinate were used as surfactants in the experiments. [Igepal has the structure $C_9H_9—C_6H_4—O—(C_2H_4O)_{n-1}CH_2CH_2OH$; the number designation is its approximate molecular weight.] In particular, the α-tocopherol acid succinate was chosen for its high molecular weight and consequent low volatility at operating conditions; for its large nonpolar, hydrophobic groups which minimize its solubility in TEA; and for its polar acid succinate group which is necessary for specific adsorption and orientation of the molecule in the TEA interface. Each surfactant was first dissolved in a volatile solvent (heptane for erucic acid, acetone for the Igepal compounds, and methylethyl ketone for the α-tocopherol acid succinate). Then approximately 20 μl of this solution was deposited on the tip of the glass probe, and the solvent was allowed to evaporate, leaving microgram quantities of surfactant on the tip of the probe.

When the tip of the probe was touched to the working surface, each of the surfactants began to spread over the liquid surface and stabilize convection, creating a torpid island and decreasing the evaporation rate. In the case of erucic acid and Igepal CO-210, the stabilizing effect was limited to approximately 10% of the total liquid surface and lasted for only 30 s. Apparently, the lower molecular weight erucic acid and Igepal CO-210 evaporated from the hot TEA surface, since all traces of interfacial stability disappeared in less than one minute.

Igepal CO-970 and α-tocopherol acid succinate had far more permanent effects. Deposition of just 0.34 mg of α-tocopherol acid succinate (equivalent to a surface concentration of $\sim 10^{-8}$ mole/cm^2) was sufficient to wipe out all vapor recoil instabilities on the liquid surface and to maintain fluid stability for the duration of the experiment. Evaporation rates were noticeably decreased by at least a factor of three. After several hours, the torpid film was overflowed to discard the surfactant and regain a working surface. However, once overflowing ceased, a torpid area returned and increased in size with time reflecting adsorption of dissolved surfactant from the bulk liquid. In fact, the system required 2 wk of continuous repurification with liquid surface overflow to eliminate the stabilizing effect of the α-tocopherol acid succinate on the TEA in the main flask. Addition of ~0.1 mg of Igepal CO-970 surfactant to the working TEA surface produced equivalent effects.

In addition, an experiment was conducted to determine the degree of superheat necessary to regain the working surface after surfactant deposition. Prior to the addition of 0.1 mg of

Igepal CO-970, the bulk temperature was 111°C, and the degree of superheat was 10°C. After deposition of the Igepal CO-970 on the surface, the heating rate was gradually increased until at a bulk liquid temperature of 169°C the stability limit of the system was finally exceeded and the liquid literally exploded out of the flask. Thus, the presence of the surfactant not only increased the stability of the system more than fivefold, but it also introduced the potential for uncontrollable evaporation via the mechanism described in the introduction.

MATHEMATICAL ANALYSIS

Quiescent System

Consider the steady evaporation of a liquid at reduced pressure. The liquid surface is flat and is infinite in lateral extent. The liquid is unbounded from below, and the rate of evaporation is a function of the surface temperature as described by the Hertz-Kundsen equation (see Schrage, 1953).

Prior to the onset of convection, the surface temperature and evaporation rate are assumed to be independent of surface position, and the concentration of surfactant is uniform throughout the liquid. The surfactant concentration in the surface, however, is greater (possibly much greater) than it is in the bulk liquid. This surfactant imparts an elasticity to the surface which resists surface dilations (see Berg, 1972) and therefore can have a profound effect on the stability of systems subject to destabilizing mechanisms which require interfacial mobility, such as instabilities induced by differential surface tension and differential vapor recoil. In general, the bulk of the liquid will be circulating either by mechanical agitation or by natural convection. However, in the absence of interfacial instabilities, a quiescent boundary layer may exist in the vicinity of the interface through which heat is transported primarily by conduction. The thickness of this boundary layer necessarily depends on the intensity of the bulk circulation. It is this interfacial region whose stability is to be analyzed.

The steady evaporation rate results in a net liquid flow upwards through the thermal boundary layer. Because of its relative insignificance and for simplicity, the effect of this liquid flow on the stable temperature profile in the thermal boundary layer is ignored in the present analysis. Therefore, prior to an instability, the temperature profile in the boundary layer is assumed to be linear, while the liquid temperature outside the boundary layer is assumed constant (see Palmer, 1976). In addition, the rate of cooling of the liquid surface by heat conduction in the vapor phase is assumed to be negligible compared with the heat removed by the phase change. Furthermore, all physical properties of the two fluid phases except surface tension and vapor pressure are assumed to be independent of temperature.

Formulation

The linear stability of the interfacial region is analyzed by introducing to the quiescent system an infinitesimal disturbance, exponential in time and periodic in the planform spatial variables, but of arbitrary wavelength. Following the formulation by Palmer for pure liquids, this disturbance is then made to obey the conservation equations of mass, momentum and energy subject to the appropriate boundary conditions and, in addition, is made to satisfy the equation of mass conservation for the solute. The rectangular coordinate system used in this development moves with the unperturbed interface, with the z coordinate normal to the interface and increasing into the vapor phase.

In the present analysis, only stationary modes of instability will be considered. Thus, conditions will be sought for which the time growth constant γ equals zero. While this assumption of exchange of stabilities appears to be justified for pure liquids, the competing effects of surfactant stabilization may favor oscillatory modes of instability (see Palmer and Berg, 1972). Consequently, the present analysis will provide an upper bound on the conditions for stability of the surfactant laden interface.

For the quiescent system conservation of mass, momentum and energy at the interface require that

$$\rho_L W_L^* = \rho_V W_V^* = \eta^* \tag{1}$$

$$P_L^* - P_V^* = \eta^{*2}(\rho_V^{-1} - \rho_L^{-1}) \tag{2}$$

$$\lambda_{\text{vap}}\eta^* = -k_L \partial T_L^*/\partial z \tag{3}$$

where the effects of heat conduction in the vapor phase and energy transport from the surface as kinetic energy have been neglected in (3). The right-hand side of Equation (2) represents the discontinuity in linear momentum which occurs at the interface during phase change and which equals the recoil force of the vapor on the liquid surface.

If the system variables are now perturbed an infinitesimal amount from their quiescent values and the requirement that γ equals zero is imposed, the boundary conditions at the free surface become

$$\rho_V W_V' = \eta' = (\partial\eta/\partial T)^* T_L' \tag{4}$$

$$\rho_L W_L' - \rho_V W_V' = 0 \tag{5}$$

$$\eta^*(\rho_L^{-1} - \rho_V^{-1})\nabla_{II}^2 B' = \frac{\partial W_L'}{\partial z} - \frac{\partial W_V'}{\partial z} \tag{6}$$

$$\begin{aligned}(P_V' - P_L') &+ 2\eta^*\eta'(\rho_V^{-1} - \rho_L^{-1}) \\ &+ 2[\mu_L \partial W_L'/\partial z - \mu_V \partial W_V'/\partial z] - \sigma^* \nabla_{II}^2 B' = 0\end{aligned} \tag{7}$$

$$\begin{aligned}(\partial\sigma/\partial T)^* \nabla_{II}^2 T_L' &+ (\partial\sigma/\partial\Gamma)^* \nabla_{II}^2 \Gamma' \\ &- \mu_s\left[\nabla_{II}^2 \frac{\partial W_L'}{\partial z} - \frac{\eta^*}{\rho_L}\nabla_{II}^4 B'\right] = \mu_L[\nabla_{II}^2 W_L' \\ &- \partial^2 W_L'/\partial z^2] - \mu_V[\nabla_{II}^2 W_V' - \partial^2 W_V'/\partial z^2]\end{aligned} \tag{8}$$

$$\eta'\lambda_{\text{vap}} + k_L \partial T_L'/\partial z = 0 \tag{9}$$

where (4) relates the perturbation in evaporation rate to the perturbation in gas phase velocity at the interface, (5) is the equation of mass conservation at the interface, (6) guarantees continuity of tangential velocity, (7) is the normal component of the equation of momentum conservation at the interface, (8) is the surface divergence of the momentum conservation equation, and (9) provides for conservation of energy at the interface. Included in Equation (8) are the destabilizing effects of surface tension gradients produced by local variations in surface temperature (Marangoni instability), the surface restoring forces produced by local variations in surfactant concentration in the interface, and the stabilizing influence of surface viscosity which resists interfacial motion. The potential for Marangoni instability is included in the analysis to determine the effect of surfactants on the coupling between the vapor recoil and the surface tension destabilizing mechanism. Because Palmer (1976) has shown that kinetic energy transport and viscous heating at the interface are generally insignificant, these effects have been neglected in (9).

In addition, conservation of the nonvolatile solute at the interface requires that (see Palmer and Berg, 1972)

$$\Gamma^*\left[\frac{\partial W_L'}{\partial z} - \frac{\eta^*}{\rho_L}\nabla_{II}^2 B'\right] + \mathcal{D}_s \nabla_{II}^2 \Gamma' = \mathcal{D}_b \frac{\partial C'}{\partial z}. \tag{10}$$

Surfactant interchange between the interface and the bulk liquid may be affected by adsorption and desorption barriers (England and Berg, 1971; Antoniades and Palmer, 1976), and the importance of such barriers in the surfactant stabilization of surface tension driven instability has been considered by Palmer and Berg (1972). To simplify the present analysis, however, adsorption and desorption rates are assumed to be rapid, compared to the rate of bulk diffusion, to permit the assumption of local equilibrium at the interface. Thus

$$\Gamma' = (\partial\Gamma/\partial C)^{*}C'. \qquad (11)$$

Strictly, (4) to (11) are valid at the interface, that is, at $z = B'$. To modify these equations for application at $z = 0$, the variation of P' and T_L' with z must be accounted for with the aid of a Taylor series expansion about $z = 0$:

$$[P_L' - P_V']_{z=B'} = [P_L' - P_V']_{z=0} - gB'(\rho_L - \rho_V) \qquad (12)$$

and

$$[T_L']_{z=B'} = [T_L']_{z=0} - \beta B' \qquad (13)$$

Equations (12) and (13) may now be combined with (4) to (11) to yield free surface boundary conditions which apply at $z = 0$.

Far from the interface, all perturbations in velocity, temperature, and solute concentration must approach zero:

$$W_L' = W_L'/\partial z = T_L' = C' = 0 \quad \text{as} \quad z \to -\infty \qquad (14)$$

and

$$W_V' = W_V'/\partial z = 0 \quad \text{as} \quad z \to \infty \qquad (15)$$

Finally, at the bottom boundary of the thermal boundary layer, the liquid temperature T_L' and the heat flux $k_L\partial T_L'/\partial z$ must be continuous.

The linearized equations of mass, momentum, and energy conservation together with the boundary conditions presented in (4) to (15) completely describe the response of the system to infinitesimal disturbances. The general form of the perturbations in W, P, T, C, and Γ which satisfies these equations is

$$\mathcal{P}'(x, y, z, t) = e^{\gamma t}f(x, y)\overline{\mathcal{P}}(z)$$

where

$$\nabla_{II}^2 f + \alpha^2 f = 0.$$

After nondimensionalization and requiring that $\gamma = 0$, the appropriate equations of mass, momentum, and energy conservation which define the neutrally stable state of the system become

$$(D^2 - \alpha^2)\overline{W}_V - N_{RE}N_\mu D\overline{W}_V - D\overline{P}_V = 0 \qquad (16)$$

$$(D^2 - \alpha^2)\overline{W}_L - N_{RE}D\overline{W}_L - D\overline{P}_L = 0 \qquad (17)$$

$$(D^2 - \alpha^2)(D^2 - \alpha^2 - N_{RE}N_\mu D)\overline{W}_V = 0 \qquad (18)$$

$$(D^2 - \alpha^2)(D^2 - \alpha^2 - N_{RE}D)\overline{W}_L = 0 \qquad (19)$$

$$(D^2 - \alpha^2)\overline{P}_V = 0 \qquad (20)$$

$$(D^2 - \alpha^2)\overline{P}_L = 0 \qquad (21)$$

$$(D^2 - \alpha^2 - N_{RE}N_{PR}D)\overline{T}_L = \begin{cases} -\overline{W}_L \text{ for } -1 \leq \zeta \leq 0 & (22a) \\ 0 \text{ for } -\infty \leq \zeta \leq -1 & (22b) \end{cases}$$

$$(D^2 - \alpha^2 - N_{RE}N_{SC}D)\overline{C} = 0. \qquad (23)$$

Equations (16) and (17) are the equations of momentum conservation for each phase, (18) and (19) derive from the curl of the vorticity equation for each phase, (20) and (21) are the divergence of the equation of momentum conservation for each phase, (22*a*) and (22*b*) are those of energy conservation in the liquid, and (23) is the equation of mass conservation of solute in the liquid.

Similarly, the complete set of boundary conditions in dimensionless form is as follows. At $\zeta = 0$

$$[N_{RE}N_{PR}N_{CR}(1 - N_\rho^{-1})]\overline{W}_V - N_H[\overline{T}_L - \overline{B}] = 0 \qquad (24)$$

$$N_\rho\overline{W}_L - N_\mu\overline{W}_V = 0 \qquad (25)$$

$$N_\mu D\overline{W}_V - D\overline{W}_L + N_{RE}N_{PR}(N_\rho - 1)\alpha^2\overline{B} = 0 \qquad (26)$$

$$N_{CR}(\overline{P}_L - \overline{P}_V) + 2N_{CR}(D\overline{W}_V - D\overline{W}_L) - 2N_H(N_\mu/N_{PR})(\overline{T}_L - \overline{B}) - (\alpha^2 + N_{BO})\overline{B} = 0 \qquad (27)$$

$$\alpha^2N_{MA}(\overline{T}_L - \overline{B}) + \alpha^2N_{EL}\overline{\Gamma} + D^2\overline{W}_L - D^2\overline{W}_V + \alpha^2(\overline{W}_L - \overline{W}_V) + \alpha^2N_{SV}[D\overline{W}_L + N_{RE}N_{PR}\alpha^2\overline{B}] = 0 \qquad (28)$$

$$N_{RE}N_{PR}D\overline{T}_L + \overline{W}_L = 0 \qquad (29)$$

$$D\overline{W}_L + N_{RE}N_{PR}\alpha^2\overline{B} - \alpha^2N_{SD}\overline{\Gamma} - D\overline{C} = 0 \qquad (30)$$

$$\overline{\Gamma} - \overline{C} = 0. \qquad (31)$$

As $\zeta \to \infty$ $\overline{W}_V = D\overline{W}_V = 0.$ (32), (33)

As $\zeta \to -\infty$ $\overline{W}_L = D\overline{W}_L = \overline{T}_L = \overline{C} = 0.$ (34) to (37)

At $\zeta = -1$, both $\overline{T}_L$ and $D\overline{T}_L$ must be continuous. (38), (39)

In (16) to (39), the scaling factors for ζ, $\overline{W}_V$, $\overline{W}_L$, $\overline{P}_V$, $\overline{P}_L$, $\overline{T}_L$, $\overline{C}$, $\overline{\Gamma}$, and $\overline{B}$ are δ, $\kappa_L\mu_L/\mu_V\delta$, κ_L/δ, $\mu_L\kappa_L/\delta^2$, $\mu_L\kappa_L/\delta^2$, $\beta\delta$, $\Gamma^{*}\kappa_L/\mathcal{D}_b\delta$, $\Gamma^{*}\kappa_L(\partial\Gamma/\partial C)^{*}/\mathcal{D}_b\delta$, and δ, respectively. The dimensionless groups in the above equations are defined as follows:

Hickman number	$N_H = \left(\frac{\partial\eta}{\partial T}\right)^{*}\frac{\eta^{*}\beta\delta^2\mu_V}{\rho_L\kappa_L\sigma^{*}}\left[\frac{1}{\rho_V} - \frac{1}{\rho_L}\right]$
Marangoni number	$N_{MA} = -\left(\frac{\partial\sigma}{\partial T}\right)^{*}\frac{\beta\delta^2}{\kappa_L\mu_L}$
Crispation number	$N_{CR} = \mu_L\kappa_L/\sigma^{*}\delta$
Viscosity ratio	$N_\mu = \mu_L/\mu_V$
Density ratio	$N_\rho = \rho_L/\rho_V$
Reynolds number	$N_{RE} = \eta^{*}\delta/\mu_L$
Prandtl number	$N_{PR} = \nu_L/\kappa_L$
Schmidt number	$N_{SC} = \nu_L/\mathcal{D}_b$
Bond number	$N_{BO} = \delta^2g(\rho_L - \rho_V)/\sigma^{*}$
Elasticity number	$N_{EL} = -(\partial\sigma/\partial C)^{*}\Gamma^{*}/\mu_L\mathcal{D}_b$
Surface diffusion number	$N_{SD} = (\partial\Gamma/\partial C)^{*}\mathcal{D}_s/\mathcal{D}_b\delta$
Surface viscosity number	$N_{SV} = \mu_s/\mu_L\delta$

Notice that both N_H and N_{MA} contain the thermal gradient in the boundary layer and, consequently, are extremely useful for defining the stability limit for the system. In the absence of surface tension driven instabilities, $N_{MA} = 0$, and the stability criteria are best expressed in terms of the Hickman number, which is the ratio of the destablilizing forces of differential vapor recoil and vapor viscosity to the stabilizing action of surface tension and thermal diffusivity. Likewise, in the absence of lateral variations in evaporation rate, $N_H = 0$, and the stability criteria for the system should be expressed in terms of the Marangoni number, which is the ratio of the destabilizing surface forces to the stabilizing action of viscosity and thermal diffusivity.

The degree of influence that the surface active solute has on the system is determined by the magnitude of N_{EL}, N_{SD}, N_{SV}, and to a lesser extent N_{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 surface viscosity number N_{SV} relates the importance of surface viscosity to bulk liquid viscosity in resisting interfacial movement. For soluble surfactants, surface viscosity and rates of surface diffusion are generally negligible, and N_{EL} alone characterizes the stabilizing effect of the surfactant on the system. However, for insoluble surfactants, the surface viscosity can be high, and surface diffusion is the only mechanism for redistribution of surfactant in the interface. Consequently, N_{EL}, N_{SD}, and N_{SV} may all play a role in determining the stabilizing effect of an insoluble surfactant.

Solution

The general solution to Equations (18), (19), (22*a*), (22*b*), and (23) which satisfies boundary conditions (32) to (37) is easily found to be

$$\overline{W}_V = A_{11}\exp(-\alpha\zeta) + A_{12}\exp(-r_V\zeta)$$

$$\overline{W}_L = A_{21}\exp(\alpha\zeta) + A_{22}\exp(r_L\zeta)$$

$$\begin{aligned}\overline{T}_L &= A_{31}\exp(q\zeta) + A_{32}\exp[(N_{RE}N_{PR} - q)\zeta] \\ &\quad + A_{21}\exp(\alpha\zeta)/(\alpha N_{RE}N_{PR}) + A_{22}\exp(r_L\zeta)/ \\ &\qquad [r_L N_{RE}(N_{PR} - 1)] \quad \text{for} \quad \zeta \geqq -1\end{aligned}$$

$$\overline{T}_L = A_{33}\exp(q\zeta) \quad \text{for} \quad \zeta < -1$$

$$\overline{C} = A_{41}\exp(s\zeta)$$

where

$$r_V = \frac{1}{2}[-N_{RE}N_\mu + (N_{RE}^2N_\mu^2 + 4\alpha^2)^{1/2}]$$

$$r_L = \frac{1}{2}[N_{RE} + (N_{RE}^2 + 4\alpha^2)^{1/2}]$$

$$q = \frac{1}{2}[N_{RE}N_{PR} + (N_{RE}^2N_{PR}^2 + 4\alpha^2)^{1/2}]$$

and

$$s = \frac{1}{2}[N_{RE}N_{SC} + (N_{RE}^2N_{SC}^2 + 4\alpha^2)^{1/2}]\,.$$

The relationships between the integration constants A_{ij} may be determined from boundary conditions (24) to (27), (29) to (31), (38), and (39) with the aid of (16), (17), (20), and (21). Substitution of the results into the shear stress balance at the interface [Equation (28)] then yields the following characteristic equation relating the Hickman number to α and the other dimensionless groups at the condition of neutral stationary instability:

$$\begin{aligned}N_H = &\{N_{RE}^2N_{PR}^2N_{CR}(N_\rho - 1)N_\mu\} \\ &\{\alpha q N_\rho^{-1}[\lambda_1 + \alpha(\alpha - r_V)\lambda_6F_s] - \alpha(\alpha - r_V) \\ &\times\lambda_3N_{MA}/N_{RE}N_{PR}\}/[\lambda_2 + \alpha(\alpha - r_V)\lambda_7F_s] \qquad (40)\end{aligned}$$

where

$$F_s = N_{SV} + N_{EL}/[\alpha^2N_{SD} + s]$$

$$\begin{aligned}\lambda_1 = &N_\mu(r_L - r_V)(\alpha^2 + N_{BO})/(\alpha N_\rho N_{RE}N_{PR}N_{CR}) \\ &+ N_{RE}N_\mu(1 - N_\rho^{-1})[r_V(r_L - \alpha)/(r_L + \alpha) \\ &- r_L(\alpha - r_V)/(\alpha + r_V)]\end{aligned}$$

$$\begin{aligned}\lambda_2 = &\lambda_3[N_{RE}(r_L + N_\rho r_V) + 2\alpha(\alpha - r_V)(1 - N_\rho/N_\mu)] \\ &+ N_\mu[N_\rho - 2 + (r_L + \alpha N_\rho)/(\alpha - r_V) \\ &+ 2r_L(1 - N_\mu^{-1})/N_{RE}]\ [r_VN_{RE}(1 - N_\rho^{-1}) \\ &\times (\lambda_4 - \lambda_5) + qN_{RE}(r_L - r_V)/N_\rho^2] + \lambda_1[\lambda_5 - \alpha/N_\rho]\end{aligned}$$

$$\begin{aligned}\lambda_3 = &N_\mu N_\rho^{-1}(\lambda_4 - \lambda_5)[(\alpha^2 + N_{BO})/(\alpha N_{RE}^2N_{PR}N_{CR}) \\ &- \alpha(N_\rho - 1)/(\alpha + r_V)] - qN_\mu N_\rho^{-2}(r_L - \alpha) \\ &\times [(\alpha + r_V)^{-1} + (\alpha + r_L)^{-1}]\end{aligned}$$

$$\lambda_4 = N_\rho^{-1}(q - \alpha)[1 - \exp(N_{RE}N_{PR} - \alpha - q)]$$

$$\lambda_5 = \alpha N_{PR}(q - r_L)[1 - \exp(N_{RE}N_{PR} - r_L - q)]/[r_LN_\rho(N_{PR} - 1)]$$

$$\begin{aligned}\lambda_6 = &\{N_\mu N_\rho^{-1}r_L/(r_L + \alpha)\} \\ &\{(\alpha^2 + N_{BO})/(\alpha N_{RE}N_{PR}N_{CR}) \\ &- \alpha N_{RE}[N_\rho(\alpha + r_V)^{-1} + (\alpha + r_L)^{-1}]\}\end{aligned}$$

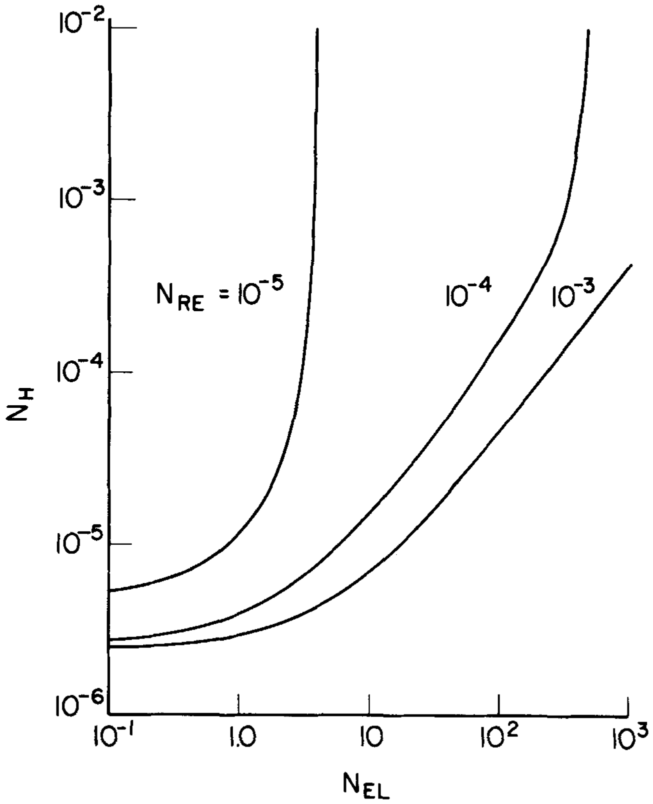

Fig. 3. The dependence of the critical Hickman number on the elasticity number for a soluble surface-active solute. $N_{PR} = 10^2$, $N_{SC} = 10^3$, $N_\rho = 10^8$, $N_\mu = 10^2$, $N_{BO} = 0.1$, $N_{CR} = 10^{-5}$, $N_{MA} = N_{SV} = N_{SD} = 0$.

$$\lambda_7 = r_L\lambda_3 + N_\mu N_\rho^{-1}[N_\rho - 2 + (r_L + \alpha N_\rho)/(\alpha - r_V) + 2r_L(1 - N_\mu^{-1})/N_{RE}]\,[q r_L N_{RE} N_\rho^{-1}/(\alpha + r_L) - \alpha(\lambda_4 - \lambda_5)] + \lambda_6[\lambda_5 - \alpha/N_\rho]$$

Since the wavelength of the infinitesimal disturbance α is arbitrary, the stability limit for the system is determined by locating the minimum in the curve of N_H vs. α.

In the next section, the effect of a surface active solute on the stability limit of a rapidly evaporating liquid in the absence of destabilizing surface tension gradients is discussed. Then the effect of the surfactant on the coupling between the vapor recoil mechanism and the surface tension destabilizing mechanism (Marangoni instability) will be explored.

RESULTS

To isolate the effect of surface active solutes on the criteria for vapor recoil instability, the Marangoni number is set equal to zero, and the stability limit is expressed in terms of the Hickman number. The stabilizing effect of the surface active solute depends on the magnitude of F_s which embodies all the dimensionless groups pertaining to the solute. For a soluble surfactant, N_{SV} and N_{SD} are negligible, and $F_s = N_{EL}/s$. Figure 3 exposes the marked increase in the criterion for vapor recoil instability as the elasticity number is increased. Notice also that for a given value of N_{RE}, an elasticity number exists which eliminates the potential for vapor recoil instability.

An increase in the Schmidt number increases the importance of convective transport of surfactant in diminishing lateral variations in surfactant concentration in the interface, thereby decreasing the stabilizing effect of soluble surfactants on the vapor recoil mechanism. In particular, for large values of N_{SC} (namely, $N_{RE}N_{SC} >> \alpha$), $s = N_{RE}N_{SC}$ and the stabilizing effect of the soluble surfactant depends solely on the value of $N_{EL}/N_{RE}N_{SC}$.

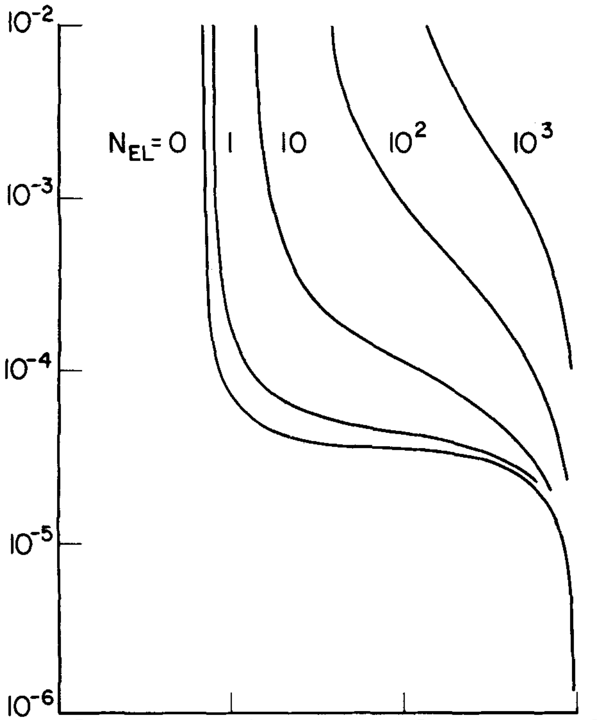

Fig. 4. The influence of a soluble surfactant on the relationship between N_H and N_{RE} for conditions similar to those in the TEA experiments. $N_{PR} = 10^2$, $N_{SC} = 10^3$, $N_\rho = 10^7$, $N_\mu = 10^2$, $N_{BO} = 0.1$, $N_{CR} = 10^{-5}$, $N_{MA} = N_{SV} = N_{SD} = 0$.

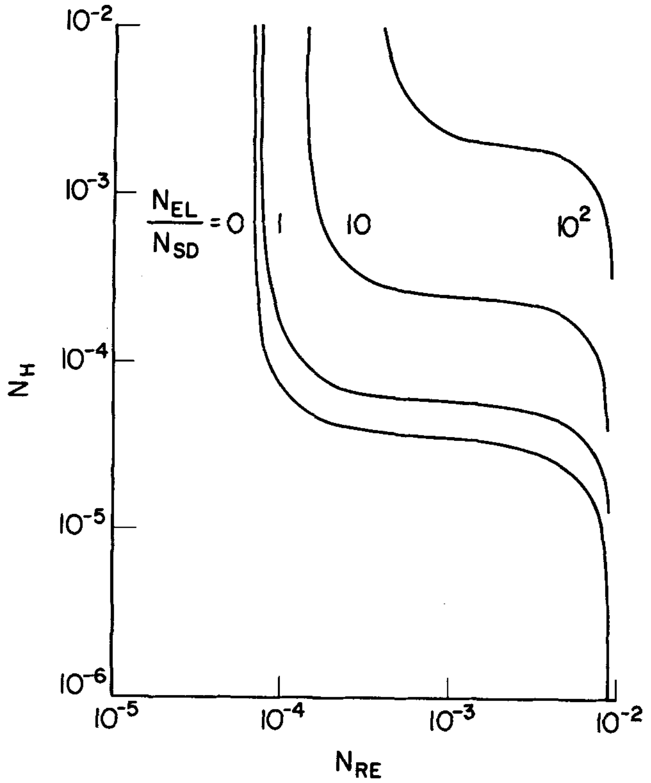

Fig. 5. The influence of an insoluble surfactant on the relationship between N_H and N_{RE}. $N_{PR} = 10^2$, $N_{SC} = 10^3$, $N_\rho = 10^7$, $N_\mu = 10^2$, $N_{BO} = 0.1$, $N_{CR} = 10^{-5}$, $N_{MA} = N_{SV} = 0$.

Figure 4 presents the effect of N_{EL} on the critical Hickman number in a slightly different manner, with values of dimensionless groups chosen to coincide with the conditions of the TEA experiments. In particular, notice that the minimum Reynolds number necessary to produce an instability (for which $N_H < \infty$) increases as N_{EL} is increased. As the Reynolds number is continuously increased beyond this critical value, a condition is eventually reached at which inertial forces are capable of producing instability even in the absence of local variations in evaporation rate, as indicated by the sharp decrease in N_H to zero at high values of N_{RE} (see Palmer, 1976). In contrast to the stabilizing effect of the surfactant on vapor recoil instability, the criterion for instability via this fluid inertia mechanism is essentially unaffected by surfactant addition. In fact, for $F_s \to \infty$ and $N_\rho >> 1$, the criteria for fluid inertia instability (with $N_H = 0$) becomes

$$N_I \equiv N_{RE}^2 N_{PR} N_{CR}(N_\rho - 1) = (\alpha + r_V)(1 + N_{BO}/\alpha^2) \tag{41}$$

While this equation is different than that derived for a pure liquid [see Palmer, 1976; Equation (38)], the result is still the same. The minimum value of N_I occurs at $\alpha \sim N_{BO}^{1/2}$, with $N_I = \epsilon N_{BO}^{1/2}$, where ϵ is a weak function of the vapor phase Reynolds number and varies between two and four.

Also embodied in the present analysis is the potential for instability via the moving boundary mechanism described by Miller (1973). The criteria for moving boundary instability may be identified by taking the limit of

Table 1. Comparison of the Effect of Soluble and Insoluble Surfactants on the Critical Marangoni Number and Associated Wavenumber for Neutral Stationary Instability. $N_{RE} = 10^{-4}$, $N_{PR} = 10^2$, $N_{SC} = 10^3$, $N_\rho = 10^7$, $N_\mu = 10^2$, $N_{BO} = 0.1$, $N_{CR} = 10^{-5}$, $N_{SV} = 0$, $N_H = 0$

Soluble surfactant			Insoluble surfactant		
N_{EL}	N_{MA}	α	N_{EL}/N_{SD}	N_{MA}	α
0	4.739	0.062	0	4.739	0.062
1.0	5.622	0.033	1.0	15.22	0.44
10	9.740	0.012	10	78.42	0.76
10^2	34.02	0.0050	10^2	684.2	0.88
10^3	228.9	0.0022	10^3	6733	0.90

Equation (40) as $\alpha \rightarrow 0$ (see Palmer, 1976). For gas-liquid interfaces, calculations reveal that elastic and viscous interfacial properties derived from surfactant addition have no significant effect on the criteria for moving boundary instability. The unimportance of surfactants to the criteria for fluid inertia and moving boundary instabilities is not surprising. Both destabilizing mechanisms are surface-wave amplification phenomena which do not depend on vapor shearing of the interface to produce auto amplification of infinitesimal disturbances.

In the limit as the solubility of the surfactant approaches zero, $(\partial\Gamma/\partial C)$ and $(\partial\sigma/\partial C)$ approach infinity, $\alpha^2 N_{SD} >> s$, and $F_s = N_{SV} + N_{EL}/\alpha^2 N_{SD}$. Thus, the key parameters which determine the maximum stabilizing effect of an insoluble surfactant on vapor recoil instability are N_{SV} and a modified elasticity number $N_{EL}/N_{SD} = -(\partial\sigma/\partial\Gamma)^*\Gamma^*\delta/\mu_L\mathfrak{D}_s$. Figure 5 illustrates the increase in system stability with increasing N_{EL}/N_{SD} for the case of an insoluble surfactant. Because bulk convective transport has no effect on surface concentration gradients when the surfactant is insoluble, the product $N_{RE}N_{SC}$ does not moderate the effect of N_{EL} in F_s for this case. Consequently, the central portion of each curve in Figure 5 is more horizontal (reflecting less dependence on N_{RE}) than the corresponding curve in Figure 4. Furthermore, inspection of the limiting form of F_s for an insoluble surfactant indicates that N_{EL}/N_{SD} will have an even greater stabilizing effect as the wave number of the disturbance is decreased. Consequently, with an insoluble surfactant, the critical wave number for the system is shifted to higher values as N_{EL}/N_{SD} is increased.

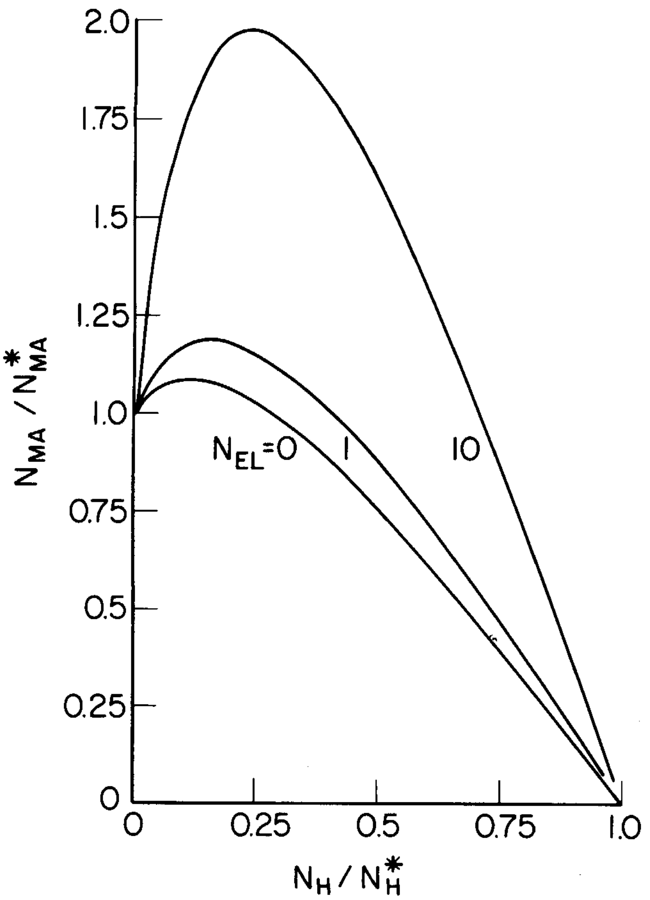

Fig. 6. The effect of a soluble surfactant on the coupling between the destabilizing surface tension and vapor recoil mechanisms. $N_{RE} = 5 \times 10^{-4}$, $N_{PR} = 10^2$, $N_{SC} = 10^3$, $N_\rho = 10^7$, $N_\mu = 10^2$, $N_{BO} = 0.1$, $N_{CR} = 10^{-5}$, $N_{SV} = N_{SD} = 0$.

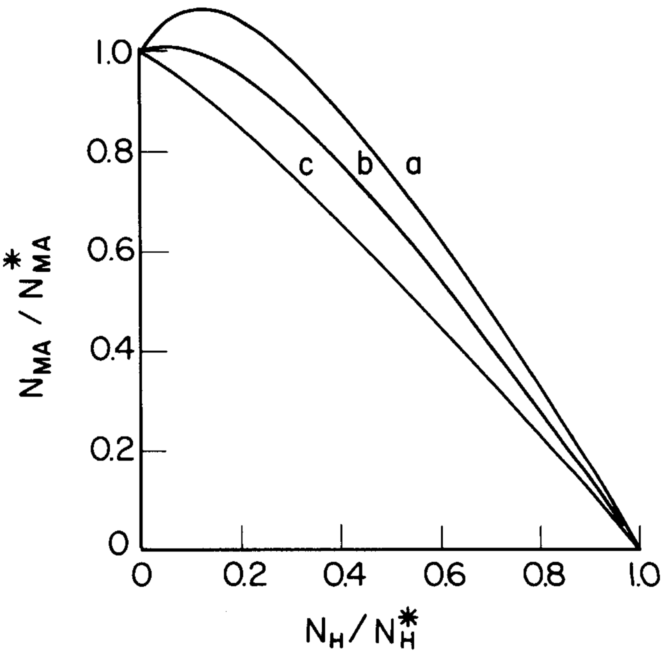

Fig. 7. The effect of an insoluble surfactant on the coupling between the destabilizing surface tension and vapor recoil mechanisms. Curve (a) is for $N_{EL}/N_{SD} = 0$, (b) is for $N_{EL}/N_{SD} = 0.1$, (c) is for $N_{EL}/N_{SD} = 1.0$. Curves for $N_{EL}/N_{SD} = 10$ and 100 are almost indistinguishable from curve (c). $N_{RE} = 5 \times 10^{-4}$, $N_{PR} = 10^2$, $N_{SC} = 10^3$, $N_\rho = 10^7$, $N_\mu = 10^2$, $N_{BO} = 0.1$, $N_{CR} = 10^{-5}$, $N_{SV} = 0$.

To explain the effect of surface active solutes on the coupling between the destabilizing surface tension and vapor recoil mechanisms, it is necessary first to discuss the stabilizing effect of the solute on surface tension driven instability in the absence of vapor recoil effects, that is, with $N_H = 0$. Table 1 presents the typical influence of both soluble and insoluble surfactants on the critical Marangoni number and wave number for surface tension driven instability. (The effect of N_{RE} on N_{MA} is small and consequently is not presented.) For both cases, an increase in N_{EL} produces a marked increase in system stability. However, trends in the critical wave number with increasing elasticity number are quite different for the two cases. If the surfactant is soluble, the critical wave number shifts to ever smaller values as N_{EL} is increased, while if the surfactant is insoluble, the critical wave number increases with increasing N_{EL}. In comparison, the effect of N_{EL} on the critical wave number for vapor recoil instability is small, with α ranging from 0.4 to 1.6 for the criteria presented in Figures 4 and 5 and with variations in α due mainly to changes in N_{RE}.

Following Nield (1964), the coupling between the vapor recoil and surface tension destabilizing mechanisms may be revealed by first determining the critical value of N_H as a function of N_{MA} from Equation (40) and then plotting N_{MA}/N_{MA}^* vs. N_H/N_H^*, where N_{MA}^* denotes the critical Marangoni number with $N_H = 0$ and N_H^* denotes the critical Hickman number with $N_{MA} = 0$. The closer the curve is to a line with slope equal to minus one, the greater is the coupling (cooperation) between mechanisms. The extent to which the vapor recoil and surface tension destabilizing mechanisms cooperate to produce convection depends on the similarity between the wave numbers of the disturbances most effectively amplified by each mechanism. In the absence of a surface active solute, the critical wave numbers for the two mechanisms differ by a factor of 10, and consequently the two mechanisms compete to determine the stability limit for the system. As shown in Figure 6, this competition is increased further by the addition of a soluble surfactant which increases the difference between the critical values of α for the two mechanisms. On the other hand, addition of an insoluble surfactant increases the critical value of α for surface tension driven instability and thus increases cooperation between the two destabilizing mechanisms as shown in Figure 7. In fact, for a value of $N_{EL}/N_{SD} \geqq 1.0$, the coupling between mechanisms is extremely tight.

CONCLUSION

Both experimental observation and linear stability analysis demonstrate that surface active solutes have a profound stabilizing influence on convection induced by differential vapor recoil. Because the analysis only considers stationary modes of instability, the stability predictions represent upper bounds on the sufficient conditions for interfacial instabilities in liquids evaporating under vacuum. Of particular significance in this regard is the discovery that surfactants have no noticeable effect on the criteria for instability via the fluid inertia mechanism. Consequently, while addition of surfactants may eliminate the potential for vapor recoil instability, the practical upper limit of stability for the system is determined by the conditions necessary for fluid inertia instability.

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NOTATION

A_{ij} = integration constants
B = the displacement of the interface from its equilibrium position
C = bulk concentration of surfactant
D = $\partial/\partial\zeta$ = dimensionless z derivative
$\mathcal{D}_b$ = bulk diffusion coefficient
$\mathcal{D}_s$ = surface diffusion coefficient
f = planform spatial dependence of the perturbations which satisfies the wave equation
F_s = term in the equation describing neutral stability which embodies all the surfactant related dimensionless groups, Equation (40)
g = gravitational acceleration
k_L = liquid thermal conductivity
N_I = inertial number defined by Equation (41)
P = fluid pressure
$\mathcal{P}'$ = arbitrary perturbation
t = time
T = temperature
W = z component of velocity
x, y = coordinates in the plane of the unperturbed interface
z = coordinate normal to the unperturbed interface

Greek Letters

α = dimensionless wave number of the disturbance
β = unperturbed temperature gradient in the thermal boundary layer (positive for evaporation)
γ = time growth constant of the perturbations
Γ = surface concentration of surfactant (mass/area)
δ = depth of the thermal boundary layer
∇_{II}^2 = $\partial^2/\partial x^2 + \partial^2/\partial y^2$ = surface divergence
ζ = dimensionless z coordinate
η = mass flux of evaporation
κ = thermal diffusivity
λ_{vap} = latent heat of vaporization of the liquid
μ = fluid viscosity
μ_s = surface viscosity
ν = μ/ρ = kinematic viscosity
ρ = fluid density
σ = surface tension

Subscripts

L = liquid phase
v = vapor phase

Superscripts

* = values for the unperturbed state
$'$ = infinitesimal perturbation in dimensional form
bar = ζ dependent part of the perturbation in dimensionless form

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