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Initial flow development due to Marangoni convection in a mass transfer system

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Abstract—A linear stability analysis is used to investigate the onset of convection in a mass transfer system due to surface tension differences. Instead of a steady linear concentration distribution as basic state we make a detailed analysis of the mass transfer due to diffusion in the initially quiescent medium and obtain a time-dependent basic concentration distribution. The critical wavenumber, at neutral stability, and the preferred wavenumber, with largest growth factor, are time dependent and both decrease in time.

INTRODUCTION

Spontaneous interfacial movements, in an initially quiescent horizontal layer of fluid, caused by some interfacial instability are of interest when accompanying a heat or mass transfer process. Although such movements can have a variety of form [1], in many instances an array of convection cells develops. In the presence of such cells the transfer rate will be larger compared to the rate obtained with diffusion as the only transfer force. Since diffusion is in general a slow process, convective flow is a beneficial influence in practical areas where fast transfer is desired.

Two mechanisms can be responsible for the development of the convective flow. The first is based on a density stratification [2] and the second is based on surface tension differences and the Marangoni effect [3].

In their paper on convective instability Normand *et al.* [4] gave a review on the historical development of explaining the experiments by Bénard; Bénard [5] observed cellular patterns in a shallow liquid layer heated from below and cooled from above by a gas.

By now it is known [6] that the controlling mechanism of thermal instability depends upon the depth of the liquid layer. Instabilities in thinner films are of Marangoni type while deeper liquid layers are more likely to be unstable with respect to buoyancy forces.

Both instability mechanisms also act when instead of temperature differences, differences in the concentration of a solute occur. These again lead to differences in density and surface tension since the latter is a function of the concentration. In this way a mass transfer system is obtained.

Sternling and Scriven [7] applied stability analysis to the study of the initiation of cellular patterns (roll cells) in mass transfer systems. Their criteria, based only on the surface tension mechanism, to predict interfacial instability in a ternary liquid–liquid system, that is a system consisting of a solute and a pair of immiscible solvents, have been extensively confirmed by experimental results.

In practical applications, such as crystal growth, it is interesting to know the influence of both mechanisms, both active on earth, on that roll cell pattern which will reach a (quasi) steady state. By comparing experiments on earth to those in space, where gravity is weak and density differences will not cause fluid motion, one can study each mechanism separately.

The Department of Chemical Engineering of the University of Groningen, the Netherlands, is performing experiments on roll cells in a rectangular container (Fig. 1) containing an acetone solution in water with air above the free surface. To keep the acetone concentration in the gas constant the acetone is absorbed by active carbon. The aim is to study the influence, on earth and in space, of the initial solute concentration on the developing flow and the mass transfer coefficient.

In this paper we propose a model for analysing the onset of the instability, under zero gravity conditions, which will eventually lead to roll cells (in space). The beginning of the phenomenon can be described by a linear theory valid as long as the velocities are still small. If the system is unstable, small perturbations of the basic state grow exponentially in time. As basic state we assume a motionless medium but instead of taking a steady linear concentration distribution, as many authors do, we analyse the mass transfer process due to diffusion only. To describe this we use two models, film theory and penetration theory. Both models predict a time-dependent concentration distribution.

The linear stability analysis of this basic state leads to the following results. The critical Marangoni number, at neutral stability, is time dependent and with it the critical wavenumber, since both depend upon the time-dependent concentration distribution. The critical wavelength increases with time. For our particular system, with the Marangoni number dependent on initial concentration, the growth factors (one for each wavelength) are also time dependent. The preferred

NOMENCLATURE

A	arbitrary constant
B	arbitrary constant
c	concentration [kg m^{-3}]
c_0	initial concentration, 16 kg m^{-3}
dc	$\partial c/\partial z$
$\mathbb{D}$	diffusivity, $\mathbb{D}_l = 12.7 \times 10^{-10}$, $\mathbb{D}_g = 1.5 \times 10^{-5}$ m^2 s^{-1}
g	concentration disturbance
h_{ns}	amplitude of concentration disturbance at neutral stability
h	amplitude of concentration disturbance
H	height of the experimental container, 2.5×10^{-2} m
I_{ns}	particular integral (neutral case)
I	particular integral
k_1	$\sqrt{\mathbb{D}_g/\mathbb{D}_l}$
k_{ft}	$mH/(R_{ft}\mathbb{D}_l)$
k_{pt}	$mH/(R_{pt}\mathbb{D}_l)$
k	either k_{ft} or k_{pt}
L	length of the experimental container, 1.5×10^{-1} m
m	distribution coefficient, 1.03×10^{-3} kg m^{-3} (kg m^{-3})$^{-1}$
Ma	Marangoni number, $-\dfrac{\delta\gamma^*}{\delta c_l^*} c_0 H/(\mu_l \mathbb{D}_l)$
p	$\sqrt{1+(\beta Re/\alpha^2)}$
Pe	$WH/\mathbb{D}_l$, Péclet number of the liquid, $Pe = 20{,}000$
q	$\sqrt{\alpha^2+\beta Pe}$
Re	WH/ν_l, Reynolds number of the liquid, $Re = 25$
R_{ft}	resistance to mass transfer due to the gas in the film theory [s m^{-1}]
R_{pt}	resistance to mass transfer due to the gas in the penetration theory, $\sqrt{\pi t Pe/(k_1 W)}$ [s m^{-1}]
R	either R_{pt} or R_{ft} [s m^{-1}]
t	time coordinate [s]
u	horizontal velocity [m s^{-1}]
v	vertical velocity [m s^{-1}]
W	characteristic velocity, 10^{-3} m s^{-1}
x	horizontal coordinate [m]
z	vertical coordinate [m].

Greek symbols

α	wavenumber [m^{-1}]
β	growth factor
γ	surface tension [N m^{-1}]
$\partial\gamma/\partial c$	concentration gradient of surface tension, $\partial\gamma^*/\partial c_l^* = -3.25 \times 10^{-4}$ m^3 s^{-2}
Δ	Laplace operator [m^{-2}]
λ	wavelength [m]
λ_1	dimensionless constant, $\mu_l W \Big/ \left(\dfrac{\delta\gamma^*}{\partial c_l^*} c_0\right)$
μ	dynamic viscosity, $\mu_l = 10^{-3}$ kg m^{-1} s^{-1}
ν	kinematic viscosity, $\nu_l = \mu_l/\rho_l$ [m^2 s^{-1}]
ρ	density, $\rho_l = 10^3$ kg m^{-3}
τ	shear stress [N m^{-2}]
ϕ_{ns}	amplitude of the streamfunction disturbance at neutral stability
ϕ	amplitude of the streamfunction disturbance
ψ	streamfunction [m^2 s^{-1}]
ω	vorticity [s^{-1}].

Subscripts and superscripts

0	initial
f, ft	film theory
g	gas
l	liquid
m	either f or p
max	maximum
min	minimum
ns	neutral stability
p, pt	penetration theory
$\bar{}$	fixed value
*	dimension indication
$'$	z-derivative.

wavelength, defined as the one with the largest growth factor in time, increases with time.

FORMULATION OF THE MODEL

We consider a liquid layer of infinite horizontal extent, bounded by a rigid plane at $z^* = 0$ and a free surface at $z^* = H$. The layer, shown in Fig. 2, is composed of an incompressible Newtonian liquid with constant viscosity μ_l and density ρ_l. Above the free surface is a gas with constant viscosity μ_g and density ρ_g. For simplicity we consider a two-dimensional situation and denote the horizontal and vertical coordinates by x^* and z^*, respectively.

A single solute is transferring between the phases, having diffusivity $\mathbb{D}_l$, $\mathbb{D}_g$ and concentration c_l^*, c_g^* in the liquid and gas phase, respectively. We assume both phases to be initially at rest with $c_l^* = c_0$ and $c_g^* = 0$. In considering the dynamics of this system we make the following assumptions:

1. There is no gravity force.
2. Only the surface tension is a function of the concentration.
3. The free surface remains flat.

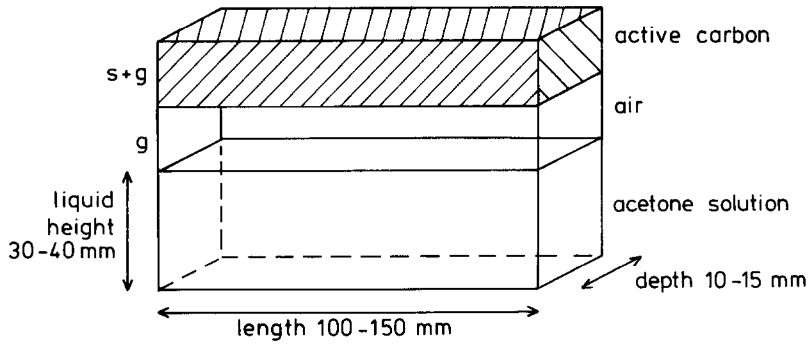

FIG. 1. Experimental set-up with some typical dimensions.

4. The gas above the surface does not exert shear forces on the interface.
5. The problem is essentially two-dimensional, so there is no influence of the back or front wall of the container.

The differential equations governing the flow are the Navier–Stokes equations. In streamfunction–vorticity formulation these are (in the absence of body forces)

$$\frac{\partial\omega^*}{\partial t^*}+\frac{\partial\psi^*}{\partial z^*}\frac{\partial\omega^*}{\partial x^*}-\frac{\partial\psi^*}{\partial x^*}\frac{\partial\omega^*}{\partial z^*}=\nu_l\Delta^*\omega^*, \quad (1)$$

$$\omega^*=-\Delta^*\psi^*, \quad (2)$$

where ψ^* is the streamfunction, ω^* the vorticity, ν_l the kinematic viscosity of the liquid and Δ^* the Laplace operator. The horizontal and vertical velocities are expressed by $u^*=\partial\psi^*/\partial z^*$ and $v^*=-\partial\psi^*/\partial x^*$, respectively.

The mass balance for the solute is

$$\frac{\partial c_l^*}{\partial t^*}+\frac{\partial\psi^*}{\partial z^*}\frac{\partial c_l^*}{\partial x^*}-\frac{\partial\psi^*}{\partial x^*}\frac{\partial c_l^*}{\partial z^*}=\mathbb{D}_l\Delta^*c_l^*. \quad (3)$$

By introduction of a characteristic velocity W and a standard length H we define dimensionless quantities

$$x=x^*/H,\quad z=z^*/H,\quad t=t^*W/H,$$

$$\psi=\psi^*/WH,\quad \omega=\omega^*H/W,\quad c=c_l^*/c_0,$$
$$\alpha=\alpha^*H,\quad \lambda=\lambda^*/H,$$

where α^* and λ^* denote the wavenumber and wavelength, respectively, both defined in Fig. 2.

Equations (1)–(3) become

$$\frac{\partial\omega}{\partial t}+\frac{\partial\psi}{\partial z}\frac{\partial\omega}{\partial x}-\frac{\partial\psi}{\partial x}\frac{\partial\omega}{\partial z}=Re^{-1}\Delta\omega, \quad (4)$$

$$\omega=-\Delta\psi, \quad (5)$$

$$\frac{\partial c}{\partial t}+\frac{\partial c}{\partial x}\frac{\partial\psi}{\partial z}-\frac{\partial\psi}{\partial x}\frac{\partial c}{\partial z}=Pe^{-1}\Delta c, \quad (6)$$

where Re denotes the Reynolds number $Re=WH/\nu_l$ and Pe the Péclet number $Pe=WH/\mathbb{D}_l$.

The boundary conditions are as follows

$$z=0:\psi=\frac{\partial\psi}{\partial z}=\frac{\partial c}{\partial z}=0. \quad (7)$$

$$x=0 \quad\text{and}\quad x=\pi/\alpha:\psi=\frac{\partial^2\psi}{\partial x^2}=\frac{\partial c}{\partial x}=0. \quad (8)$$

At the free boundary $z=1$:

(a) $\psi=0.$ (9)

(b) The boundary condition at $z=1$ for the concentration follows from the mass balance of the solute at the interface. From Fick's law the mass flux from the liquid is

$$\Phi_m''=-\frac{\mathbb{D}_lc_0}{H}\frac{\partial c}{\partial z}. \quad (10)$$

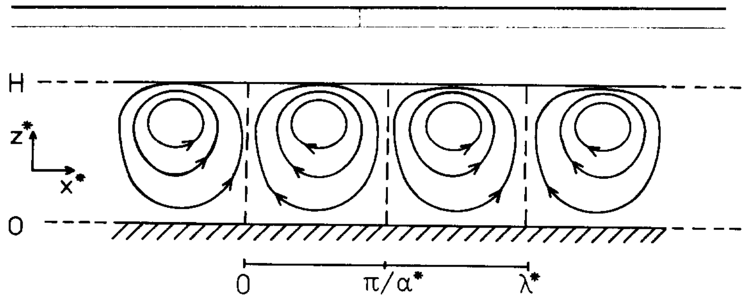

FIG. 2. Schematic view of the geometric model. Coordinate axes, the wavelength λ^* and the wavenumber α^* are defined.

In the gas phase Φ''_{m} is proportional to the concentration difference between the interface and bulk and inversely proportional to the resistance R of the gas phase to mass transfer from the liquid. We assume the bulk gas concentration to be negligibly small. Hence

$$\Phi''_{\mathrm{m}} = \frac{mc_0 c}{R}, \tag{11}$$

where m is the distribution coefficient. From (10) and (11) we obtain

$$\frac{\partial c}{\partial z} = -\frac{mH}{\mathbb{D}_{\mathrm{l}} R} c. \tag{12}$$

(c) The last boundary condition is obtained from the tangential stress balance at the interface. With γ^* the surface tension and τ^* the shear stress, the equation is

$$\frac{\partial \gamma^*}{\partial x^*} = \tau^*. \tag{13}$$

Using assumptions 2 and 4 this becomes

$$\frac{\partial \gamma^*}{\partial c_{\mathrm{l}}^*} \frac{\partial c_{\mathrm{l}}^*}{\partial x^*} = \mu_{\mathrm{l}} \left(\frac{\partial u^*}{\partial z^*} + \frac{\partial v^*}{\partial x^*} \right), \tag{14}$$

where μ_{l} is the dynamic viscosity of the liquid. The term $\partial v^*/\partial x^*$ vanishes because of (9). In dimensionless variables the Marangoni boundary condition becomes

$$\frac{\partial c}{\partial x} = \lambda_1 \frac{\partial^2 \psi}{\partial z^2}, \tag{15}$$

with $\lambda_1 = \mu_{\mathrm{l}} W / [(\partial \gamma^* / \partial c_{\mathrm{l}}^*) c_0]$ a dimensionless constant, which is negative due to the negative value of $\partial \gamma^* / \partial c_{\mathrm{l}}^*$.

CONCENTRATION DISTRIBUTION FOR THE QUIESCENT MEDIUM

We look for solutions of the model equations in the case $\psi = \omega = 0$. The equations reduce to

$$\frac{\partial c}{\partial t} = Pe^{-1} \Delta c, \tag{16}$$

$$z = 0 : \frac{\partial c}{\partial z} = 0 \tag{17}$$

$$z = 1 : \frac{\partial c}{\partial z} = -\frac{mH}{\mathbb{D}_{\mathrm{l}} R} c, \frac{\partial c}{\partial x} = 0, \tag{18}$$

$$t = 0 : \quad c = 1. \tag{19}$$

The solution of (16)–(19) is a concentration distribution only due to diffusion in the liquid and evaporation at the free surface. This solution does not depend on x.

The expression for the resistance R, occurring in the first equation of (18), depends upon the mass transfer model describing the transfer of the solute through the interface. In the film theory [8] R is taken constant R_{ft}.

For small times it is expected that the concentration in the liquid will differ only from the initial concentration close to the interface. So the fluid layer can be thought as semi-infinite. In this case the solution of (16)–(19) is straightforward [9]

$$c_{\mathrm{l}}^{\mathrm{f}}(z,t) = 1 - \operatorname{erfc}\left(\frac{1-z}{2} \sqrt{\frac{Pe}{t}} \right) + \exp\left[(1-z) k_{\mathrm{ft}} + k_{\mathrm{ft}}^2 \frac{t}{Pe} \right] \times \operatorname{erfc}\left(\frac{1-z}{2} \sqrt{\frac{Pe}{t}} + k_{\mathrm{ft}} \sqrt{\frac{t}{Pe}} \right), \tag{20}$$

where $k_{\mathrm{ft}} = mH/(\mathbb{D}_{\mathrm{l}} R_{\mathrm{ft}})$ and the superscript f indicates film theory.

To investigate the dependence on the mass transfer model we determined also the concentration distribution of the solute using penetration theory. The penetration theory, originally due to Higbie [10], takes diffusion in both the gas and fluid phase into account in describing the mass transfer process. For two semi-infinite layers the solutions are well known [8], and in our case, details are given in [11], we find

$$c_{\mathrm{l}}^{\mathrm{p}}(z,t) = 1 - \frac{mk_1}{1 + mk_1} \operatorname{erfc}\left(\frac{1-z}{2} \sqrt{\frac{Pe}{t}} \right), \tag{21}$$

where $k_1 = \sqrt{\mathbb{D}_{\mathrm{g}} / \mathbb{D}_{\mathrm{l}}}$ and the superscript p indicates penetration theory.

The resistance R turns out to be

$$R = R_{\mathrm{pt}} = \frac{\sqrt{\pi t Pe}}{k_1 W}. \tag{22}$$

This resistance is zero at $t = 0$ and then increases with time. In itself this picture is more realistic than the constant R_{ft} from the film theory. So initially we expect the penetration theory to give the best description.

In Figs. 3(a) and (b) plots of both concentration distributions $c_{\mathrm{l}}^{\mathrm{p}}$ and $c_{\mathrm{l}}^{\mathrm{f}}$ are shown for different times t. It is clear from these figures that it is permissible to assume the liquid layer to be semi-infinite.

LINEAR STABILITY ANALYSIS

The solute will not evaporate uniformly along the interface, resulting in local velocities at the interface due to the Marangoni effect, expressed by equation (15).

The question is now whether these disturbances will decay in time by viscous forces (the system is stable) or will grow in time (the system is unstable). A necessary condition for the disturbances to develop into roll cells is the instability of the linearised system. In view of experiments we expect this instability to occur. To analyse the development of disturbances we take for the concentration of the solute

$$c(x,z,t) = c_{\mathrm{l}}^{\mathrm{m}}(z,t) + g(x,z,t), \tag{23}$$

where the superscript m (mass transfer model) is either p or f and we assume the disturbance g to be small.

Since an arbitrary disturbance is composed of Fourier components it is sufficient in a linear theory to

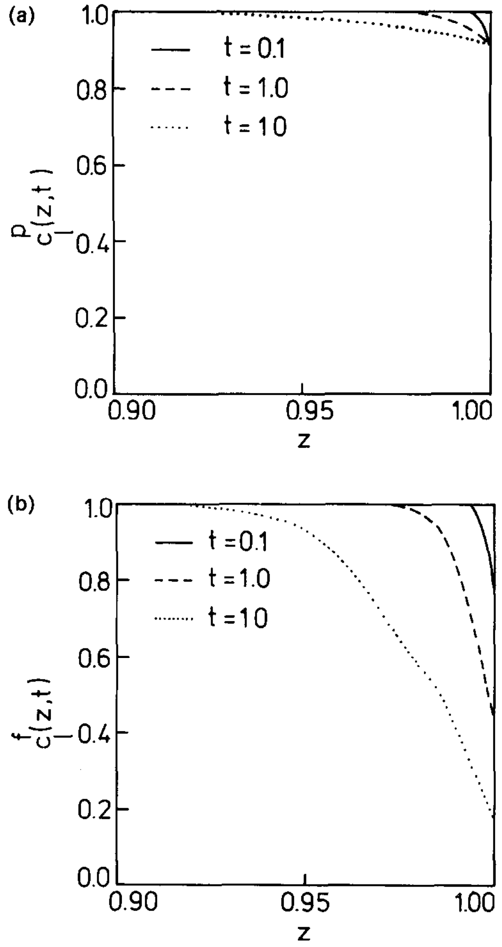

FIG. 3. The concentrations (a) c_l^p and (b) c_l^f at different times t.

consider only one component in studying the local stability of the system.

The linearised system becomes

$$\frac{\partial\omega}{\partial t} = Re^{-1}\Delta\omega, \quad \omega = -\Delta\psi,$$

$$\frac{\partial g}{\partial t} - \frac{\partial\psi}{\partial x}\frac{\partial c_l}{\partial z} = Pe^{-1}\Delta g$$

with boundary conditions

$$x = 0 \quad \text{and} \quad x = \pi/\alpha : \psi = \frac{\partial^2\psi}{\partial x^2} = \frac{\partial g}{\partial x} = 0$$

$$z = 0 : \psi = \frac{\partial\psi}{\partial z} = \frac{\partial g}{\partial z} = 0 \qquad (24)$$

$$z = 1 : \psi = 0, \quad \lambda_1\omega - \frac{\partial g}{\partial x} = 0, \quad \frac{\partial g}{\partial z} + kg = 0.$$

At the moment $t = t_0$, ω, ψ and g suddenly differ from zero.

The solution is written in the form

$$\psi(x,z,t) = \varphi(z)\exp(\mathrm{i}\alpha x + \beta\tau),$$
$$g(x,z,t) = h(z)\exp(\mathrm{i}\alpha x + \beta\tau), \qquad (25)$$

where $\tau = t - t_0$,

In the differential equation c_l is a function of time and in the boundary condition k also depends on time in the case of the penetration theory. We consider β as a constant complex number of which the value obtained depends on the parameter t_0. In reality β will be a function of t and also of z.

However, it can be shown that for $\tau \to 0$

$$\exp\beta\tau \sim 1 + \tau\beta(t_0) + o(\tau)$$

where $o(\tau) = O(\tau^2)$ for the film theory and $O(\tau\sqrt{\tau})$ for the penetration theory. Hence, the instantaneous value $\beta(t_0)$ corresponds to the true value β with an error $o(1)$. The real part of β, also denoted as growth factor, determines stability. It is obtained correctly by the procedure described hereafter, assuming β to be a constant.

Substitution of (25) into the differential equations and boundary conditions gives, after linearisation in the disturbances

$$\beta(\phi'' - \alpha^2\phi) = Re^{-1}(\phi^{\mathrm{IV}} - 2\alpha^2\phi'' + \alpha^4\phi), \qquad (26)$$

$$\phi(0) = \phi(1) = \phi'(0) = 0, \qquad (27)$$

$$h'' - q^2h = -\mathrm{i}\alpha Pe\phi\,\mathrm{d}c_l^{\mathrm{m}}, \qquad (28)$$

$$h'(0) = 0, \quad h'(1) = -kh(1), \quad \mathrm{i}\alpha h(1) = \lambda_1\phi''(1), \qquad (29\text{a,b,c})$$

where $k = mH/(\mathbb{D}_l R)$ with R either R_{ft} or R_{pt} depending on the mass transfer model and

$$q = \sqrt{\alpha^2 + \beta Pe}, \mathrm{d}c_l^{\mathrm{m}} = \partial c_l^{\mathrm{m}}/\partial z.$$

We assume β to be real, so we are neglecting the possibility of oscillatory convection. For an account on this oscillatory convection the reader is referred to [12].

First we determine the critical conditions for the onset of stationary convection (neutral stability). We set $\beta = 0$ and solve the system (26)–(29). Solutions are

$$\phi_{\mathrm{ns}}(z) = A\left(\sinh\alpha z - z\sinh\alpha z + \frac{\alpha z\sinh\alpha(z-1)}{\sinh\alpha}\right), \qquad (30)$$

$$h_{\mathrm{ns}}(z) = I_{\mathrm{ns}}(z) - \frac{[I'_{\mathrm{ns}}(1) + kI_{\mathrm{ns}}(1)]\cosh\alpha z}{\alpha\sinh\alpha + k\cosh\alpha}, \qquad (31)$$

$$I_{\mathrm{ns}}(z) = -\mathrm{i}Pe\int_0^z \phi_{\mathrm{ns}}(s)\,\mathrm{d}c_l^{\mathrm{m}}(s)\sinh\alpha(z-s)\,\mathrm{d}s. \qquad (32)$$

The Marangoni number is defined by

$$Ma = -\frac{Pe}{\lambda_1} = \frac{-(\partial\gamma^*/\partial c_l^*)c_0H}{\mu_l\mathbb{D}_l}. \qquad (33)$$

From condition (15) a relation between the Marangoni number and the wavenumber is obtained (neutral curve)

$$Ma = \frac{2A\left(\dfrac{\alpha}{\sinh\alpha} - \cosh\alpha\right)(\alpha\sinh\alpha + k\cosh\alpha)}{\alpha\displaystyle\int_0^1 \phi_{\mathrm{ns}}(s)\,\mathrm{d}c_1^{\mathrm{m}}(s)\cosh\alpha s\,\mathrm{d}s}. \tag{34}$$

The constant A is arbitrary, dependent on the initial disturbance amplitude, but drops out of equation (34). Because $\mathrm{d}c_1^{\mathrm{m}}$ is slowly varying with time, equation (34) determines for each time value a neutral curve. The minimum of this curve gives the critical Marangoni number and the critical wavenumber of the system. When the Marangoni number exceeds slightly this critical value the system is unstable, the critical wavenumber being the wavenumber amplified first.

For $\beta \neq 0$ the solutions of the system (26)–(29) are

$$\phi(z) = B\left[(\cosh\alpha - \cosh\alpha p)\left(\sinh\alpha z - \frac{1}{p}\sinh\alpha pz\right) - \left(\sinh\alpha - \frac{1}{p}\sinh\alpha p\right)(\cosh\alpha z - \cosh\alpha pz)\right], \tag{35}$$

$$h(z) = I(z) - \frac{[I'(1) + kI(1)]\cosh qz}{q\sinh q + k\cosh q}, \tag{36}$$

$$I(z) = -\frac{\mathrm{i}\alpha Pe}{q}\int_0^z \phi(s)\,\mathrm{d}c_1^{\mathrm{m}}(s)\sinh q(z-s)\,\mathrm{d}s, \tag{37}$$

where

$$p = \sqrt{1 + \frac{\beta Re}{\alpha^2}}.$$

From condition (15) we now obtain a transcendental equation for β

$$\alpha^2 Ma\int_0^1 \phi(s)\,\mathrm{d}c_1^{\mathrm{m}}(s)\frac{\cosh qs}{\cosh q}\,\mathrm{d}s = B\beta Re\,(q\tanh q + k)\left(\sinh\alpha\cosh\alpha p - \frac{1}{p}\cosh\alpha\sinh\alpha p\right). \tag{38}$$

The interval of α values for which β turns out to be positive determines the wavenumbers for which the linearised system is unstable. The preferred wavenumber is defined as that wavenumber for which β is maximal. Note that if at a fixed time the Marangoni number (of our experimental system) is less than the critical one, equation (38) cannot have a positive solution.

RESULTS

The integrals in equations (34), (37) and (38) are evaluated after coordinate transformations (see ref. [11] for details) by aid of the Gauss–Laguerre method [13], where eight weight points are sufficient to obtain accurate values. Neutral curves at different times, using

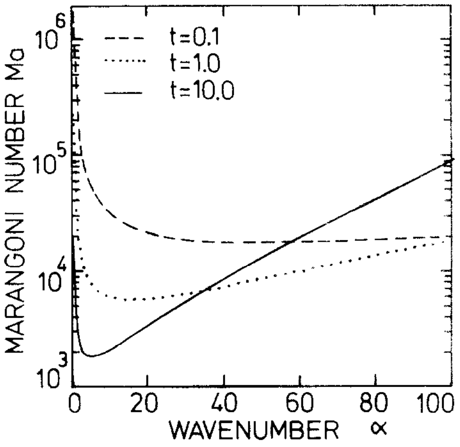

FIG. 4. Neutral curves at different time values t calculated for the penetration theory.

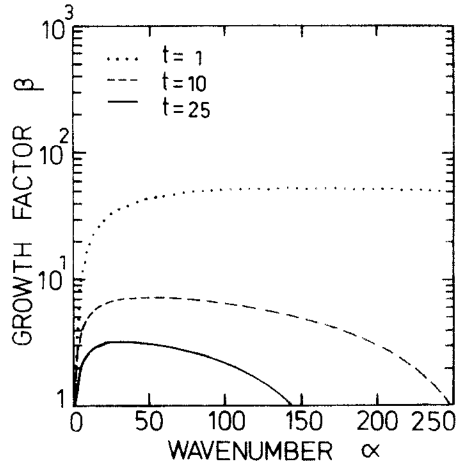

FIG. 5. Time t vs growth factor β at different wavenumber α calculated with the penetration theory.

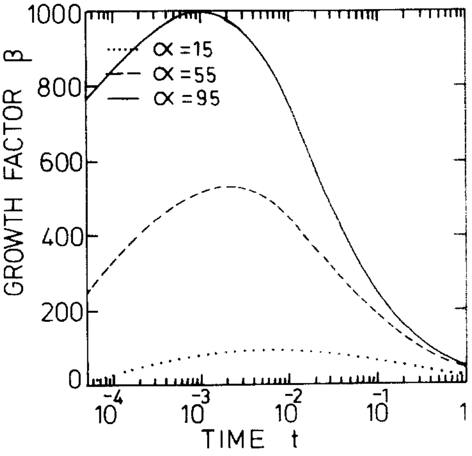

FIG. 6. Wavenumber α vs growth factor β at different times t calculated using penetration theory.

penetration theory, are drawn in Fig. 4. From this it is clear that the concentration distribution, due to diffusion only, influences the critical conditions for instability.

The Marangoni number of our experimental system turns out to be 10^8. Using this value we solved (38) by bisection and obtained at every time t for a given wavenumber α a growth factor β. Results are shown in Figs. 5 and 6, using penetration theory. For fixed time $\bar{t}$ there exists a wavenumber $\alpha_{\max}$ at which the corresponding β is maximal. As $\bar{t}$ increases $\alpha_{\max}$ decreases, which is consistent with the decrease of the critical wavenumber with increasing time.

For every fixed wavenumber $\bar{\alpha}$ there exists a very small $t_{\min}$ at which the corresponding β becomes larger than zero. As $\bar{\alpha}$ increases, $t_{\min}$ decreases, illustrating that as $t < t_{\min}$ the Marangoni number is less than the critical one (at that particular $\bar{\alpha}$).

Similar results are obtained using film theory. A difference in results between the mass transfer models is that $t_{\min}$ values are larger for the film theory (at any wavenumber). So instability is predicted to happen sooner by the penetration theory. This is due to the low resistance at small time, so a low resistance to mass transfer promotes instability.

In Figs. 7 and 8 the solutions ϕ and h are shown for some values of α and time t. As time increases the disturbance extends over deeper liquid layers.

From the results we can make the following picture of the initial stages of development of the roll cells. Initially, roll cells of small size will develop near the interface. In this stage penetration modelling seems to be preferred. For larger times, and assuming that the linear theory still holds, larger cells will develop since $\alpha_{\max}$ decreases. Remember again that the theory used here only describes the start of the instability. Thus the conclusions drawn for larger times start from concentration distributions which are developed in the liquid in which the velocities are still zero.

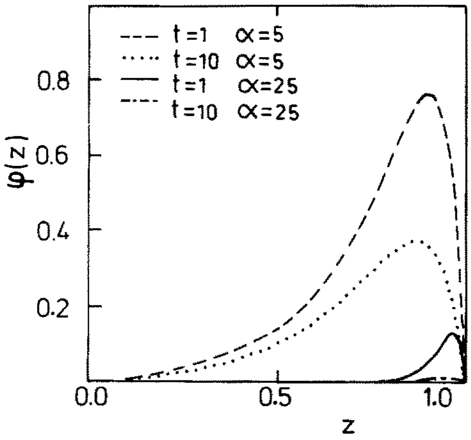

FIG. 7. Amplitude of the streamfunction disturbance at different times t and wavenumber α calculated using penetration theory.

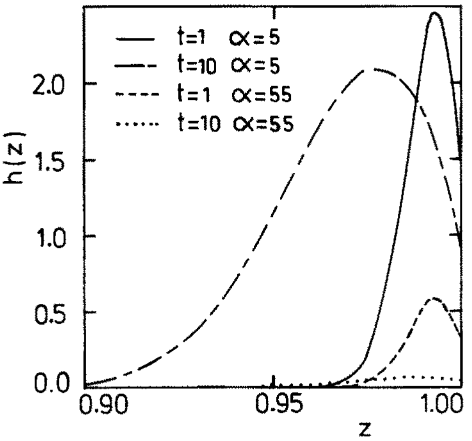

FIG. 8. Amplitude of the concentration disturbance at different times t and wavenumber α calculated using penetration theory.

After a short while there will be a supply of solute due to convection from the bulk to the interface [the term g in equation (23)]. This destroys the basic assumption—that only diffusion occurs—of the penetration theory. Because of the much larger diffusivity in the gas phase, extension in this phase is much larger than in the liquid. After a relatively short time the solute will occupy the available space, of the gas, in the container (up to the carbon sink). Then the description of the mass transfer process for the gas phase should shift to the film model due to the constant resistance of the gas layer to mass transfer from the liquid. So we can use this description in investigating later (nonlinear) stages of development of roll cells.

This picture of initial development of roll cells is in agreement with the experimental results, for small time, of Linde and Schwarz [14].

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DEVELOPPEMENT INITIAL DE L'ECOULEMENT RESULTANT DE CONVECTION MARANGONI DANS UN SYSTEME DE TRANSFERT DE MASSE

Résumé—Une analyse de stabilité linéaire a été utilisée pour examiner le commencement de la convection due aux variations en tension superficielle dans un système de transfert de masse. Au lieu de supposer comme situation initiale une distribution de concentration linéaire et stationnaire, nous faisons une analyse detaillée du transfert de masse résultant de la diffusion dans le système initialement sans mouvement, ce qui amène à une distribution de concentration dépendant du temps. Le nombre d'onde critique correspondant à la stabilité neutre et le nombre d'onde préferé correspondant au plus grand facteur d'amplification décroissent avec le temps.

ANFANGSENTWICKLUNG DER STRÖMUNG INFOLGE MARANGONI KONVEKTION IN EINEM STOFFÜBERTRAGUNGSSYSTEM

Zusammenfassung—Eine lineare Stabilitätsanalyse der durch Oberflächenspannungskräfte bewirkten Zellularkonvektion in einem Stofftransportsystem wird beschrieben. Statt einer stationären linearen Konzentrationsverteilung als Grundzustand anzunehmen untersuchen wir den Stofftransport infolge Diffusion in einer im Anfang bewegungslose Flüssigkeit und erzielen damit eine zeitabhängige Konzentrationsverteilung. Die kritische Wellenzahl, bei neutraler Stabilität, und die dominante Wellenzahl, mit grösster Wachsfaktor, sind zeitabhängig und nehmen ab in die Zeit.

РАЗВИТИЕ НАЧАЛЬНОГО ПОТОКА ВСЛЕДСТВИЕ КОНВЕКЦИИ МАРАНГОНИ В СИСТЕМЕ ПЕРЕНОСА МАССЫ

Аннотация—Анализ линейной устойчивости используется, чтобы исследовать введение конвекции в систему переноса массы вследствие разниц поверхностного натяжения. Вместо устойчивого линейного распределения концентрации как основного состояния, мы вводим подробный анализ переноса массы по причине диффузии в начальном неподвижном потоке; получается основное распределение концентрации, которое зависит от времени. Критическое волновое число, при нейтральной устойчивости, и избранное волновое число, имеющее самый большой фактор увеличения, зависят от времени и оба уменьшаются во времени.