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International Journal of Heat and Mass Transfer 48 (2005) 135–144

International Journal of HEAT and MASS TRANSFER

www.elsevier.com/locate/ijhmt

Predicting Marangoni convection caused by transient gas diffusion in liquids

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Received 21 August 2003; received in revised form 30 April 2004
Available online 22 October 2004

Abstract

The onset of convection driven by surface tension during gas diffusion in a liquid is investigated. Gas diffusion at the gas–liquid interface results in the variation of concentration of the solute that may cause an increase in surface tension leading to Marangoni convection. The onset of convection for unsteady-state gas desorption can be predicted from the maximum transient Ma_t, which is here derived by analogy with its equivalent in thermal convection. It is a function of the transient Biot number (Bi_D) for interfacial gas diffusion, which depends strongly on the state of vapour–liquid equilibrium at the interface. The transient Marangoni numbers, critical times for stable mass diffusion and the critical sizes of convection cells have been formulated. The desorption of ethyl-ether from chloro-benzene in L.M. Blair's [The onset of cellular convection in a fluid layer with time-dependent density gradients, PhD thesis, University of Illinois, Urbana, 1968] experiments is liquid phase-controlled, hence, the highly soluble system is characterized by $Bi_D = 0$. Therefore, his experiments that were initiated with a step-change in pressure cannot be analyzed by a step-function boundary that is characterized by $Bi_D = \infty$. The surface concentration may change very slowly, it has been approximated to be about 0.1% of the initial pressure change at the point of onset of convection. The average critical Marangoni number for this condition was estimated to be 53.3, which is fairly close to the theoretical value of 67 for an interface with a Biot number of 0. Therefore, the high value of 3100 calculated by I.F. Davenport and C.J. King [The initiation of natural convection caused by time-dependent profiles, Lawrence Berkeley Lab, Report NBR LBL-600, 1972] is wrong, who wrongly assumed a fixed surface-concentration boundary that is applicable only to a sparingly soluble solute. The critical sizes of convection cells predicted by theory are generally less than 1 mm for reported critical times of less than 20 s, they would be difficult to measure.

Keywords: Surface-tension driven convection; Gas diffusion; Transient Biot and Marangoni number; Critical times and cell sizes

1. Introduction

The desorption of a solute gas from liquid leads to an increase in surface tension in the liquid surface which can consequently cause convection or Marangoni effect, which may develop into 'interfacial turbulence' and result in rapid mass transfer. For example Brian et al. [3] detected 3.6-fold enhancement of the mass transfer coefficient in the liquid phase by desorbing surface tension-reducing solutes from aqueous solution in a short wetted-wall column. O'Brien [4] employed the Marangoni effect to enhance the drying of a wet silicone wafer

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doi:10.1016/j.ijheatmasstransfer.2004.05.039

Nomenclature

$\tilde{a}_c$	critical dimensionless wavenumber = ad
B_m	linear surface-concentration variation, kmol/m^3/s
c_b	bulk concentration, kmol/m^3
c_s	surface concentration, kmol/m^3
c^*	gas–liquid interfacial equilibrium concentration, kmol/m^3
d	depth of fluid layer, m
D	diffusion coefficient, m^2/s
H	Henry's law constant, J/kmol
H'	quasi Henry's law constant, kmol/m^3 atm
H^*	dimensionless Henry's law constant, $H^* = H/RT$
j	interfacial mass flux, kmol/m^2 s
j°	constant mass flux, kmol/m^2 s
k	thermal conductivity of the fluid, W/m °C
l	thickness of fluid layer, m
L	diameter of optical cell used by Okhotsimskii and Hozawa [8], m
p	partial pressure, Pa
p^{sat}	saturated vapour pressure, Pa
q°	constant heat flux, W/m^2
t_c	critical time of stable gas diffusion before the onset of convection, s
x	mole fraction
z	vertical distance in fluid measured from the bounding surface, m

Greek symbols

β	linear temperature gradient, K/m
ϕ	coefficient for temperature variation of surface tension, N/m K
γ	activity coefficient
φ	coefficient for concentration variation of surface tension, N m^2/kmol
κ	thermal diffusivity, m^2/s
λ	wavelength, m
μ	dynamic viscosity, Pa s
ρ	density, kg/m^3
ρ°	molar density, kmol/m^3
σ	surface tension, N/m

Abbreviations

CMF	constant mass flux boundary condition
LCR	linear concentration rate
FSC	fixed surface-concentration boundary condition
VLE	Vapour liquid equilibrium

Subscripts

c	critical
g	gas phase
l	liquid phase
0	initial state
s	surface

by using an alcohol, leaving them almost completely dry and extremely clean. Skurygin and Dil'man [5] have shown that the thermal effect of water evaporation is about 30 times greater than that of carbon dioxide desorption in a combined process of desorption and evaporation. This is expected as the square root of the ratio of thermal diffusivity to that of the mass diffusivity is approximately $\sqrt{10^{-7}/10^{-9}} = 10$, and the effect of advection will enhance the heat transfer further by a factor of about three, so that the overall effect will be about 30. Vazqueez et al. [6] had measured rather high surface velocity exceeding 0.1 m/s at the interface between air and various aqueous solutions, where the shear at the free surface is effectively zero since $du/dy = 0$. The high velocity is about 100 times faster than those encountered in buoyancy convection, which tend to occur in deeper fluids.

The onset of convection driven by surface tension during gas desorption in a quiescent cell has been studied systematically only by Blair [1], and qualitatively by Preven [7] and Okhotsimskii and Hozawa [8]. Blair [1] observed Marangoni effect induced by the desorption of ethyl-ether from a solution of chloro-benzene containing 10 mol% of ethyl-ether, and suppressed the convection by adding a trace amount of dimethylpolysiloxane. The short onset times, below 20 s, are an indication of Marangoni convection since the depth involved was very shallow. He correctly showed that the transient Marangoni number was proportional to the square root of the critical time, which was inversely proportional to the initial concentration difference, but he did not estimate the critical value of Ma_c due to the lack of accurate physical properties of the organic liquids, especially the coefficient for concentration variation of surface tension. Davenport and King [2] estimated a critical Marangoni number ($Ma_c = (\varphi Ra_c\sqrt{t_{Ma}/t_{Ra}^3})/g\alpha D$) of 3100 from Blair's [1] data for buoyancy and Marangoni experiments, this is very much higher than Pearson's [9] theoretical value of 79.6, where the Marangoni number for steady-state linear stability analysis is defined as ($Ma = \beta l^2\phi/(\mu\kappa)$). Their values of Marangoni number were calculated from physical properties crudely estimated with doubtful basis, for instance the Henry's law constant was derived from data of buoyancy-driven convection in aqueous solutions and a Rayleigh number of 300. If their data are corrected for buoyancy in an organic liquid and a Rayleigh number of 1000 as reported by Blair [1], then the critical Marangoni number would be 11,000, which is unacceptably high.

Okhotsimskii and Hozawa [8] observed the desorption of carbon dioxide from methanol and obtained an extremely large value for their version of the Marangoni number ($Ma = L\Delta\sigma/(\mu D)$) of 2×10^6, which is unreasonable since surface tension is a weak force. The senseless value was due to the use of the wrong length scale, i.e. diameter L of the optical cell, and also to the high value of surface tension difference being used in the calculation of the Marangoni number; defining the Marangoni number in terms of L is in clear contradiction of Pearson's [9] instability theory for a thin layer of liquid.

Tan [10] and Tan and Thorpe [11] have shown that Marangoni effect caused by transient heat conduction can be characterized by a newly defined transient Marangoni number which predicted the onset of convection successfully. Transient gas diffusion in liquid is analogous to transient heat conduction, hence the principles of their approach should apply here. It is thus desirable to develop a theory of onset of Marangoni convection induced by gas desorption and to formulate the criteria and equations for its prediction.

2. Theory of transient Marangoni convection induced by gas desorption

The principle and mechanism of the onset of transient Marangoni convection are identical to those of transient thermal convection, that is the increase in surface tension as a result in this case of the decrease of surface solute concentration during gas desorption causes liquid to be drawn to the surface leading to convection. The stable diffusion process before convection will be very brief and the affected layer will accordingly be very thin. The same Biot number-dependence of the onset of convection will also apply here, and the effect of vapour–liquid equilibrium at the interface is incorporated in a diffusive Biot number (Bi_D) defined by Tan [10] and Tan and Thorpe [12]. These have been clearly shown to be valid in buoyancy-driven convection during gas absorption. The influence of $Bi_D(=D_gH^*/D_l)$ on Marangoni number for some gas–liquid systems as predicted by Nield [13] from linear stability analysis are shown in Table 1. As expected, a highly soluble gas will lead to a low Bi_D and Ma_c, and vice versa for a sparingly soluble gas. The highly soluble ethyl-ether (in chlorobenzene) leads to zero in Biot number and a corresponding Marangoni number of 80. Conversely, the high Biot number for CO_2 desorption in water has a corresponding large critical Marangoni number and ensures that surface-tension driven convection will not occur. Plevan and Quinn [14] were unable to observe surface-tension driven convection in the CO_2–water system. It is thus very important to ascertain the actual Biot number of the fluid system with accurate physical properties before any attempt to analyze the data with linear stability criteria.

The detailed formulation of the instability criteria and mathematical derivations are identical to those provided by Tan [10] and Tan and Thorpe [11], and only the important results for three boundary conditions, namely: constant mass flux (CMF), linear concentration rate (LCR) and fixed surface concentration (FSC), are presented in this study. The transient Marangoni number for surface-tension change due to concentration variation which results is:

$$Ma = \frac{\varphi z^2}{D\mu}\left(\frac{\partial c}{\partial z}\right)_t \tag{1}$$

where φ is the coefficient of surface-tension variation with concentration defined as $\varphi = \mathrm{d}\sigma/\mathrm{d}c$.

2.1. Transient Marangoni number for CMF boundary condition

The transient Marangoni number for an interface that is governed by $Bi_D = 0$, or a constant mass flux, j°, can similarly be derived from the heat transfer analogue, $Ma_{\max} = 0.663\phi q^\circ t/(\mu k)$, as follows:

$$Ma_{\max} = \frac{0.663\varphi j^\circ t}{\mu D} \tag{2}$$

at the critical depth of penetration $z_c = 1.684\sqrt{Dt}$. Substituting the change in surface concentration for the constant mass flux $j^\circ(= (c_b - c_s)\sqrt{D\pi/4t})$, Eq. (2) becomes

$$Ma_{\max} = \frac{0.587\varphi(c_b - c_s)}{\mu}\sqrt{\frac{t}{D}} \tag{3}$$

from which the time when convection commences, t_c, can be calculated if the critical Marangoni number and the interfacial concentration, c_s at that instant are known. If it is assumed that the critical Marangoni number is 79.6, the critical time is then:

$$t_c = \frac{120\mu D}{\varphi j^\circ} \tag{4}$$

or in terms of the surface-concentration change $\Delta c_s = (c_b - c_s)$,

$$t_c = \left(\frac{136\mu\sqrt{D}}{\varphi\Delta c_s}\right)^2 \tag{5}$$

The critical Marangoni number for a deformable surface was found to be 67 by Davis and Homsy [17]. Eqs. (4) and (5) can then be modified to become $t_c = 101\mu D/\varphi j^\circ$ and $t_c = 114\mu D/\varphi\Delta c_s$ respectively.

Table 1
Transient Biot number for gas diffusion in water at 25 °C and the corresponding theoretical values of Marangoni numbers from Nield [13]

Parameter	Ethyl-ether[a]	NH_3	SO_2	CO_2	O_2
Bi_D	0.02	0.053	0.79	89.5	2780
Ma_c	80	82.6	108	2583	40,000
$D_g \times 10^5\,\text{m}^2/\text{s}$	0.88	2.34	1.40	1.25	2.80
$D_l \times 10^9\,\text{m}^2/\text{s}$	1.90	1.70	1.82	1.72	2.10
$\sqrt{D_g/D_l}$	68	117	87.7	85.2	95.7
$H \times 10^6$ J/kmol	0.0071	0.0011	0.022	2.56	72
H^*	0.0029	0.00045	0.00903	1.05	29.1

[a] Ethyl-ether desorbing from chloro-benzene, D_l from Davenport and King [2], H and D_g are our estimates. H from Kay and Nedderman [15] and D from Cussler [16].

2.2. Transient Marangoni number for LCR boundary condition

If the gas is modestly soluble in liquid, then the interfacial gas concentration may steadily drop at a linear rate $\Delta c_s = B_m t$. The concentration profile for a layer of saturated liquid desorbing at a linear concentration rate (LCR) is given by its thermal analogue [18]:

$$c_b - c = 4B_m t i^2\text{erfc}\left(\frac{z}{2\sqrt{Dt}}\right) \qquad (6)$$

The instantaneous adverse concentration gradient at point z is

$$\left(\frac{\partial c}{\partial z}\right)_t = -2B_m\sqrt{\frac{t}{D}}\left[i\text{erfc}\left(\frac{z}{2\sqrt{Dt}}\right)\right] \qquad (7)$$

The transient Marangoni number from Eq. (1) becomes:

$$Ma_t = \frac{\varphi z^2}{\mu}\sqrt{\frac{t}{D}}2B_m i\text{erfc}\left(\frac{z}{2\sqrt{Dt}}\right) \qquad (8)$$

The maximum Marangoni number is found by differentiating Eq. (8):

$$\left(\frac{\partial}{\partial z}Ma_t\right)_t = \frac{2\varphi B_m z}{\mu}\sqrt{\frac{t}{D^3}}\left[2i\text{erfc}\left(\frac{z}{2\sqrt{Dt}}\right) - \frac{z}{2\sqrt{Dt}}\text{erfc}\left(\frac{z}{2\sqrt{Dt}}\right)\right] = 0$$

which gives the depth of penetration for the maximum Ma as

$$z_c = 1.465\sqrt{Dt} \qquad (9)$$

The local concentration gradient is $\partial c/\partial z = 0.4398B_m\sqrt{t/D}$ and the maximum Marangoni number is

$$Ma_{\max} = \frac{0.472\varphi B_m}{\mu}\sqrt{\frac{t^3}{D}} \qquad (10)$$

or in terms of the surface-concentration drop Δc_s,

$$Ma_{\max} = \frac{0.472\varphi\,\Delta c_s}{\mu}\sqrt{\frac{t}{D}} \qquad (11)$$

There is no known theoretical value of Marangoni number for the boundary condition here under consideration. The surface concentration decreases faster than a constant mass flux boundary condition, i.e. $Bi > 0$. This moderately soluble interface may be assumed to correspond to a Biot number of 1.0. The corresponding Ma_c is estimated from Nield's [13] analysis to be 116.1 with $\tilde{a}_c = 2.246$. A conducting bottom surface seems more appropriate for a semi-infinite fluid. The critical time for a critical Marangoni number of 116 (in the absence of the exact theoretical value) is

$$t_c = \left(\frac{246\mu\sqrt{D}}{\varphi B_m}\right)^{2/3} \qquad (12)$$

or in terms of the concentration difference Δc_s,

$$t_c = \left(\frac{246\mu\sqrt{D}}{\varphi\,\Delta c_s}\right)^2 \qquad (13)$$

which is independent of the depth of the liquid.

2.3. Transient Marangoni number for FSC boundary condition

A gas absorption process is here postulated with constant interfacial concentration which apparently does not allow a change of surface tension when such a change is to be caused by a change in gas concentration. Theoretically (for example from gas penetration analysis) therefore there will be no surface-tension induced convection. In any experiment however the interfacial concentration would not be spatially uniform during gas absorption even if the time average is a constant value everywhere at the interface. However, during gas absorption the increased gas concentration in the liquid phase will usually lead to a drop of surface tension, and hence there is no driving force for convection. Conversely during gas desorption the surface tension at the surface will increase and may cause Marangoni convection as the solute escapes from the liquid.

If it is supposed that a local perturbation does lead to a local imbalance in surface tension, this can cause convection. The transient Marangoni number can be similarly defined as in the case of transient heat conduction,

$$Ma_{\mathrm{t}} = (\phi z^2/\mu\kappa)(\mathrm{d}T/\mathrm{d}z)_{\mathrm{t}} = (\phi(T_0 - T_{\mathrm{s}})z^2/\mu\sqrt{\pi\kappa^3 t})\mathrm{e}^{-\frac{z^2}{4\kappa t}}$$

and is given by

$$Ma_{\mathrm{t}} = \frac{\varphi c^* z^2}{\mu\sqrt{\pi D^3 t}}\mathrm{e}^{-\frac{z^2}{4Dt}} \tag{14}$$

The maximum Marangoni number at any time can be found by differentiating Eq. (14)

$$\left(\frac{\mathrm{d}}{\mathrm{d}z}Ma_{\mathrm{t}}\right)_{\mathrm{t}} = \frac{\varphi c^* z}{\mu\sqrt{\pi D^3 t}}\mathrm{e}^{-\frac{z^2}{4Dt}}\left[2 - \frac{z^2}{2Dt}\right] = 0$$

which gives the position of the maximum value of Ma_{t} as

$$z = 2\sqrt{Dt} \tag{15}$$

which is confined to the top surface layer of the liquid. Therefore, the maximum Marangoni number after time t is

$$Ma_{\max} = \frac{0.8302\varphi(c^* - c_{\mathrm{b}})}{\mu}\sqrt{\frac{t}{D}} \tag{16}$$

from which the time when convection commences, t_{c}, can be calculated if the critical Marangoni number is known.

Nield [13] obtained a large critical Marangoni number of 3304 corresponding to a Bi of 100. The critical time for a critical Marangoni number of 3304 is:

$$t_{\mathrm{c}} = \left(\frac{Ma\mu\sqrt{D}}{0.8302\varphi c^*}\right)^2 = \left(\frac{3980\mu\sqrt{D}}{\varphi c^*}\right)^2 \tag{17}$$

Comparing this with Eq. (5) indicates that this may only occur in a relatively longer time than that predicted for constant mass flux; but again it is well to recall that it is a short time for surface tension to drive a thin layer of liquid into motion. The real problem with using Eq. (17) is that φ has not been measured; our prediction of φ is using the method of Winterfield et al. [19]. It has a sound thermodynamic basis as show in Appendix A.

3. Sizes of convection cells induced by surface-tension convection

It is expected from linear stability theory that the sizes of the small convection cells are determined by the critical Marangoni number and the critical dimensionless wavenumber, which depend on the boundary conditions, the Biot number, the modes and rates of gas diffusion. The wavelengths of the cells can be formulated from those derived by Tan [10] and Tan and Thorpe [11] for thermal convection.

3.1. CMF boundary condition

The onset of Marangoni convection at an interface is predicted by Pearson's [9] critical Marangoni number of 79.6 with a critical dimensionless wavenumber of 1.993 and a critical depth of $1.684\sqrt{Dt_{\mathrm{c}}}$. The wavelength of the hexagonal cell can be expressed as:

$$\lambda_{\mathrm{c}} = \frac{4\pi \times 1.684\sqrt{Dt_{\mathrm{c}}}}{\sqrt{3}\tilde{a}_{\mathrm{c}}} = 6.13\sqrt{Dt_{\mathrm{c}}} \tag{18}$$

which can be rewritten with the critical time substituted by Eq. (5) as:

$$\lambda_{\mathrm{c}} = 6.13\sqrt{D\left(\frac{120\mu D}{\varphi j^\circ}\right)} = 67.17\sqrt{\frac{\mu k D}{\varphi j^\circ}} \tag{19}$$

which shows that the wavelength is dependent upon $\sqrt{j^\circ}$, i.e. the cell size decreases with increasing mass flux. It can also be expressed in terms of the surface-concentration drop as:

$$\lambda_{\mathrm{c}} = 6.13\sqrt{D}\left(\frac{135.6\mu\sqrt{D}}{\varphi\,\Delta c_{\mathrm{s}}}\right) = \frac{831\mu D}{\varphi\,\Delta c_{\mathrm{s}}} \tag{20}$$

3.2. LCR boundary condition

The onset of convection will commence at a critical Marangoni number of 116.1, a critical dimensionless wavenumber of 2.246 and a critical depth of $1.465\sqrt{Dt_{\mathrm{c}}}$. The wavelength of a hexagonal cell can be expressed as:

$$\lambda_{\mathrm{c}} = \frac{4\pi \times 1.465\sqrt{Dt_{\mathrm{c}}}}{\sqrt{3}\tilde{a}_{\mathrm{c}}} = 4.73\sqrt{Dt_{\mathrm{c}}} \tag{21}$$

which can be also be rewritten with the critical time predicted by Eq. (12) as:

$$\lambda_{\mathrm{c}} = 4.73\sqrt{D}\left(\frac{246\mu\sqrt{D}}{\varphi B_{\mathrm{m}}}\right)^{1/3} = 29.63\left(\frac{\mu D^2}{\varphi B_{\mathrm{m}}}\right)^{1/3} \tag{22}$$

which shows that the cell size is proportional to $B_{\mathrm{m}}^{-1/3}$, and it decreases with the increasing rate of mass transport. It can be rewritten in terms of the surface-concentration drop Δc_{s} as:

$$\lambda_{\mathrm{c}} = 4.73\sqrt{D}\left(\frac{246\mu\sqrt{D}}{\varphi\,\Delta c_{\mathrm{s}}}\right) = \frac{1164\mu D}{\varphi\,\Delta c_{\mathrm{s}}} \tag{23}$$

which is independent of the fluid depth, but is dependent upon the concentration driving force and the physical properties of the liquid.

Table 2
Equations for predicting the wavelengths of the Marangoni-convection cells for hexagonal and circular shapes under different boundary conditions

Boundary conditions and equations for λ_c	Hexagon	Circle
CHF, $\lambda_c(Dt_c)^{-1/2}$	6.13	6.48
LCR, $\lambda_c(Dt_c)^{-1/2}$	4.73	5.00
FSC, $\lambda_c(Dt_c)^{-1/2}$	4.88	5.16
CHF, $\lambda_c\left(\frac{\mu D^2}{\varphi j^\circ}\right)^{-1/2}$	67.17	70.96
CHF, $\lambda_c\left(\frac{\mu D}{\varphi\,\Delta c}\right)^{-1}$	831	878
LCR, $\lambda_c\left(\frac{\mu D^2}{\varphi B_m}\right)^{-1/3}$	29.63	31.32
LCR, $\lambda_c\left(\frac{\mu D}{\varphi\,\Delta c}\right)^{-1}$	1164	1230
FSC, $\lambda_c\left(\frac{\mu D}{\varphi\,\Delta c}\right)^{-1}$	16,110	17,030

3.3. FSC boundary condition

It has been noted in Section 2.3 that gas desorption may lead to Marangoni convection with a fixed surface concentration. This will occur at a Biot number of 100 with a Marangoni number of 3304 and a critical wavenumber of 2.976. The wavelength of the hexagonal cell can be predicted from:

$$\lambda_c = \frac{4\pi \times 2\sqrt{Dt_c}}{\sqrt{3}\tilde{a}_c} = 4.88\sqrt{Dt_c} \tag{24}$$

which can also be rewritten with the critical time predicted by Eq. (25) as:

$$\lambda_c = 4.88\sqrt{D}\left(\frac{3304\mu\sqrt{D}}{0.8302\varphi c^*}\right) = \frac{16110\mu D}{\varphi c^*} \tag{25}$$

The sizes of the convection cells are very small (generally less than 1 mm) due to the short critical time, and the shape is generally polygonal or roughly circular. The prediction of cell sizes for the hexagonal and circular shapes at various boundary conditions are summarized in Table 2. The sizes of the circular cells are only 6% bigger than those of the hexagonal ones, which will be difficult to distinguish and measure since they are tiny. However, the tiny convection cells may be very effective in mixing solute into fluid and enhancing mass transfer at the interface.

These equations may be readily transformed for liquid–liquid systems with the partition coefficients replacing the Henry's law constant.

4. Verification of Marangoni convection induced by gas desorption

The correct application of the various equations for the onset of convection is dependent upon the knowledge of the true Biot number and concentration profile of the interface during transient gas diffusion. The Biot number of the system is determined by the diffusion coefficients and Henry's law constant of the gas–liquid phases in contact, which may not be necessarily in equilibrium as shown by the case of highly soluble solute where the Biot number is zero, when extremely small constant flux of solute will diffuse across the interface. The surface concentration will change slowly with time, since the bulk of the highly soluble solute is retained in the liquid. The diffusion is therefore liquid phase-controlled. Such is the experiment conducted by Blair [1], although they wrongly thought the system is one of FSC as the experiment had been initiated with a step-change in pressure. Our calculation of the Henry's law constant for the desorption of ethyl-ether from a solution of chloro-benzene showed that it is small, $H = 7100$ J/kmol, and represents a very soluble system with a Biot number of zero. The Marangoni effect was induced by desorption from a solution pre-saturated with only 10 mol% of ethyl-ether, it is thus expected from the flux equation, $j^\circ = (c_b - c_s)\sqrt{D\pi/4t}$, that the surface concentration will change in very minute amount over the short onset time, notwithstanding the large pressure drop employed in the initiation of the experiments, and there would be no instantaneous equilibrium at the interface. This parallels the case of thermal Marangoni convection induced by evaporative cooling where the surface temperature decreased very slowly as the gas phase is insulating, and therefore the interface is characterized by $Bi = 0$. This has been resolved by Tan and Thorpe [12] successfully with a zero Biot number boundary condition and a critical Marangoni number of 80 for experiments of Vidal and Acrivos [20], who obtained critical Marangoni number between 280 and 820, and experiments performed in Apollo 17 mission, Grodzka and Bannister [21] that recorded very large Marangoni numbers of 400 and 1320 corresponding to very large Biot number or conducting boundaries.

It is no surprise that Blair's [1] plot of critical times versus the initial pressure change yielded a slope of −1.8, which is less than −2 for a FSC boundary condition as indicated by Eq. (16); the correct plot according to Eq. (3) would be for critical times versus actual surface-concentration change at the onset of convection. It is thus expected for Davenport and King [2] to obtain very large Marangoni number of 3310 using the large initial step-change in pressure in their calculations, which have been masked by the small Henry's law constant, H', used by them.

Blair [1] did not measure the surface concentration as it would be very difficult to do so with any instrument, however, we can make an order-of-magnitude estimation by assuming a very small change in the surface concentration, such as a 0.1% change in the initial step-pressure change. This will also give a 0.1% change in the surface concentration, which in Blair's [1] experiments were between 33×10^{-6} and 130×10^{-6} kmol/m^3. The constant mass fluxes for the stable diffusion period are found to be in 10^{-9} kmol/m^{2}s (Table 3), which seem reasonable when compared to the desorption rate of 1.17×10^{-8} kmol/m^{2}s for sparingly soluble ether (0.009 wt.%) from water ($Bi_D \sim 11$) in a wetted-wall column (with a contact time of 0.1 s) measured by Brian et al. [3]. The average critical Marangoni number for an assumed interfacial pressure change equal to 0.1% of the initial step-change in pressure calculated from Eq. (3) is 53.3, which is fairly close to the theoretical value in 67 for a deformable surface Pēres-Garcia and Carneiro [22], Fig. 1 and Table 3. The critical Marangoni numbers can also be calculated with Eq. (2) by using the mass flux predicted from the change of surface concentration and critical times. It is interesting to note that the resultant force as represented by the numerator of the Marangoni number is very small for the surface pressure change of 7.58×10^{-5} atm, it is only $0.587\varphi H'\Delta p\sqrt{Dt_c} = 7.88 \times 10^{-11}$ N, compared to the more certain value of the denominator of $\mu D = 1.41 \times 10^{-12}$ N. The critical times may also likewise be predicted by a critical Marangoni number of 67 with fair accuracy as shown in Table 3. The prediction of the Marangoni number may be improved if the masss flux or the change in surface concentration can be measured accurately.

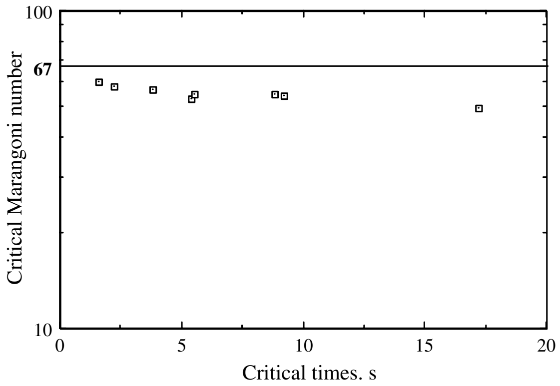

Fig. 1. Critical Marangoni numbers predicted by Eq. (3) for the desorption of ethyl-ether from chloro-benzene by assuming 0.1% change of Δp at the interface.

The prediction may also have to take account of the ensuing evaporative cooling that may cause and enhance the surface-tension convection. Our study of thermal Marangoni convection has shown that a very small change in surface temperature change of 0.1 °C is sufficient to induce Marangoni convection within a few seconds, and the mass loss due to evaporation provided a heat loss approximately equal to that due to convective heat transfer in the air layer. Blair's [1] experiments for a initial pressure change of 0.0233 atm to 0.0914 atm may cause a drop in surface temperature of probably more than 0.1 °C, which may be sufficient to induce the onset of convection. More important there may exist a synergistic effect of thermal and mass diffusion, thus causing the onset of convection to occur in advance of either cause of convection. Nevertheless the onset of convection will still begin at the critical Marangoni number of about 67 induced by a more rapid increase of surface tension. It is therefore necessary to build a theory based on simultaneous heat and mass diffusion in order to predict the onset of Marangoni convection successfully. The analysis of combined effect of thermal and mass diffusion of Skurygin and Dil'man [5] should be tested by comprehensive experiments.

5. The sizes of Marangoni convection cells

The sizes of the Marangoni convection cells predicted from Eq. (18) for the short range of critical times of 1.6 s to 17.1 s measured in Blair's [1] experiments are only

Table 3
Prediction of the critical times and Marangoni numbers for the onset of surface tension driven convection

Initial Δp atm	Critical time t_c (s)		$j^\circ \times 10^9$ (kmol/m^{2}s)	Predicted Ma_c
	Experimental	Predicted		
0.0233	17.2	31.2	0.22	48.2
0.0346	9.2	14.1	0.44	52.3
0.0358	8.8	13.2	0.47	53.0
0.0442	5.4	8.7	0.74	51.2
0.0454	5.5	8.2	0.75	53.1
0.0567	3.8	5.3	1.12	55.1
0.0758	2.2	2.9	1.97	56.1
0.0914	1.6	2.0	2.29	57.7
			Average	53.3

Note: t_c is predicted with $Ma_c = 67$. Our estimated $\varphi = -1.93 \times 10^{-3}$ N m^2/kmol and $H' = 14.2$ kmol/m^3 atm, while $\rho_o = 1106.6$ kg/m^3, $\mu = 7.4 \times 10^{-4}$ Pa s and $D = 1.9 \times 10^{-9}$ m^2/s are from Davenport and King [2].

Table 4
Prediction of the critical wavelengths

Initial Δp (atm)	Experimental t_c (s)	Predicted λ_c (mm)
0.0233	17.2	1.11
0.0346	9.2	0.81
0.0358	8.8	0.79
0.0442	5.4	0.62
0.0454	5.5	0.63
0.0567	3.8	0.52
0.0758	2.2	0.40
0.0914	1.6	0.33

between 0.3 and 1.10 mm respectively, Table 4. These will be difficult to observe in any experiment as gas desorption is a very rapid transient process. This will require a very sensitive visual technique to monitor the growing convection cell in a brief moment. Unlike the larger convection cells observed in transient evaporative cooling of organic liquids [23], ranging from 1.7 to 8.5 mm, there has been no known measurement and photograph of the Marangoni cells for gas diffusion being reported. Pearl-like convection cells of about 2 mm photographed by Okhotsimskii and Hozawa [8] for the evaporation of ethyl acetate from toluene in the presence of flowing nitrogen are rather large, and are primarily induced by cooling. It will be a major challenge to design a visualisation technique to record the rapid development of the tiny Marangoni convection cells.

6. Mass transfer coefficient at the onset of Marangoni convection

The liquid-phase mass transfer coefficient, k_L, can be estimated from a Sherwood number defined as $Sh = (D/\delta_e)/(D/z_c) = z_c/\delta_e$, which for CMF boundary is $Sh = 1.684/0.587 = 2.87$, i.e. $k_L = 2.87\sqrt{D\pi/4t_c} = 2.54\sqrt{D/t_c}$. Hence, the rate of mass transfer at convection is about 2.9 times that of the diffusion rate, which is comparable to the enhancement factor of 3.6 reported by Brian et al. [3] in Marangoni convection-driven desorption. The large enhancement of mass transfer is expected as the liquid may travel at rather high velocity near the gas–liquid interface. However, this may be confined to the thin layer near the interface of few cell sizes, i.e. few mm thick. Therefore, Marangoni convection is very effective in thin film processes, such as the drying of wafer using alcohol, O'Brien [4].

7. Conclusions

The onset of Marangoni convection caused by gas desorption in liquid is analogous to thermal convection induced by transient heat conduction. It can be predicted by newly defined transient Marangoni numbers corresponding to CMF, LCR and FSC boundary conditions, which are characterized by their respective diffusive Biot numbers. The transient Marangoni numbers incorporate the mode and rate of diffusion that strongly depends on the interfacial vapour–liquid equilibrium. The critical times and the sizes of convection cells have also been formulated to allow the prediction of Marangoni convection.

The estimated value of Henry's law constant of ethyl-ether-chloro-benzene system, H, was very low, thus indicating a very soluble system with a Biot number = 0. hence, the desorption of ethyl-ether from chloro-benzene in Blair's [1] experiments is liquid phase-controlled. The average critical Marangoni number was estimated to be 53.3, which is fairly close to the theoretical value of 67 for a flexible interface with a Biot number of 0. Therefore, the high value of 3100 calculated by Davenport and King [2] is wrong, who mistook the experiments that have been initiated by a step-change in pressure as a fixed surface-concentration boundary, that is applicable only to a sparingly soluble solute.

The sizes of the convection cells were predicted to be very small, between 0.3 and 1.1 mm for the brief onset times of 1.6–17.2 s. Their smallness and rapidly evolving structure may pose great difficulties in measuring them in a gas desorption experiment.

The synergistic effect of thermal and mass diffusion in causing the onset of convection must be accounted for in order to provide a more successful theory of Marangoni convection.

Acknowledgment

The author is grateful to Professor Rex Thorpe for his critical comments and the estimation of the Henry's law constant and concentration surface-tension coefficient.

Appendix A

A.1. Prediction of Henry's law constant

At low to moderate pressures and at temperatures below the critical temperature, where the vapour phase can be assumed ideal and the molar volume of the gas is much less than that of the liquid, simple thermodynamic considerations yields the partial pressure of component 1,

$$p_1 = \gamma_1 x_1 p_1^{\mathrm{sat}}$$

or

$$p_1/c_1 = H = \gamma_1 p_1^{\mathrm{sat}}/\rho_{\mathrm{m}}$$

Provided the other component(s) do(es) not cause the activity coefficient to deviate significantly from its ideal values of 1, the Henry's law constant is the same irrespective of the other component involved. This is good approximation for mixtures of simple hydrocarbons. However for gas and molecules with hydrocarbon character in water it is a poor assumption to make.

The activity coefficient for ethyl-ether in chloro-benzene is close to the ideal value of unity. Both are mostly hydrocarbon in nature with some polarity due to oxygen and chlorine atoms respectively. therefore the nature and strength of their van der Walls intermolecular bonding will be similar and little disruption will be caused on mixing the two molecules. Unfortunately there are no VLE or Henry's law data in the literature for the system ethyl-ether and choro-benzene. we are therefore forced to estimate the Henry's law constant for this system.

Gmehling et al. [24] calculated from the data of Schmidt [25] that for the very similar system of ethyl-ether in benzene, the activity coefficient of ethyl-ether at infinite dilution is 1.03 at both 0 and 20 °C. Thus it seems likely that the activity coefficient for ethyl-ether in chloro-benzene is close to 1, whereas a value of 80 for ethyl-ether in water has been assumed to obtain the value of H (=845,000 J/kmol) by Davenport and King [2], this is significantly in error. As we demonstrate in the main text, this error is sufficient to explain the values obtained by Davenport and King [2] for the critical Marangoni number of 3100, which is anomalously large. A change in H also changes the value of the Biot number, as it is found to be close to zero.

Using an activity coefficient of unity and the experimental vapour pressure of Signer et al. [26] gives a Henry's law constant at 25 °C of

$$H = \gamma_1 p_1^{\text{sat}}/\rho_{\text{m}} = 1 \times 7.05 \times 10^4/9.97 = 7100\,\text{J/kmol}$$

Unsurprisingly this is two orders of magnitude less than the value for ethyl-ether in water. We estimate that the accuracy of this value is ±20%. At 20 °C, based on the data of Schmidt [25] for vapour pressure, H is 5734 J/kmol.

A.2. Prediction of coefficient for concentration variation of surface tension, φ

The method recommended by Perry and Green [27] for the prediction of the surface tension of mixtures not involving water is the method of Winterfield et al. [19]. It has a sound thermodynamic basis whilst also using the experimental values of the surface tension of the two pure components, and it can predict the surface tension of binary mixtures of organic liquids within 2×10^{-5} N/m.

For a binary mixture of components 1 and 2, Winterfield et al. [19] suggest

$$\rho^\circ = \left(\frac{x_1}{\rho_1^{\text{o}}} + \frac{1-x_1}{\rho_2^{\text{o}}}\right)^{-1}$$

$$\sigma = \rho^{\text{o}2}\left(\frac{x_1^2\sigma_1}{\rho_1^{\text{o}2}} + \frac{2x_1(1-x_1)}{\rho_1^{\text{o}}\rho_2^{\text{o}}}\sqrt{\sigma_1\sigma_2} + \frac{(1-x_1)^2\sigma_2}{\rho_2^{\text{o}2}}\right)$$

where ρ° is the molar density, σ is the surface tension and x is the mole fraction.

With the known values of surface tension of diethyl-ether and chloro-benzene of 0.01701 and 0.03356 N/m respectively, we calculated a value of φ from two molar concentrations of 0.09 and 0.11 to be $-0.00193\,\text{N}\,\text{m}^2$/kmol, which is close to the value of $-0.00168\,\text{N}\,\text{m}^2$/kmol obtained from linear interpolation between the two experimental values of surface tension of the pure components as used by Davenport and King [2]. Our predicted value is 15% larger and takes account the almost universally observed non-linearity of surface tension with concentration in a binary mixture. It is likely to be accurate to ±5%.

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