J. Fluid Mech. (1983), *vol.* 126, *pp.* 491–506
Printed in Great Britain

Interfacial stability of binary mixtures evaporating at reduced pressure

By ARIJIT BOSE† AND HARVEY J. PALMER
Department of Chemical Engineering, University of Rochester, New York 14627

(Received 2 December 1980 and in revised form 9 August 1982)

When a liquid evaporates under vacuum, its free surface is potentially unstable to local variations in evaporative flux, surface depressions being produced by the recoil force of the departing vapour and sustained convection in the liquid being driven by the shearing action of the vapour on the distorted liquid surface. For a binary mixture, local variations in evaporative flux may be produced by fluctuations in both surface concentration and temperature. With the aid of linear hydrodynamic-stability theory, this paper examines the extents to which key mass-transfer properties affect the interfacial stability of the system. The mass-transfer aspects that distinguish this problem from its heat-transfer analogue centre on the dependence of relative volatility on temperature and composition as well as the importance of the bulk-flow term in Fick's law. Results indicate that the stability criteria for interfacial convection are extremely sensitive to the difference in volatility between the two components, that the destabilizing effects of surface concentration and temperature on evaporative flux are additive in determining stability limits, and that for certain operating pressures spontaneous convection can only be induced by adverse concentration gradients. Attention is limited to low-surface-tension mixtures for which there are no concentration effects on surface tension (Marangoni instability).

1. Introduction

When a liquid vaporizes, the density change that accompanies the phase transition gives rise to a discontinuity in the transport of linear momentum normal to the vapour–liquid interface. The result is a recoil force on the interface directed towards the liquid phase, whose magnitude is directly proportional to the square of the local evaporative flux and inversely proportional to the pressure (or density) of the vapour phase (see equation (5)). A linear stability analysis of a pure liquid evaporating into a partial vacuum reveals that local variations in this recoil force may disrupt the vapour–liquid interface and induce interfacial convection (Palmer 1976; Maheshri & Palmer 1979). Local fluctuations in surface temperature are accompanied by fluctuations in evaporative flux and recoil force. Regions of interface that are hotter and are exhibiting a higher evaporative flux are depressed owing to the associated increase in recoil force, and sustained liquid flows are driven by the resultant shear stress exerted on the walls of these craters by the departing vapour. Besides elucidating the basic features of this differential vapour recoil mechanism, the linear stability analysis indicates that vapour-recoil convection can be induced only if the ratio of liquid to vapour density is greater than 10^6. Practically speaking, this means

---

† Present address: Department of Chemical Engineering, University of Rhode Island, Kingston, RI 02881.

that the operating pressure must be below 50 Pa before differential vapour recoil becomes a significant surface-disruption mechanism.

The stability analysis of Palmer (1976) was motivated by the experiments of Hickman (1952, 1972, 1976), who observed curious schizoid interfacial behaviour, erratic explosive activity, and visible, steady small-scale interfacial convection patterns in a wide variety of liquids vaporizing into a partial vacuum. One unique feature of the phenomenon that Hickman observed is the large increase in interfacial heat and mass transfer that accompanies the onset of interfacial convection in these systems. Subsequent quantitative experimental measurements of evaporative heat transfer rates for triethanolamine under vacuum clearly show (i) that vapour-recoil convection can produce interfacial transport rates which are 20 times greater than the rates associated with buoyancy-driven convection, and (ii) that the interfacial heat-transfer coefficients for the liquid phase are strong functions of evaporative flux and gas-phase pressure (Palmer & Maheshri 1981). In contrast, interfacial transport rates associated with free convection via the differential surface-tension or buoyancy mechanisms depend on the temperature gradient at the interface and show no explicit dependence on evaporative flux or gas-phase pressure. In brief, all the observed trends in the rate of heat transfer during evaporation under vacuum are consistent with the phenomenological model of natural convection via the differential vapour-recoil mechanism. Unfortunately, no experiments have been done to determine the necessary conditions for inducing spontaneous convection by differential vapour recoil to provide a quantitative verification of the linear stability theory. Such experiments are under way in our laboratory at the present time.

In addition to the high interfacial transport rates, the schizoid interfacial behaviour observed by Hickman is especially important. Under most conditions, the evaporating interface segregates into two regions of interfacial activity, with portions of the surface exhibiting rapid small-scale movement and a substantially increased evaporation rate (which Hickman called working), while the rest of the surface remains torpid and stable. The large difference in evaporation rate from the two adjacent regions is dramatically revealed by a difference in their surface elevations (~ 2 mm), caused by the difference in momentum transfer (recoil force) to the surface by the departing vapour. The torpid surface represents a source of inefficiency in the evaporation process, and Hickman's experiments show that it is also the cause of the erratic, sometimes explosive, activity and abnormally high degrees of superheat (~ 60 °C) observed in vacuum distillation processes.

It is important to recognize that the spontaneous formation of a schizoid surface is observed on a wide variety of liquids of moderate to low surface tension, including silicone fluids. For liquids of moderate surface tension we have demonstrated with linear stability theory and experiments that the torpid surface is produced by surface-active contamination (Palmer 1977). The addition of trace amounts of a surface-active solute suppresses interfacial convection and induces the schizoid surface, the size of the torpid regions being proportional to the amount of surface-active solute added and to the magnitude of the evaporative flux. On the other hand, for low-surface-tension fluids like oils and silicone fluids, Hickman and ourselves have been unable to uncover a specific additive that will induce torpidity on a working surface. This is not surprising since low-surface-tension liquids like silicones are highly resistant to surface-active contaminants and their stabilizing effects (Palmer 1971). Nevertheless, the existence of the schizoid surface on these liquids seems to be due to the presence of a chemical artefact in the system, since a torpid surface can be transformed temporarily into a working surface by carefully overflowing (discarding) the interfacial layer in an evaporation experiment.

Our contention is that the extra interfacial stability observed during the vacuum distillation of oils and silicone fluids is associated with a concentration-polarization phenomenon. All these fluids are mixtures of chemically similar materials of varying molecular weight. During the vaporization process, low-volatility constituents tend to accumulate near the interface as the higher-volatility components vaporize. As the local concentration of the less-volatile material increases at the interface, the evaporation rate is suppressed. Our own preliminary experiments with mixtures of two pure, low-surface-tension liquids of different volatility verify that the extent of torpidity is indeed dependent on the composition of the mixture; no torpid region is observed in experiments done with each pure liquid separately (Bose 1981).

Yet, from the point of view of interfacial stability, the presence of stable patches on a two-component mixture is entirely unexpected. For example, if we consider a local increase in the evaporative flux, the resultant increase in the recoil force depresses the surface locally and exposes the liquid surface to shear by the departing vapour. Flow patterns are induced, which bring to this local interfacial disturbance liquid which is not only hotter but also more volatile than the original interfacial layer. Both these factors contribute additively to increase further the local evaporative flux and thus amplify the original disturbance. Therefore the presence of a second component should *reduce* the intrinsic stability of the system.

The purpose of the present work is to provide insight into the schizoid interfacial phenomena observed when a binary mixture of low surface tension evaporates into a partial vacuum. Linear stability theory is used to predict the degree to which the second component increases the potential for interfacial convection in such systems, and to establish the relevant interrelationships between the physical properties of the mixture and its intrinsic stability. The predicted stability criteria are then used to interpret the schizoid behaviour that is observed experimentally.

2. The quiescent system

Consider the steady evaporation of a binary liquid (A plus B) at reduced pressures. The liquid surface is flat and infinite in lateral extent, and the liquid is unbounded from below. The evaporative flux is a function of both the surface temperature and composition, and at reduced pressures is given by a modified form of the Hertz–Knudsen equation which assumes no interaction between species A and B:

$$\eta_A = E\left(\frac{M_A}{2\pi R}\right)^{\frac{1}{2}}\left[\frac{X_A P_A^0}{T_S^{\frac{1}{2}}} - \frac{Y_A P_V}{T_V^{\frac{1}{2}}}\right], \tag{1}$$

$$\eta_B = E\left(\frac{M_B}{2\pi R}\right)^{\frac{1}{2}}\left[\frac{X_B P_B^0}{T_S^{\frac{1}{2}}} - \frac{Y_B P_V}{T_V^{\frac{1}{2}}}\right], \tag{2}$$

where η_A and η_B are the mass evaporative fluxes of A and B, E is the evaporation coefficient (commonly equal to unity), R is the gas constant, M_A and M_B are the molecular weights of A and B, P_A^0 and P_B^0 are their pure-component vapour pressures at the surface temperature T_S, X and Y denote their mass fractions in the liquid and gas phase at the surface, and P_V and T_V are the pressure and temperature of the gas phase.

Prior to the onset of convection, the surface temperature and composition are assumed to be independent of surface position. As in Palmer (1976, 1977) and Maheshri & Palmer (1979), the hydrodynamic stability of the quiescent boundary layer adjacent to the interface is analysed. For simplicity we presume that the thickness of this stagnant layer δ is the thickness of both the thermal and concentration boundary layers. This situation is reasonable if the depth of the boundary layer is influenced by the intensity of bulk circulation far from the interface.

The steady evaporation rate results in a net liquid flow upwards through this stagnant layer. The effect of this bulk flow is to distort the otherwise linear temperature and concentration profiles in the quiescent state. The nonlinear nature of the quiescent profiles has a significant stabilizing effect under conditions of high Prandtl and Schmidt numbers, and therefore its effect has been incorporated into the present analysis. The temperature and concentration outside the boundary layer are assumed constant. The use of such a 'broken-line' profile should not restrict the usefulness of this analysis (cf. Palmer 1976).

All physical properties of the vapour and liquid phases are assumed independent of composition and, except for vapour pressure, they are assumed independent of temperature. In particular, the coupling between surface-tension gradients (Marangoni instability) and differential vapour recoil is ignored in the present analysis, as is the destabilizing influence of an adverse density gradient. In earlier work, the interaction of thermally induced surface-tension variations with local fluctuations in evaporative flux was considered extensively for a pure fluid (Palmer 1976) and the stabilizing effect of compositional elasticity on vapour-recoil instability was evaluated (Palmer 1977). In addition, the rate of cooling of the liquid surface by heat conduction in the vapour phase and by the discontinuity in kinetic-energy transfer due to the phase change are assumed to be negligible compared with latent-heat effects. Furthermore, energy generation by viscous dissipation is ignored because of its insignificance in practical situations (cf. Palmer 1976).

For the quiescent state, the temperature and concentration profiles are

$$T^* - T^*_{\mathrm{s}} = -\frac{\lambda_{\mathrm{vap}}}{C_p}\left[\exp\frac{\eta^* z}{\rho_{\mathrm{L}}\kappa_{\mathrm{L}}} - 1\right], \tag{3}$$

$$\frac{X^*_{\mathrm{A}} - \eta^*_{\mathrm{A}}/\eta^*}{X^*_{\mathrm{As}} - \eta^*_{\mathrm{A}}/\eta^*} = \exp\frac{\eta^* z}{\rho_{\mathrm{L}}\mathscr{D}}, \tag{4}$$

where T is liquid temperature, η^* $(=\eta^*_{\mathrm{A}}+\eta^*_{\mathrm{B}})$ is the total mass evaporative flux, z is the spatial coordinate normal to the unperturbed vapour–liquid interface and increasing into the vapour phase, ρ is mass density, κ is thermal diffusivity, λ_{vap} is the latent heat of vaporization, C_p is the specific heat of the liquid, and $\mathscr{D}$ is molecular diffusivity. Throughout the analysis, the subscript s denotes conditions at the interface, the asterisk refers to the quiescent unperturbed state, and the subscripts L and V refer to the liquid and vapour phases respectively.

Conservation of linear momentum at the free surface for the unperturbed state requires

$$P^*_{\mathrm{L}} - P^*_{\mathrm{V}} = \eta^{*2}\left(\frac{1}{\rho_{\mathrm{V}}} - \frac{1}{\rho_{\mathrm{L}}}\right). \tag{5}$$

The right-hand side of this equation is the recoil force, which acts toward the liquid phase and is seen to increase with the square of the local evaporative flux and with decreasing vapour density (or pressure). Consequently the magnitude and thus the importance of this vapour-recoil force increases markedly as the overbearing pressure is reduced.

3. Mathematical formulation

The linear stability analysis is performed in the usual manner, the infinitesimal disturbance being exponential in time and periodic in the planform spatial variables, but of arbitrary wavelength. This disturbance is made to obey the conservation equations of mass, momentum and energy, subject to the appropriate boundary conditions.

For simplicity, only stationary modes of instability are considered in the present analysis. Oscillatory modes of instability are not expected since the presence of a second component does not appear to introduce a competing effect. Regardless of this, with the assumption of exchange of stabilities, the analysis defines the necessary conditions for interfacial instability. With the system variables perturbed an infinitesimal amount from their quiescent values, and with both the real and imaginary parts of the time-growth constant set equal to zero, the boundary conditions at the free surface (i.e. at $z = B'$) become

$$\rho_V W'_V = \eta' = \left(\frac{\partial \eta}{\partial T}\right)^* T' + \left(\frac{\partial \eta}{\partial X_A}\right)^* X'_A, \tag{6}$$

$$\rho_L W'_L = \rho_V W'_V, \tag{7}$$

$$\eta^* \left(\frac{1}{\rho_L} - \frac{1}{\rho_V}\right) \nabla^2_{II} B' = \frac{\partial W'_L}{\partial z} - \frac{\partial W'_V}{\partial z}, \tag{8}$$

$$(P'_V - P'_L) + 2\eta^* \eta' \left(\frac{1}{\rho_V} - \frac{1}{\rho_L}\right) + 2\left(\mu_L \frac{\partial W'_L}{\partial z} - \mu_V \frac{\partial W'_V}{\partial z}\right) - \sigma^* \nabla^2_{II} B' = 0, \tag{9}$$

$$\mu_L \left[\nabla^2_{II} W'_L - \frac{\partial^2 W'_L}{\partial z^2}\right] - \mu_V \left[\nabla^2_{II} W'_V - \frac{\partial^2 W'_V}{\partial z^2}\right] = 0, \tag{10}$$

$$k_L \frac{\partial T'}{\partial z} = -\lambda_{vap} \eta', \tag{11}$$

$$\rho_L \mathscr{D} \frac{\partial X'_A}{\partial z} = X^*_A \eta' + X'_A \eta^* - \eta'_A, \tag{12}$$

where k_L is the thermal conductivity of the liquid, W is the vertical component of velocity, ∇^2_{II} is the surface Laplacian operator and B' is the deflection of the interface in the z-direction from its equilibrium position. Equation (6) relates the perturbation in evaporative flux to the perturbation in vapour-phase velocity at the interface, (7) is the equation of mass conservation at the interface, (8) guarantees continuity of tangential velocity, (9) is the normal component of the interfacial momentum balance, (10) is the surface divergence of the interfacial momentum balance, and (11) is the energy-conservation equation for the interface.

Unique to this analysis of a binary mixture is (12), which requires continuity of flux of the more-volatile component A at the interface. In addition, fluctuations in the local evaporative flux η' are produced by perturbations in both temperature and composition (see (6)). If (6) and (12) are combined, we obtain

$$\rho_L \mathscr{D} \frac{\partial X_A}{\partial z} = -(X^*_A \eta^0_B + X^*_B \eta^0_A) X'_A + (\eta^*) X'_A - (X^*_A X^*_B) \left(\frac{\partial \eta^0_A}{\partial T} - \frac{\partial \eta^0_B}{\partial T}\right) T', \tag{13}$$

where η^0_A and η^0_B are the evaporative fluxes that would exist if pure A and B were to vaporize into a perfect vacuum at the prevailing surface temperature T^*_s.

Careful inspection of (13) reveals how the presence of a second component affects the interfacial stability of the system. In (13) and its heat-transfer analogue, (11), negative terms on the right-hand side of the equations represent stabilizing influences (effects that counter the auto-amplification of a disturbance) while positive terms represent destabilizing effects.

Recall the mechanism by which spontaneous convection is initiated in this system. A local increase in surface temperature and/or surface concentration of species A produces a local increase in evaporative flux and thus a local surface depression. Convective flows are initiated, by the shearing force of the departing vapour, which bring to this portion of surface liquid that is not only hotter but also richer in the more-volatile component. Thus, the local evaporative flux is increased still further, and the original disturbance becomes self-amplifying. Any factor that moderates the local increase in surface temperature or the local increase in surface concentration of A at surface depressions will stabilize the system. For example, from the perspective of heat transfer, the local increase in evaporative flux creates additional evaporative cooling, which diminishes the local increase in surface temperature and stabilizes the system. The greater the latent heat of vaporization λ_{vap} the faster local increases in surface temperature are diminished by evaporative cooling, as indicated by the negative term in (11).

In an analogous manner, the local increase in evaporative flux increases the rate at which species A is removed from the surface, which diminishes the local increase in surface concentration of A at surface depressions and stabilizes the system. The greater the inherent volatility of the mixture (as indicated by the magnitudes of η_{A}^{0} and η_{B}^{0}) the faster local increases in surface concentration are diminished by evaporative transport, as indicated by the first negative term in (13). However, while species A is being removed from the surface by evaporation, bulk flow in the unperturbed state is enhancing the transport of A up to the surface. This bulk-flow term helps to sustain local increases in surface concentration and thus is a destabilizing factor in the system, as indicated by the positive sign in front of the second term on the right-hand side of (13).

Finally, because species A is more volatile than B, the evaporative flux of A increases more rapidly with an increase in temperature.† Therefore a local increase in surface temperature will always result in a *preferential* depletion of A relative to B at the surface. This *preferential* increase in the evaporative flux of A at surface depressions diminishes the local surface concentration of A and stabilizes the system. The more volatile A is relative to B, the faster local increases in surface concentration are diminished by associated increases in surface temperature, as indicated by the last term in (13).

This coupling between composition and temperature fluctuations, as exposed in (13), as well as the destabilizing effect of bulk flow on mass transfer, distinguish this stability analysis of a binary mixture from the heat-transfer analogue with a pure liquid. In short, the mass-transfer aspects of this problem are *not* mathematically equivalent to a heat-transfer analogue with a pure liquid.

Aside from the composition effects on evaporative flux introduced in (6), the equation of continuity of mass flux (12), and the diffusion equation for the conservation of species A in the boundary layer, the analysis presented here is identical with that presented in an earlier paper (Palmer 1976). For convenience, the

---

† It may be shown with the aid of (1) and (2) and the Clausius–Clapeyron equation that $\partial\eta_{\text{A}}^{0}/\partial T$ is always greater than $\partial\eta_{\text{B}}^{0}/\partial T$ if A is more volatile than B.

complete set of differential equations and boundary conditions that describe the spatial variation of perturbations in the neutral stationary state are presented in dimensionless form in the appendix. The numerous dimensionless groups that appear in these equations are defined as follows:

Hickman number for heat transfer

$$\mathscr{H}_T = \left(\frac{\partial \eta}{\partial T}\right)^* \frac{\eta^* \beta_T \delta^2 \mu_\mathrm{V}}{\rho_\mathrm{L} \kappa_\mathrm{L} \sigma^*} \left[\frac{1}{\rho_\mathrm{V}} - \frac{1}{\rho_\mathrm{L}}\right],$$

Hickman number for mass transfer

$$\mathscr{H}_X = \left(\frac{\partial \eta}{\partial X_\mathrm{A}}\right)^* \frac{\eta^* \beta_X \delta^2 \mu_\mathrm{V}}{\rho_\mathrm{L} \mathscr{D} \sigma^*} \left[\frac{1}{\rho_\mathrm{V}} - \frac{1}{\rho_\mathrm{L}}\right],$$

Relative-vaporization number

$$\mathscr{Rv} = \frac{\beta_T}{\beta_X} \frac{X_\mathrm{A}^* (1 - X_\mathrm{A}^*) \delta}{\rho_\mathrm{L} \mathscr{D}} \left[\frac{\partial}{\partial T} (\eta_\mathrm{A}^0 - \eta_\mathrm{B}^0)\right],$$

Biot number for mass transfer

$$\mathscr{Bi} = \frac{\delta}{\rho_\mathrm{L} \mathscr{D}} [X_\mathrm{B}^* \eta_\mathrm{A}^0 + X_\mathrm{A}^* \eta_\mathrm{B}^0],$$

Crispation number $\mathscr{Cr} = \dfrac{\mu_\mathrm{L} \kappa_\mathrm{L}}{\sigma^* \delta}$,

Viscosity ratio $\mathscr{N}_\mu = \dfrac{\mu_\mathrm{L}}{\mu_\mathrm{V}}$, Density ratio $\mathscr{N}_\rho = \dfrac{\rho_\mathrm{L}}{\rho_\mathrm{V}}$,

Reynolds number $\mathscr{Re} = \dfrac{\eta^* \delta}{\mu_\mathrm{L}}$, Prandtl number $\mathscr{Pr} = \dfrac{\nu_\mathrm{L}}{\kappa_\mathrm{L}}$,

Schmidt number $\mathscr{Sc} = \dfrac{\nu_\mathrm{L}}{\mathscr{D}}$, Bond number $\mathscr{Bo} = \dfrac{\delta^2 g (\rho_\mathrm{L} - \rho_\mathrm{V})}{\sigma^*}$,

where ν is kinematic viscosity, and all quantities are evaluated at interfacial conditions.

The stability limit for the system is defined best in terms of the Hickman numbers for heat and mass transfer. Both groups are functions of the evaporative flux and the appropriate transfer gradient. Furthermore, they both reflect the relative importance of the destabilizing forces of differential vapour recoil and vapour viscosity to the stabilizing action of surface tension and diffusive transport. In $\mathscr{H}_T$ the vapour-recoil forces originate from local variations in surface temperature, while for $\mathscr{H}_X$ the recoil forces are due to local variations in surface composition. In the limiting case of $\mathscr{H}_X \rightarrow 0$, the local evaporative flux is independent of composition, vapour-recoil forces originate solely from local variations in surface temperature, and the mixture behaves as a pure liquid with stability criteria expressed in terms of $\mathscr{H}_T$ alone. On the other hand, if compositional effects dominate over temperature effects in a steadily evaporating mixture, then $\mathscr{H}_T \approx 0$ and the stability criteria are expressed solely in terms of $\mathscr{H}_X$.

As usual, the stability limit for the system is considered to be the minimum positive value of the function $\mathscr{H}_X$ (or $\mathscr{H}_T$) versus the wavenumber α of the disturbance (see the appendix for further details). Because the limiting case of a single-component liquid evaporating under vacuum has been discussed extensively in a previous paper (Palmer 1976), the presentation of results in § 4 will emphasize the effects of pertinent dimensionless groups on the value of the critical Hickman number for mass transfer

$\mathscr{H}_X$ with $\mathscr{H}_T$ equal to zero. In addition, the coupling between the heat- and mass-transfer destabilizing mechanisms will be assessed. The predictions of the linear stability analysis will then be used to interpret experimental observations of schizoid interfacial behaviour in binary liquids of low surface tension.

4. Results

The primary objective of the present paper is to evaluate how the presence of a second, volatile component in an evaporating liquid influences its interfacial stability at reduced pressures. As stated previously, (13) symbolizes the manner in which the second component affects the stability limit. In dimensionless form, (13) becomes

$$DX_A = -\mathscr{Rv}\,(T-B) + (\mathscr{Re}\,\mathscr{Sc} - \mathscr{Bi})\,(X_A - B), \tag{14}$$

at $\xi = 0$. Recall that, on the right-hand side of the equation, terms that are negative represent stabilizing influences while positive terms are destabilizing. Thus increases in the relative vaporization number $\mathscr{Rv}$ and Biot number $\mathscr{Bi}$ will increase the stability limit for the system, while increases in the Schmidt number will decrease the stability limit.

The Biot number, relative-vaporization number, and Schmidt number have no effect on the Hickman number for heat transfer $\mathscr{H}_T^*$ when $\mathscr{H}_X$ equals zero. Therefore the magnitude of their effects on interfacial stability is evaluated by considering the limiting case of vapour-recoil convection produced solely by adverse concentration gradients. The stability limit for this case is represented by the Hickman number for mass transfer $\mathscr{H}_X^*$ with $\mathscr{H}_T$ set equal to zero.

The stabilizing effect of the Biot number for this case is illustrated in figure 1. Note that the critical Hickman number for mass transfer increases in direct proportion to the magnitude of $\mathscr{Bi}$ for Biot numbers greater than unity, and that $\mathscr{H}_X^*$ approaches a limiting value as the Biot number approaches zero. Physically the Biot number reflects the efficiency with which local increases in the surface concentration of species A are diminished by associated increases in the evaporative flux of A away from the surface.

The magnitude of the relative-vaporization number $\mathscr{Rv}$ reflects the degree to which a local increase in surface temperature induces the stabilizing effect of a local depletion of the more-volatile component at the surface. The greater the difference in volatility between the two components, the more accentuated this effect becomes. Figure 2 presents the quantitative effect of the relative-vaporization number on the critical Hickman number for mass transfer. For values of $\mathscr{Rv}$ less than ten, the stability criteria seem to be unaffected by selective depletion of the more-volatile constituent at hot spots on the surface. However, for $\mathscr{Rv} > 10$ the stability limit increases sharply, and for $\mathscr{Rv} \sim 10^3$ the stability limit approaches infinity. The implication is that the system is universally stable to fluctuations in interfacial concentration when the difference in volatility between the two components of the mixture is sufficiently large.

The product of Reynolds number and Schmidt number $\mathscr{Re}\,\mathscr{Sc}$ reflects the importance of bulk flow on mass transfer in the quiescent state. From (14), we infer that this effect is destabilizing. However, this interpretation is contradicted by the results presented in figure 1, which show the critical Hickman number for mass transfer increasing with increasing Schmidt number. The paradox exists because of the complicated way in which the Schmidt number (and bulk-flow effects) enters into the analysis. In addition to (14), the Schmidt number has a significant effect on the

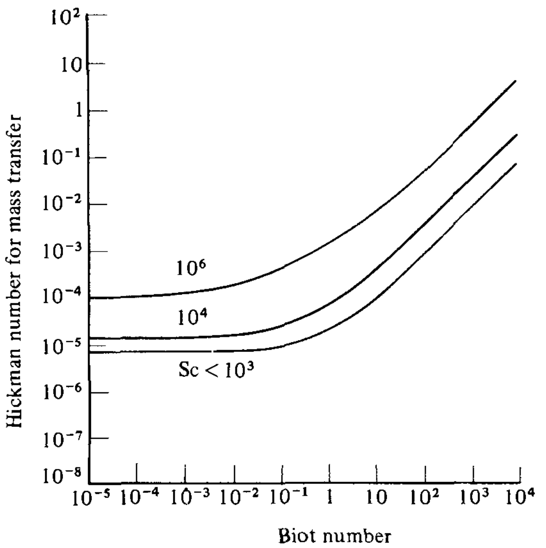

FIGURE 1. The influence of Biot number on the stability limit for vapour-recoil convection due to mass transfer. $\mathscr{R}e = 10^{-3}$, $\mathscr{P}r = 10$, $\mathscr{N}_\rho = 10^8$, $\mathscr{C}r = 10^{-5}$, $\mathscr{B}o = 1$, $\mathscr{N}_\mu = 100$, $\mathscr{H}_T = 0$, $\mathscr{R}v = 0$.

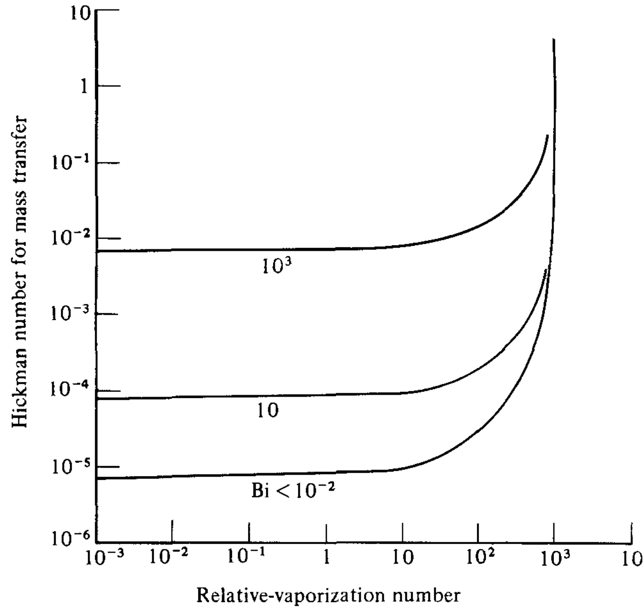

FIGURE 2. The effect of relative-vaporization number on the stability limit for vapour-recoil convection due to mass transfer. $\mathscr{R}e = 10^{-3}$, $\mathscr{P}r = 10$, $\mathscr{N}_\rho = 10^8$, $\mathscr{C}r = 10^{-5}$, $\mathscr{B}o = 1$, $\mathscr{N}_\mu = 100$, $\mathscr{S}c = 10^3$, $\mathscr{H}_T = 0$.

concentration profile in the quiescent state (see (A 8) in the appendix). At large values of $\mathscr{R}e\,\mathscr{S}c$ the initial concentration profile deviates considerably from a straight line. Such nonlinear concentration (and temperature) profiles in the quiescent state are known to increase the stability criteria for spontaneous convection (Batchelor 1959). The full effect of Schmidt number is shown in figure 3. At low Reynolds numbers the Schmidt number is destabilizing, as suggested by (14). However, at high Reynolds numbers this trend is reversed, with increases in Schmidt number producing increases

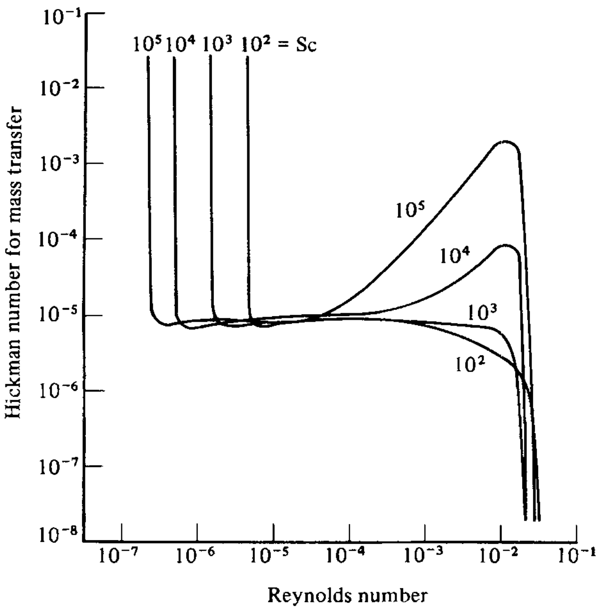

FIGURE 3. The effect of Reynolds number on the Hickman number for mass transfer for vapour-recoil convection. $\mathscr{N}_\rho = 10^8$, $\mathscr{C}r = 10^{-5}$, $\mathscr{B}o = 1$, $\mathscr{N}_\mu = 100$, $\mathscr{R}v = 10^{-2}$, $\mathscr{P}r = 10$, $\mathscr{H}_T = 0$.

in the stability limit because the quiescent concentration profiles become increasingly nonlinear.

The stabilizing effect of the nonlinear, unperturbed concentration profile may be more easily seen by analogy with the heat-transfer aspect of this problem. The importance of bulk flow in heat transfer is reflected in the magnitude of the product $\mathscr{R}e\, \mathscr{P}r$, and its effect on the unperturbed temperature profile is introduced on the right-hand side of (A7) in the appendix (compare this with (A8)). The results of the analysis are presented in figure 4, with the critical Hickman number for heat transfer $\mathscr{H}_T^*$ (with $\mathscr{H}_X = 0$) plotted as a function of Reynolds number and Prandtl number. The solid lines are the stability predictions of the present analysis while the dotted lines are the results of the previous analysis (Palmer 1976), in which the unperturbed temperature profile was assumed to be linear. The difference between the two curves at high Reynolds numbers represents the extent to which the system is stabilized by the effect of bulk on the shape of the quiescent profiles in the boundary layer.

The effect of the liquid to vapour phase density ratio $\mathscr{N}_\rho$ on vapour-recoil convection via the mass-transfer mechanism is shown in figure 5. Trends are similar to those observed for the heat-transfer mechanism (see Palmer 1976): the stability limit decreases as the density ratio increases, and, for each value of $\mathscr{N}_\rho$, a minimum critical Reynolds number exists below which no vapour-recoil convection is possible. At any fixed value of $\mathscr{N}_\rho$ the range of Reynolds numbers over which vapour-recoil convection is possible via the mass- or heat-transfer mechanism depends on the value of the Schmidt or Prandtl number respectively, with the range of Reynolds numbers increasing with $\mathscr{S}c$ or $\mathscr{P}r$ (see figures 3 and 4). Because thermal diffusivities for liquids are typically two orders of magnitude larger than molecular diffusivities, we expect the Prandtl number to be 100 times smaller than the Schmidt number in a given system. Under these conditions we discover that, at any fixed value of the density ratio, vapour-recoil convection via the mass-transfer mechanism can occur over a much wider range of Reynolds numbers than convection via the heat-transfer

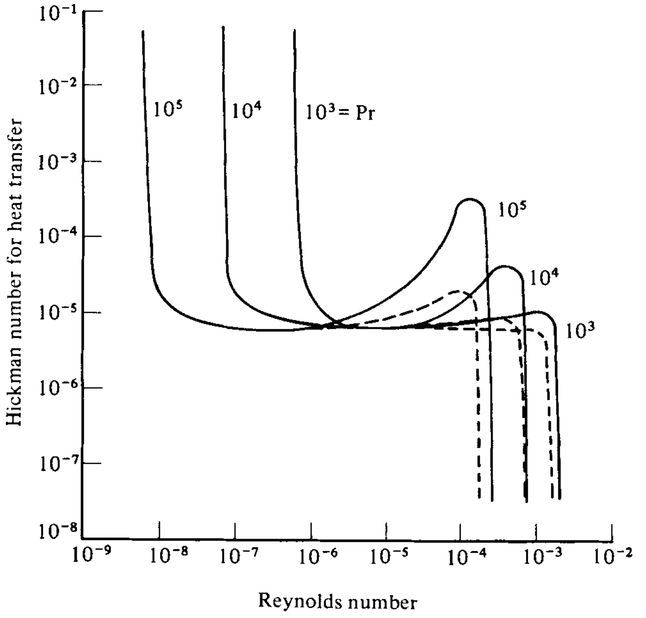

FIGURE 4. The stability limit for vapour-recoil convection with heat-transfer effects dominating; the importance of including the effect of bulk flow on the quiescent (unperturbed) temperature profile. ——, Bulk flow included; – – –, bulk flow ignored. $\mathscr{N}_\rho = 10^8$, $\mathscr{C}t = 10^{-5}$, $\mathscr{B}o = 1$, $\mathscr{N}_\mu = 100$, $\mathscr{H}_X = 0$.

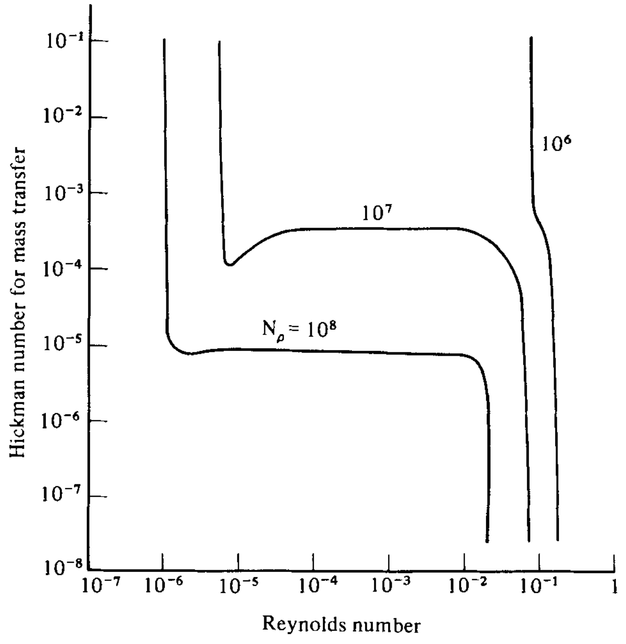

FIGURE 5. The effect of liquid to vapour density ratio on the stability limit for vapour-recoil convection due to mass transfer. $\mathscr{C}t = 10^{-5}$, $\mathscr{B}o = 1$, $\mathscr{N}_\mu = 100$, $\mathscr{R}v = 10^{-2}$, $\mathscr{B}i = 10^{-2}$, $\mathscr{P}t = 10$, $\mathscr{S}c = 10^3$, $\mathscr{H}_T = 0$.

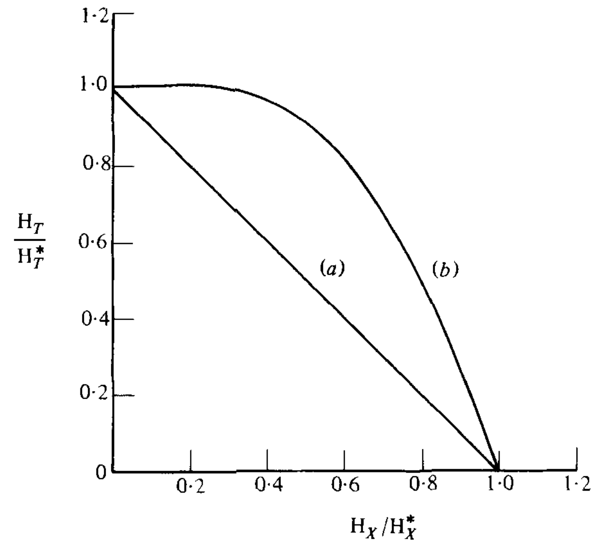

FIGURE 6. The coupling between heat transfer and mass transfer modes of vapour-recoil convection. Curve (*a*) is for $\mathscr{R}v = \mathscr{B}i = 1$ and curve (*b*) is for $\mathscr{R}v = \mathscr{B}i = 100$. Otherwise $\mathscr{R}e = 10^{-3}$, $\mathscr{P}i = 10$, $\mathscr{N}_\rho = 10^8$, $\mathscr{C}i = 10^{-5}$, $\mathscr{B}o = 1$, $\mathscr{N}_\mu = 100$.

mechanism. (Compare figure 5 with $\mathscr{S}c = 10^3$ to figure 1 in Palmer (1976) with $\mathscr{P}i = 10$.) This result suggests that at constant evaporative flux (constant $\mathscr{R}e$) a modest alteration in the overbearing pressure (and thus $\mathscr{N}_\rho$) can change the dynamics of a system from predominantly heat-transfer controlled to mass-transfer controlled.

Generally, local evaporative flux is a function of both composition and temperature, and thus the Hickman numbers for both heat and mass transfer will be non-zero. The actual stability limit then will depend on the degree to which these two destabilizing effects reinforce each other to create differential vapour-recoil forces. A convenient way to expose this interaction is to present the stability criteria in terms of a normalized Hickman number for heat transfer $\mathscr{H}_T/\mathscr{H}_T^*$ as a function of the normalized Hickman number for mass transfer $\mathscr{H}_X/\mathscr{H}_X^*$, where $\mathscr{H}_T^*$ is the stability limit with $\mathscr{H}_X = 0$ and $\mathscr{H}_X^*$ is the stability limit with $\mathscr{H}_T = 0$. Curve (*a*) in figure 6 shows the tight coupling that frequently exists between these two destabilizing mechanisms over a wide range of Biot numbers and relative-vaporization numbers. In fact, for $\mathscr{B}i = \mathscr{R}v = 1$ the coupling is extremely tight and there is a maximum additive contribution between the two driving forces to determine the stability limit for the system. However, as the stabilizing effect of the relative-vaporization number becomes significant, a shift in the preferred wavelength occurs for mass-transfer-induced convection, and the cooperation between the heat- and mass-transfer mechanisms is reduced significantly. For $\mathscr{B}i = \mathscr{R}v = 100$ the preferred wavelengths for instability via the two mechanisms differ by a factor of two, and a moderate degree of decoupling results, as shown in curve (*b*) of figure 6.

It is apparent from figure 5 and Palmer (1976) that for density ratios less than 10^6 (pressures greater than 50 Pa) vapour recoil is an unlikely mechanism for instability. For such systems two other mechanisms assume importance: the moving-boundary mechanism (Miller 1973) and the fluid-inertia mechanism (Palmer 1976). Computations suggest that the moving-boundary mechanism at vapour–liquid interfaces may be important in μ-gravity environments while the fluid inertia mechanism is important at unusually high evaporation rates, such as in sudden-depressurization experiments. Since neither situation seems to apply for typical vacuum-distillation processes, the effect of a second component on instability via these mechanisms is not discussed here (for details see Bose 1981).

5. Practical consequences

In addition to establishing the effect of key mass-transfer properties on the interfacial stability of our system, one goal of the hydrodynamic-stability analysis is to provide insight into the schizoid interfacial behaviour of binary mixtures that are resistant to surfactant contamination. To explore the practical consequences of the analysis, stability criteria for mixtures of ethyl hexyl phthalate (EHP) in ethyl hexyl sebacate (EHS) are computed. All mixtures are assumed to be at 150 °C and are steadily evaporating into a vapour phase at either 10^{-2} or 10^{-3} mmHg pressure.

Using physical property data estimated from Reid, Prausnitz & Sherwood (1977) the relevant dimensionless groups are calculated and presented in tables 1 and 2 together with predicted stability criteria for vapour-recoil convection. For a vapour-phase pressure of 10^{-3} mmHg, the normalized Hickman number for mass transfer is only slightly greater than zero for all proportions of EHP to EHS, and heat-transfer effects dominate (see figure 5). Thus the stability criteria in dimensionless form are essentially the same as that for a pure liquid. However, the ease with which this stability limit is exceeded depends on the steady evaporative flux that is achieved during the experiment. The greater the concentration of the less-volatile constituent (EHS) in the mixture, the lower will be the steady evaporative flux at a fixed bulk temperature. Imagine an experiment in which a mixture of EHP and EHS is steadily evaporating. Wherever the less-volatile constituent accumulates, the interface becomes *virtually* stable owing to the practical reduction in the overall evaporative flux. These stable patches of interface therefore may co-exist with unstable regions in much the same way as torpid regions develop on the surface of high-surface-tension liquids contaminated by trace amounts of surfactant (Palmer 1977).

Although the heat-transfer mechanism determines the conditions for spontaneous convection in mixtures of EHS and EHP at a pressure of 10^{-3} mmHg, the mass-transfer mechanism dominates at a pressure of 10^{-2} mmHg, as indicated in table 2. Note that, at this pressure, the critical Hickman number for heat transfer would have to be infinite for heat-transfer effects to be significant. As discussed earlier, a modest change in the operating pressure can have a profound effect on the predominant driving force for vapour-recoil convection and can alter entirely the relative importance of key physical properties on the stability limit for the system.

6. Conclusion

The present theoretical investigation of the interfacial stability of a binary mixture of low surface tension evaporating at reduced pressure reveals that the presence of a second volatile component may increase significantly the potential for interfacial convection in this system, and that the destabilizing effects of surface concentration and temperature on evaporative flux are usually additive in determining stability limits. In addition, the stability criterion for convection via the mass-transfer mechanism is extremely sensitive to the difference in volatility between the two components. If this difference is sufficiently great, the system becomes universally stable to fluctuations in surface concentration. Results also indicate that, at a fixed pressure, vapour-recoil convection via the mass-transfer mechanism can occur over

X_{EHP}	$\mathscr{R}e$	$\mathscr{R}v$	$\mathscr{B}i$	$\mathscr{H}_X/\mathscr{H}_X^*$	$\mathscr{H}_T/\mathscr{H}_T^*$
0·1	$2{\cdot}84\times10^{-5}$	$8{\cdot}02\times10^{-3}$	$1{\cdot}51\times10^{-1}$	$9{\cdot}22\times10^{-3}$	0·99
0·5	$5{\cdot}33\times10^{-5}$	$1{\cdot}53\times10^{-2}$	$8{\cdot}3\times10^{-2}$	$5{\cdot}01\times10^{-2}$	0·95
0·9	$7{\cdot}79\times10^{-5}$	$2{\cdot}23\times10^{-2}$	$5{\cdot}35\times10^{-2}$	$2{\cdot}68\times10^{-2}$	0·97
1·0	$8{\cdot}40\times10^{-5}$	—	—	—	1

TABLE 1. Vapour-recoil stability limits for the ethyl-hexyl-phthalate–ethyl-hexyl-sebacate system at a pressure of 10^{-3} mmHg, showing that heat-transfer effects dominate. $\mathscr{N}_\rho = 5\times10^8$, $\mathscr{S}c = 10^3$, $\mathscr{B}o = 1$, $\mathscr{C}t = 10^{-5}$, $\mathscr{N}_\mu = 100$, $\mathscr{P}t = 50$. For all compositions $\mathscr{H}_X^* \approx 7{\cdot}5\times10^{-6}$ and $\mathscr{H}_T^* \approx 1{\cdot}8\times10^{-5}$.

X_{EHP}	$\mathscr{R}e$	$\mathscr{R}v$	$\mathscr{B}i$	$\mathscr{H}_X^*$	$\mathscr{H}_T^*$
0·1	$2{\cdot}84\times10^{-5}$	$8{\cdot}02\times10^{-3}$	$1{\cdot}51\times10^{-1}$	$2{\cdot}84\times10^{-4}$	∞
0·5	$5{\cdot}33\times10^{-5}$	$1{\cdot}53\times10^{-2}$	$8{\cdot}3\times10^{-2}$	$2{\cdot}92\times10^{-4}$	∞
0·9	$7{\cdot}79\times10^{-5}$	$2{\cdot}23\times10^{-2}$	$5{\cdot}35\times10^{-2}$	$2{\cdot}93\times10^{-4}$	∞
1·0	$8{\cdot}40\times10^{-5}$	—	—	—	∞

TABLE 2. Vapour-recoil stability limits for the ethyl-hexyl-phthalate–ethyl-hexyl-sebacate system at a pressure of 10^{-2} mmHg, showing that mass-transfer effects dominate. $\mathscr{N}_\rho = 5\times10^7$, $\mathscr{S}c = 10^3$, $\mathscr{B}o = 1$, $\mathscr{C}t = 10^{-5}$, $\mathscr{N}_\mu = 100$, $\mathscr{P}t = 50$.

a much wider range of vaporization rates than convection via the heat-transfer mechanism. This result suggests that a modest change in either evaporative flux or overbearing pressure can change the dynamics of the system from predominantly heat-transfer-controlled to mass-transfer-controlled.

We are grateful to the Heat Transfer Program of the National Science Foundation and to the Rochester Gas and Electric Energy Fund for their financial support. Acknowledgement is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research. The graduate fellowship from the Elon Huntington Hooker foundation was also greatly appreciated.

Appendix

The general form of the perturbations in T', X', W' and P' which satisfy the linearized equations of mass, momentum, energy and species conservation together with the appropriate boundary conditions is

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

where

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

After non-dimensionalization and with the assumption of exchange of stabilities, the conservation equations that define the neutrally stable state of the system become

$$(D^2-\alpha^2)\,W_{\mathrm{V}} - \mathscr{R}e\,\mathscr{N}_\mu D W_{\mathrm{V}} - DP_{\mathrm{V}} = 0, \tag{A 1}$$

$$(D^2-\alpha^2)\,W_{\mathrm{L}} - \mathscr{R}e\,D W_{\mathrm{L}} - DP_{\mathrm{L}} = 0, \tag{A 2}$$

$$(D^2-\alpha^2)(D^2-\alpha^2-\mathscr{R}e\,\mathscr{N}_\mu D)\,W_{\mathrm{V}} = 0, \tag{A 3}$$

$$(D^2-\alpha^2)(D^2-\alpha^2-\mathscr{R}e\,D)\,W_{\mathrm{L}} = 0, \tag{A 4}$$

$$(D^2-\alpha^2)\,P_{\mathrm{V}} = 0, \tag{A 5}$$

$$(D^2-\alpha^2)\,P_{\mathrm{L}} = 0, \tag{A 6}$$

$$(D^2-\alpha^2-\mathscr{R}e\mathscr{P}r\,D)\,T = \begin{Bmatrix} -W_{\mathrm{L}}\exp\{\mathscr{R}e\mathscr{P}r\xi\}, \\ 0 \quad (-\infty \leqslant \xi < -1), \end{Bmatrix} \tag{A 7}$$

$$(D^2-\alpha^2-\mathscr{R}e\mathscr{S}c\,D)\,X_{\mathrm{A}} = \begin{Bmatrix} -W_{\mathrm{L}}\dfrac{\mathscr{S}c}{\mathscr{P}r}\exp\{\mathscr{R}e\mathscr{S}c\,\xi\}, \\ 0 \quad (-\infty \leqslant \xi < -1). \end{Bmatrix} \tag{A 8}$$

Equations (A 1) and (A 2) are the momentum-conservation equations for each phase, (A 3) and (A 4) are the curls of the vorticity equation for each phase, (A 5) and (A 6) are the divergences of the momentum conservation equation for each phase, (A 7) is the energy equation for the liquid phase, and (A 8) is the diffusion equation for component A in the liquid.

Similarly, the complete set of non-dimensionalized boundary conditions is as follows: at $\xi = 0$

$$\mathscr{R}e\,\mathscr{C}r\,(1-\mathscr{N}_\rho^{-1})\,W_{\mathrm{V}}-\frac{\mathscr{H}_T}{\mathscr{P}r}(T-B)-\frac{\mathscr{H}_X}{\mathscr{S}c}(X_{\mathrm{A}}-B) = 0, \tag{A 9}$$

$$\mathscr{N}_\rho W_{\mathrm{L}}-\mathscr{N}_\mu W_{\mathrm{V}} = 0, \tag{A 10}$$

$$\mathscr{R}e\mathscr{P}r\,(\mathscr{N}_\rho-1)\,\alpha^2B+\mathscr{N}_\mu DW_{\mathrm{V}}-DW_{\mathrm{L}} = 0, \tag{A 11}$$

$$\begin{aligned} &\mathscr{C}r(P_{\mathrm{L}}-P_{\mathrm{V}})+2\mathscr{C}r(DW_{\mathrm{V}}-DW_{\mathrm{L}}) \\ &\qquad -2\mathscr{N}_\mu\left[\frac{\mathscr{H}_T}{\mathscr{P}r}(T-B)+\frac{\mathscr{H}_X}{\mathscr{S}c}(X_{\mathrm{A}}-B)\right]-(\alpha^2+\mathscr{B}o)\,B = 0, \end{aligned} \tag{A 12}$$

$$(D^2+\alpha^2)\,(W_{\mathrm{L}}-W_{\mathrm{V}}) = 0, \tag{A 13}$$

$$DT = \frac{-W_{\mathrm{L}}}{\mathscr{R}e\mathscr{P}r}, \tag{A 14}$$

$$DX_{\mathrm{A}} = -\mathscr{R}v(T-B)+(\mathscr{R}e\mathscr{S}c-\mathscr{B}i)\,(X_{\mathrm{A}}-B); \tag{A 15}$$

$$\text{as } \xi \to \infty \qquad W_{\mathrm{V}} = DW_{\mathrm{V}} = 0; \qquad \text{(A 16), (A 17)}$$

$$\text{as } \xi \to -\infty \qquad W_{\mathrm{L}} = DW_{\mathrm{L}} = X_{\mathrm{A}} = T = 0; \qquad \text{(A 18)–(A 21)}$$

$$\text{at } \xi = -1 \qquad T, DT, X_{\mathrm{A}} \text{ are continuous.} \qquad \text{(A 22)–(A 25)}$$

In (A 1)–(A 25) the scaling factors for ξ, W_{L}, W_{V}, P, T, X_{A} and B are δ, $\kappa_{\mathrm{L}}/\delta$, $\kappa_{\mathrm{L}}\mu_{\mathrm{L}}/\mu_{\mathrm{V}}\,\delta$, $\mu_{\mathrm{L}}\,\kappa_{\mathrm{L}}/\delta^2$, $\beta_T\,\delta$, $\beta_X\,\delta$ and δ respectively, where κ_{L} is the thermal diffusivity of the liquid and β_T and β_X are the gradients in temperature and mass fraction in the liquid at the interface. The non-dimensionalized boundary conditions (A 9)–(A 15) derive from the equations (6)–(13) for the vapour–liquid interface (i.e. at $z = B'$), rewritten to apply at $z = 0$ with the aid of a Taylor-series expansion for each variable. Equations (A 16)–(A 21) require that all perturbations in velocity, temperature and concentrations approach zero far from the interface. Equations (A 22)–(A 25) guarantee continuity of temperature, heat flux, concentration, and mass flux at the bottom of the boundary layer.

To obtain a characteristic equation that defines the neutral stationary state of the system, the general solution to (A 1)–(A 8) is sought, and then is substituted into the boundary conditions (A 9)–(A 25) to yield a homogeneous set of linear algebraic equations for the numerous integration constants in the general solution. The characteristic equation is generated by requiring that the determinant of the coefficient matrix of these algebraic equations be zero. Because the order of the matrix is 17 × 17, the characteristic equation is exceedingly large and therefore is not presented here. It can be obtained directly from the authors or from the thesis by Bose (1981).

The final result is an equation that relates the Hickman numbers $\mathscr{H}_X$ and $\mathscr{H}_T$ to the arbitrary wavenumber α of the disturbance and to all the other dimensionless groups at the condition of neutral stationary instability. Strictly speaking, α can take on any value from zero to infinity. In the results section we present only the minimum value of $\mathscr{H}_X$ (or $\mathscr{H}_T$ where appropriate) as a function of α, since this represents the practical stability limit for the system assuming that all possible values of α are physically realizable.

REFERENCES

Batchelor, G. K. 1959 *Q. J. R. Met. Soc.* **80**, 335.

Bose, A. 1981 Ph.D. thesis, Dept of Chemical Engng, University of Rochester.

Hickman, K. 1952 *Indust. Engng Chem.* **44**, 1892.

Hickman, K. 1972 *J. Vac. Sci. Tech.* **9**, 960.

Hickman, K. 1976 *J. Vac. Sci. Tech.* **13**, 585.

Maheshri, J. C. & Palmer, H. J. 1979 *A.I.Ch.E. J.* **25**, 183.

Miller, C. A. 1973 *A.I.Ch.E. J.* **19**, 909.

Palmer, H. J. 1976 *J. Fluid Mech.* **75**, 487.

Palmer, H. J. 1977 *A.I.Ch.E. J.* **23**, 831.

Palmer, H. J. & Maheshri, J. C. 1981 *Int. J. Heat Mass Transfer* **4**, 117.

Reid, R. C., Prausnitz, J. M. & Sherwood, T. K. 1977 *The Properties of Gases and Liquids.* McGraw-Hill.