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Marangoni instability in binary liquid–liquid systems

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Abstract

The onset of Marangoni instabilities in binary partially miscible liquid–liquid systems was first explained by Perez de Ortiz and Sawistowski who formulated and solved the linear stability problem for these systems. In the present paper, the same linear stability problem is investigated but the solution is obtained in a way that leads to the presentation of the characteristic equation in a new analytical form, which can be analysed easily. The stability criterion obtained for stationary instability is the same as the one by Perez de Ortiz and Sawistowski but has been found to differ for the onset of oscillatory instabilities. Another important finding of the present work is that stationary and oscillatory instabilities cannot exist simultaneously. The stability criteria developed have been applied to six binary systems and comparisons of the results obtained are made against experimental observations available in the literature.

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1. Introduction

Marangoni convection is often observed during the transfer of a solute across an interface between two immiscible liquids, i.e. in ternary systems [1–7]. It is many times known as *solutal* Marangoni convection, and its appearance is due to variations in interfacial tension caused by local changes in solute concentrations along the interface.

Mass transfer in partially miscible liquid–liquid systems may also be accompanied by Marangoni convection [8–11]. According to the phase rule there are no degrees of freedom at the interface of a binary partially miscible liquid–liquid systems under isothermal conditions. This means that concentration gradients do not exist at the interface and therefore the interfacial tension is independent of concentration. However, temperature gradients produced by the heat of solution give the necessary degree of freedom for interfacial tension gradients to exist and *thermal* Marangoni convection may occur.

The theory of thermal and solutal Marangoni convection in ternary systems has been extensively developed since the 1950s when two seminal papers were published. In the first paper, Pearson [12] studied thermal Marangoni instability of a horizontal liquid layer placed on a hot rigid wall, with a free surface to the ambient gas phase. In the second one, Sternling and Scriven [13] considered a system of two semi-infinite immiscible liquids with a solute transferring across a planar interface. Both papers stressed the role of the interfacial tension gradient, induced either by temperature [12] or solute concentration [13] gradients along the interface, in promoting Marangoni instability and stability criteria were obtained. In the case of Pearson's work, a non-dimensional physical parameter (later named Marangoni number) was introduced and it was shown that instabilities would occur when the magnitude of this number exceeded a critical value.

The stability analysis of solutal Marangoni convection has been extended by many researchers to more complete physico-chemical models of ternary systems for both the linear and the non-linear cases [14]. For example, for the linear stability of semi-infinite layers, Hennenberg et al. [15–17] improved the physical model of bulk-diffusion controlled transfer of a surfactant across the liquid interfaces by including the adsorption–desorption mechanism at the interface with possible solute accumulation; Chu and Velarde [18] applied their model considering

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not only longitudinal, but also transversal modes of oscillation; Nakache and coworkers [19] proposed semi-empirical criteria for transfer of surface-active solutes in ternary systems and studied the solutal Marangoni effect in liquid–liquid extraction [20–23].

In the early 1970s Sternling and Scriven's linear stability approach [13] was applied to the case of partially miscible liquid–liquid systems by Perez de Ortiz and Sawistowski [24,25]. They derived stability criteria, which they compared against experimental observations for six binary systems [9]. Satisfactory agreement between the experimental and theoretical results was achieved for some systems only.

Recently, Mendes-Tatsis and Agble [26–28] studied the effect of surfactants on Marangoni convection in binary partially miscible liquid–liquid systems. They proposed a semi-empirical Marangoni coefficient [28], to predict the occurrence of Marangoni convection in the presence of a surfactant, which was based on their experimental results obtained with five binary systems and six surfactants.

Despite the theoretical and experimental studies of several research groups, the onset of Marangoni instability in binary liquid–liquid systems with or without added surfactants cannot yet be satisfactorily predicted. The ultimate aim of the continuing work by the authors in the topic is to obtain stability criteria for Marangoni convection in binary liquid–liquid systems with added surfactants. In this paper, however, the authors have started with the simpler system, i.e. binary system without surfactants. In Section 2 the linear stability problem is formulated and its solution is given in Section 3. The same method of solution has been recently applied by one of the authors to study Marangoni instability in ternary systems [29]. The characteristic equation is derived in an analytical form that allows explicit conclusions to be drawn. In Section 4 the stability analysis is performed for stationary and oscillatory instabilities. The application of the stability criteria developed is included in Section 5 where the results obtained are compared with results published in the literature as well as with experimental observations [8,11,26,32]. Conclusions are taken in Section 6.

2. Formulation of the problem

Consider a system of two semi-infinite, partially miscible liquids at room temperature, which are contacted along a plane interface of infinite extent (Fig. 1). In the general case, mass transfer occurs in both directions by molecular diffusion and the two liquids eventually dissolve in each other. However, when one of the liquids is pre-saturated with the other, mass transfer occurs in one direction only. In the present work, the transfer is in one direction only, from phase 1 to phase 2, i.e. phase 1 is pre-saturated with phase 2. Since mass transfer by diffusion is slow, there is a very thin mixing zone between the two liquids for a long time, which may be modelled as a geometrical two-dimensional Newtonian surface.

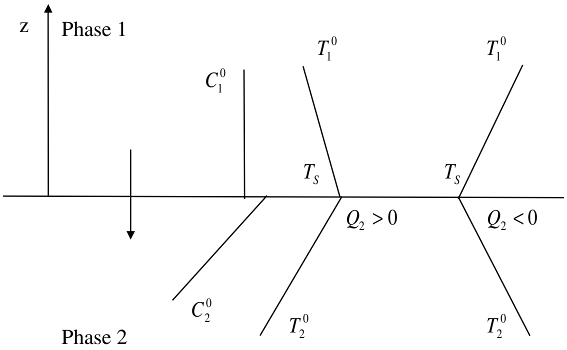

Fig. 1. Sketch of a liquid–liquid binary system at steady state.

The dissolution of the liquids may be accompanied by release or absorption of heat at the interface, leading to an increase or decrease in the interfacial temperature. In the case of heat release, the heat will transfer into both phases, whilst in the case of heat absorption the heat fluxes will be directed from the bulk of each phase to the interface. The mean interfacial tension σ_0 of the binary liquid–liquid system is taken to be large enough to prevent interfacial deformation. The interfacial tension is assumed to depend on the interfacial temperature T_s by the following expression:

$$\sigma = \sigma_0 - \gamma(T_s - T_0), \tag{1}$$

where $\gamma = \left(-\frac{\partial\sigma}{\partial T}\right)_0$ is defined as the interfacial tension coefficient and T_0 is the reference temperature. The quantity $(-\gamma)$ is the rate of change of the interfacial tension with temperature. The coefficient γ is positive for binary systems with a temperature-lowering interfacial tension (e.g. ethylacetate–water) and negative for temperature-increasing interfacial tension systems (e.g. isobutanol–water).

Cartesian coordinates are introduced with the (x, y) plane considered coincident with the liquid–liquid interface and a vertical coordinate z directed from phase 2 (negative z) towards phase 1 (positive z), i.e. in the opposite direction of mass transfer indicated by the arrow in Fig. 1.

In the reference steady state, the fluids are at rest and the concentration and temperature profiles in the phases are assumed to be linear functions of z, namely

$$\begin{aligned} &C_1^0 = C_{1s}, \qquad T_1^0 = T_s + \beta_1^T z \quad (z > 0), \\ &C_2^0 = C_{2s} + \beta_2^C z, \qquad T_2^0 = T_s + \beta_2^T z \quad (z < 0), \end{aligned} \tag{2}$$

where C_1 is the molar concentration of phase 2 in phase 1, C_2 is the molar concentration of phase 1 in phase 2, superscript “0” indicates the reference state, subscript “s” designates the interface and β_2^C and β_i^T $(i = 1, 2)$ are concentration and temperature gradients which are constant in the phases indicated. The concentrations at the interface are assumed to be equilibrium concentrations at the following interfacial temperature:

$$T_s = \frac{C_{is}}{R_i} \quad (i = 1, 2), \tag{3}$$

where R_i are assumed constants, since the temperature variations at the interface are small. For mass transfer from phase 1 to phase 2 the concentration gradient is positive, i.e. $\beta_2^C > 0$. This quantity and the temperature gradients β_i^T are not independent because the concentration and temperature distributions, given in Eq. (2), should satisfy the heat balance equation at the interface given by

$$-k_2\frac{\partial T_2}{\partial z} + Q_2 D_2 \frac{\partial C_2}{\partial z} = -k_1\frac{\partial T_1}{\partial z} + Q_1 D_1\frac{\partial C_1}{\partial z}, \tag{4}$$

where k_i is the thermal conductivity of phase i, D_1 is the diffusivity of phase 2 in phase 1, Q_1 is the heat of solution of phase 2 in phase 1 per mole of phase 2, and D_2 and Q_2 are the corresponding diffusivity and heat of solution of phase 1 in phase 2.

From Eqs. (2) and (4) the following equation is obtained:

$$Q_2 D_2 \beta_2^C = k_2\beta_2^T - k_1\beta_1^T. \tag{5}$$

The temperature gradients β_1^T and β_2^T always have opposite signs (see Fig. 1). When heat is released at the interface $(Q_2 > 0)$, $\beta_1^T < 0$ and $\beta_2^T > 0$, while in the case of heat absorption $(Q_2 < 0)$, $\beta_1^T > 0$ and $\beta_2^T < 0$.

In the linear stability study, disturbances are defined for the different variables: velocities $\mathbf{v}_i(u_i, v_i, w_i)$, pressures p_i, concentrations C_i and temperatures T_i $(i = 1, 2)$, and they satisfy the linearized equations of continuity, momentum, mass and heat balances

$$\nabla\cdot\mathbf{v}_i = 0, \qquad \rho_i\frac{\partial\mathbf{v}_i}{\partial t} = -\nabla p_i + \mu_i\nabla^2\mathbf{v}_i, \tag{6a}$$

$$\frac{\partial C_1}{\partial t} = D_1\nabla^2 C_1, \qquad \frac{\partial C_2}{\partial t} = -\beta_2^C w_2 + D_2\nabla^2 C_2, \tag{6b}$$

$$\frac{\partial T_i}{\partial t} = -\beta_i^T w_i + \kappa_i\nabla^2 T_i, \tag{6c}$$

where t is time, ρ_i the fluid density, μ_i the dynamic viscosity (the kinematic viscosity is defined by $\nu_i = \mu_i/\rho_i$), κ_i the thermal diffusivity and ∇^2 the three-dimensional Laplacian operator. This analysis neglects density effects.

The dynamic boundary conditions at the interface $(z = 0)$ expressing the no-slip condition, the non-deformability of the surface and the tangential balances between the bulk viscous stresses and the interface shear stresses, are

$$\begin{aligned}
&u_1 = u_2, \qquad v_1 = v_2, \qquad w_1 = w_2 = 0,\\
&\mu_2\left(\frac{\partial w_2}{\partial x} + \frac{\partial u_2}{\partial z}\right) - \mu_1\left(\frac{\partial w_1}{\partial x} + \frac{\partial u_1}{\partial z}\right) = \frac{\partial\sigma}{\partial x},\\
&\mu_2\left(\frac{\partial w_2}{\partial y} + \frac{\partial v_2}{\partial z}\right) - \mu_1\left(\frac{\partial w_1}{\partial y} + \frac{\partial v_1}{\partial z}\right) = \frac{\partial\sigma}{\partial y}.
\end{aligned} \tag{7}$$

At the interface the concentrations and phase temperatures satisfy Eqs. (3) and (4), and the interfacial temperature has the same value for both phases.

All disturbances, in both phases, are to vanish at large distances from the interface:

$$\begin{aligned}
&\mathbf{v}_1, C_1, T_1 \to 0 \quad \text{as } z \to \infty,\\
&\mathbf{v}_2, C_2, T_2 \to 0 \quad \text{as } z \to -\infty.
\end{aligned} \tag{8}$$

It is convenient to express the variables in dimensionless form. As there is no any characteristic length in the problem under consideration, an arbitrary length scale l is defined that will disappear in the final results. The physical parameters of phase 2 are used to introduce the quantities l^2/ν_2, ν_2/l, $\rho_2\nu_2^2/l^2$ and $\beta_2^C l$ for scales of time, velocity, pressure and concentration, respectively. The quantity $\beta_0 = \beta_2^C Q_2 D_2/k_2$ is chosen as a temperature gradient scale (see Eq. (5)), instead of β_2^T which is difficult to measure experimentally.

Keeping the same notation for the dimensionless variables, Eqs. (6) are re-written in the form

$$\begin{aligned}
&\frac{\partial w_1}{\partial t} = \frac{1}{e^2}\nabla^2 w_1, \qquad \frac{\partial w_2}{\partial t} = \nabla^2 w_2,\\
&\frac{\partial C_1}{\partial t} = \frac{1}{r^2 Pr_2 Le_2}\nabla^2 C_1, \qquad \frac{\partial C_2}{\partial t} = -w_2 + \frac{1}{Pr_2 Le_2}\nabla^2 C_2,\\
&\frac{\partial T_1}{\partial t} = \frac{\beta}{1+k\beta}w_1 + \frac{1}{h^2 Pr_2}\nabla^2 T_1,\\
&\frac{\partial T_2}{\partial t} = -\frac{1}{1+k\beta}w_2 + \frac{1}{Pr_2}\nabla^2 T_2,
\end{aligned} \tag{9}$$

where the following ratios have been introduced:

$$\begin{aligned}
&e^2 = \frac{\nu_2}{\nu_1}, \qquad r^2 = \frac{D_2}{D_1}, \qquad h^2 = \frac{\kappa_2}{\kappa_1},\\
&k = \frac{k_1}{k_2}, \qquad \beta = -\frac{\beta_1^T}{\beta_2^T} > 0,
\end{aligned} \tag{10}$$

and $Pr_2 = \frac{\nu_2}{\kappa_2}$ and $Le_2 = \frac{\kappa_2}{D_2}$ are the Prandtl and Lewis numbers for phase 2. The first to use the variables e^2 and h^2 were Sternling and Scriven [13] and r^2 was first defined by Perez de Ortiz and Sawistowski [24].

Introducing the dimensionless quantities defined above into Eqs. (3), (4) and (7) and using the continuity equation (6a), the following set of boundary conditions at the interface is obtained:

$$
\begin{aligned}
&w_1 = w_2 = 0, \qquad \frac{\partial w_1}{\partial z} = \frac{\partial w_2}{\partial z},\\
&\mu\left(\nabla_s^2 - \frac{\partial^2}{\partial z^2}\right)w_1 - \left(\nabla_s^2 - \frac{\partial^2}{\partial z^2}\right)w_2 = \frac{Ma}{Pr_2}\nabla_s^2 T_2,\\
&T_1 = T_2, \qquad -\frac{\partial T_2}{\partial z} + \frac{\partial C_2}{\partial z} = -k\frac{\partial T_1}{\partial z} + \frac{Q}{r^2}\frac{\partial C_1}{\partial z},\\
&C_1 = \frac{kr^2}{Q}\widetilde{R}_1 T_1, \qquad C_2 = \widetilde{R}_2 T_2,
\end{aligned}
\tag{11}
$$

where

$$
Q = \frac{Q_1}{Q_2}, \qquad \mu = \frac{\mu_1}{\mu_2}, \qquad \widetilde{R}_i = \frac{R_i Q_i D_i}{k_i}
\tag{12}
$$

and

$$
Ma = \frac{\gamma \beta_0 l^2}{\mu_2 \kappa_2} = \frac{\gamma Q_2 D_2 \beta_2^C l^2}{\mu_2 \kappa_2 k_2}
\tag{13}
$$

is the Marangoni number. In Eq. (11) the expression that contains the two-dimensional Laplacian operator ∇_s^2, is obtained by taking the surface divergence from the tangential force balances (7) and using Eq. (1).

The sign of the Marangoni number is the same as that of the product γQ_2 because all the other quantities in Eq. (13) are positive. For binary systems with a *temperature lowering* interfacial tension (positive γ) the Marangoni number assumes *positive* values when the heat of solution is liberated at the interface ($Q_2 > 0$) and *negative* ones in the case of heat absorption ($Q_2 < 0$). The Marangoni number has the opposite signs for systems with a *temperature increasing* interfacial tension (negative γ).

3. Solution of the problem

The solution of the system of linear equations (9) is searched in normal modes, so any function is represented in the form

$$
f = f_0(z)\exp\lfloor \omega t + \mathrm{i}(a_x x + a_y y)\rfloor,
\tag{14}
$$

where $f_0(z)$ is the disturbance amplitude, ω the complex growth constant and $a = \sqrt{a_x^2 + a_y^2}$ is the wavenumber. The oscillatory instability (overstability) will be studied defining $\omega = \mathrm{i}\varpi$, where the positive quantity ϖ is the wave frequency. The case when $\omega = 0$ corresponds to stationary instability. The solution must satisfy the boundary conditions given in (11) at $z = 0$ and Eq. (8) for large distances from the interface.

After solving the stability problem by a standard method [30], the characteristic equation is derived and is found to be given by the Marangoni number expressed as follows:

$$
\begin{aligned}
&\frac{Ma}{a^2} = \frac{P_2}{P_1},\\
&P_1 = \frac{Le_2}{(1+p_1)(q_1+p_1)} - \frac{1}{1+k\beta}\left[\frac{1}{(1+q_3)(q_1+q_3)}\right.\\
&\qquad\left. + \frac{k\beta h^2}{(1+q_4)(q_2+q_4)}\right],\\
&P_2 = [1 + q_1 + \mu(1+q_2)][q_3 - \widetilde{R}_2 p_1 + k(q_4 - \widetilde{R}_1 p_2)],\\
&q_1 = \sqrt{1+\xi}, \qquad q_2 = \sqrt{1+e^2\xi},\\
&q_3 = \sqrt{1+Pr_2\xi}, \qquad q_4 = \sqrt{1+h^2 Pr_2\xi},\\
&p_1 = \sqrt{1+Le_2 Pr_2\xi}, \qquad p_2 = \sqrt{1+r^2 Le_2 Pr_2\xi},
\end{aligned}
\tag{15}
$$

where $\xi = \omega/a^2$ is a new independent variable. Note that the ratio $\frac{Ma}{a^2}$ defined above is a complex function of this new variable only.

4. Stability analysis

4.1. Stationary instability

In the case of stationary instability, the characteristic equation has a very simple form

$$
\frac{Ma_{\mathrm{st}}}{a^2} = \frac{8(1+\mu)\lfloor 1 - \widetilde{R}_2 + k(1 - \widetilde{R}_1)\rfloor}{Le_2 - \dfrac{1+k\beta h^2}{1+k\beta}}.
\tag{16}
$$

The RHS of Eq. (16) is independent of the length scale and only depends on the ratios of the physical parameters of both phases and thus, it does not depend on the arbitrary length scale that also disappears on the LHS. The stationary Marangoni number Ma_{st} assumes only positive values because $Le_2 \gg 1$ and $|\widetilde{R}_i| \ll 1$ for most liquids. So, the stationary stability problem has a solution for *positive* Marangoni numbers. This means that binary systems will be stable when $\gamma Q_2 < 0$ and unstable when $\gamma Q_2 > 0$. Hence, *stationary instabilities* can occur when the heat of solution and the interfacial tension coefficient have the same sign, i.e. when the heat of solution and the rate of change of the interfacial tension with temperature are of different signs, which is in agreement with the predictions by Perez de Ortiz and Sawistowski [24].

4.2. Oscillatory instability

In the case of oscillatory instability ($\omega = \mathrm{i}\varpi$), the Marangoni number is a complex function of the pure imaginary variable $\xi = \mathrm{i}s$ where $s = \varpi/a^2 > 0$. Following Sternling and Scriven's stability analysis [13], one can study the behaviour of the inverse Marangoni number

$$a^2/Ma = \frac{P_1}{P_2} \equiv F(\mathrm{i}s) = F_1(s) + \mathrm{i}F_2(s), \tag{17}$$

where F_1 and F_2 are real functions of *one* variable s. Non-zero real solutions of Eq. (9) with boundary conditions (8) and (11) will exist for values of the independent variable satisfying $F_2(s) = 0$. If s_0 is a root of this last equation, the Marangoni number is given by

$$Ma = \frac{a^2}{F_1(s_0)} \tag{18}$$

for any pair of the wavenumber a and the frequency ϖ related by the equation $\varpi = s_0 a^2$. Thus, without loss of generality one can assume $a = 1$.

An explicit analysis of the inverse Marangoni number expressed in Eq. (17) is not easy because $P_1 = P_1(\mathrm{i}s)$ and $P_2 = P_2(\mathrm{i}s)$ contain combinations of square roots which introduce, together with the independent variable, a certain number of dimensionless physical parameters of the liquids. Therefore, functions $F_1(s)$ and $F_2(s)$ have been calculated and plotted for the binary systems considered in [9] and this is shown in the next section. The asymptotic behaviour of the same functions at very large s has been studied analytically.

In general, functions $F_1(s)$ and $F_2(s)$ vary quickly for very small s and slowly for large s, and vanish as the independent variable goes to infinity. Equation $F_1(s) = 0$ has only one root (denoted by s_1) and the function is positive for $0 < s < s_1$ and negative for $s_1 < s < \infty$. Function $F_2(s)$ is equal to zero at $s = 0$ and may have another root (s_2) in some cases. When the second zero exists, $F_2(s)$ is negative for $0 < s < s_2$ and positive for $s_2 < s < \infty$ approaching the abscissa from above at very large s. As a rule, $s_1 < s_2$ and the searched real solution of the characteristic equation $F_1(s_2) < 0$. Then, if for a given binary system and direction of transfer the Marangoni number (Eq. (13)) is negative, the quantity $F_1(s_2)$ represents the value of the inverse Marangoni number (for $a = 1$). When $F_1(s_2)$ and the Marangoni number have different signs, the mathematical solution obtained is not a solution of the physical problem and hence, oscillatory instabilities will not set in. But, at the same time the positive quantity $F_1(0)$ will be the reciprocal value of the Marangoni number Ma_{st} for stationary instability.

If function $F_2(s)$ does not cross the abscissa, it remains negative for any finite value of the independent variable. Then, the characteristic equation (15) has no real solution and oscillatory instabilities are not expected to appear.

4.3. Stability analysis conclusions

It can be concluded that stationary instabilities occur for positive Marangoni numbers, while oscillatory ones may develop for negative ones, i.e. both instabilities cannot exist simultaneously. As it will be shown below, the appearance of oscillatory instabilities depends on the sign of a function of the physical parameters of the system, expressed by the viscosity ratios, e^2 and μ, thermal conductivity ratio k, thermal diffusivity ratio h^2, and the Lewis and Prandtl numbers.

5. Numerical analysis

The stability criteria were applied to the binary liquid–liquid systems considered in [9] and results are shown in Table 1. Perez de Ortiz and Sawistowski's predictions [9,31] and experimental observations available in the literature are also presented there [8,11, 26,32]. However, the results for the experimental cases

Table 1
Stability predictions for selected binary systems

Liquid A	Liquid B	Direction of transfer	Predicted stationary instability [this work]	Predicted stationary instability [9]	Predicted oscillatory instability [this work]	Predicted oscillatory instability [9]	Experimental observations
Ethylacetate	Water	A → B	Unstable	Unstable	Stable	Stable	Unstable [8]
		B → A	Stable	Stable	Unstable	Unstable	Unstable [8]
Acetylacetone	Water	A → B	Stable	Stable	Unstable	Unstable	Unstable [8,11]
		B → A	Stable	Stable	Unstable	Stable	Stable [8,11]
Isobutanol	Water	A → B	Stable	Stable	Stable	Unstable	Stable [8] Unstable [26,32]
		B → A	Unstable	Unstable	Stable	Stable	Stable [8]
MEK	Water	A → B	Stable	Stable	Unstable	Stable	Stable [8]
		B → A	Unstable	Unstable	Stable	Unstable	–
Cyclohexanol	Water	A → B	Unstable	Unstable	Stable	Unstable	Unstable [8]
		B → A	Stable	Stable	Stable	Stable	Unstable [8]
Hexane	Aniline	A → B	Stable	Stable	Stable	Stable	Unstable [8]
		B → A	Stable	Stable	Unstable	Unstable	Unstable [8]

are described only in terms of the general stability observed, since it is very difficult to distinguish between stationary and oscillatory instabilities.

The stability criterion for stationary instability given by Eq. (16) was used and the results obtained show that they are in agreement with Perez de Ortiz and Sawistowski's predictions (see Table 1).

Before discussing the results for the oscillatory instability case, a method for analysing the instability conditions is presented studying numerically the behaviour of functions $F_1(s)$ and $F_2(s)$ in Eq. (17) for two binary systems: ethylacetate–water and isobutanol–water.

5.1. Ethylacetate–water

5.1.1. Transfer of ethylacetate into water

Consider first the transfer of ethylacetate (phase 1) into water (phase 2). In this case the heat of solution is liberated at the interface ($Q_2 = 12810$ kJ/kmol) [9]. For the interfacial tension coefficient $\gamma = 0.03 \times 10^{-3}$ N/m K, only positive values of the Marangoni number are physically possible. The function $F_1(s)$ plotted in Figs. 2 and 3, has a value of 11.185 at $s = 0$ (not shown in Fig. 2) that defines the value $Ma_{st} = 0.089$ for stationary instability (at $a = 1$). The function crosses the abscissa at $s_1 = 0.037$ and remains negative for larger values of the independent variable (Fig. 3). Function $F_2(s)$ has one root $s_2 = 29.0$ (Fig. 4), but the negative value $F_1(s_2)$ does not correspond to a positive Marangoni number. Therefore, stationary instabilities can only occur during the transfer of ethylacetate into water.

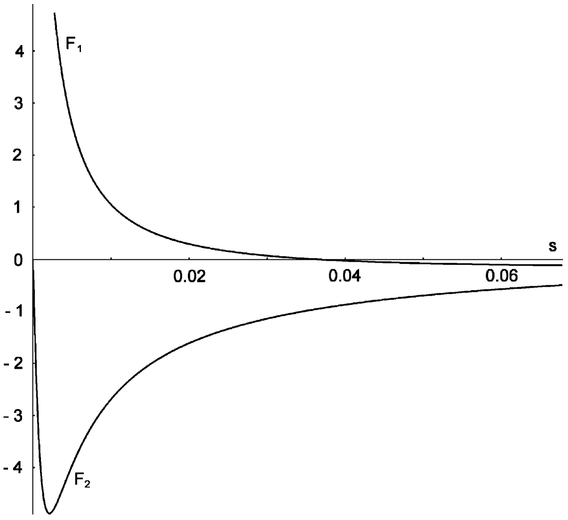

Fig. 2. Functions F_1 and F_2 for small s for transfer of ethylacetate into water.

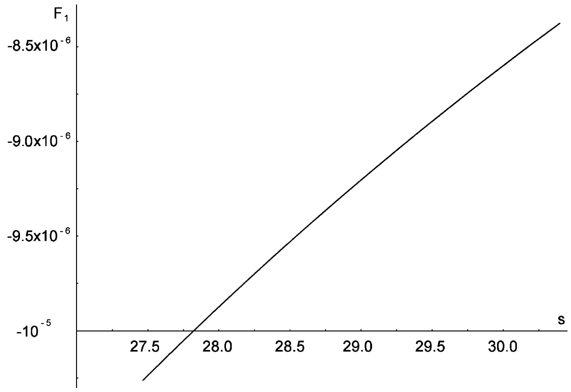

Fig. 3. Function F_1 for large s for transfer of ethylacetate into water.

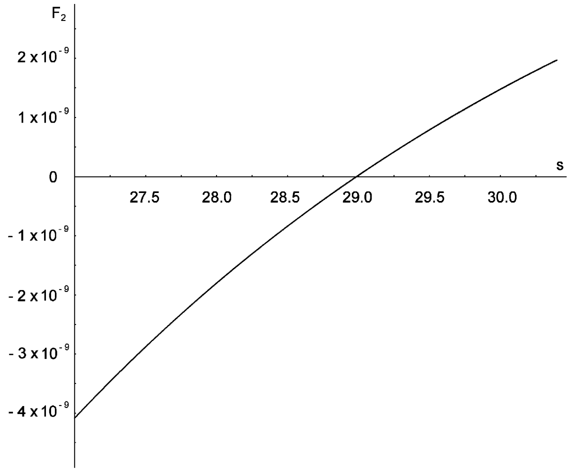

Fig. 4. Function F_2 for large s for transfer of ethylacetate into water.

5.1.2. Transfer of water into ethylacetate

For the transfer of water (phase 1) into ethylacetate (phase 2) the heat of solution is absorbed at the interface ($Q_2 = -4820$ kJ/kmol) and by definition (Eq. (13)), the Marangoni number assumes negative values. Functions $F_1(s)$ and $F_2(s)$ have the same behaviour as in the previous case, with the corresponding roots $s_1 = 0.054$ and $s_2 = 2.96$. Being stationary stable ($F_1(0) = 0.016 > 0$), the transfer of water into ethylacetate may be unstable to oscillatory perturbations. The absolute value of the Marangoni number $Ma_{osc} = -205761$, at $a = 1$, (corresponding to $F_1(s_2) = -4.68 \times 10^{-6}$) is quite large. The conclusion for the existence of oscillatory Marangoni instability is in agreement with Perez de Ortiz and Sawistowski's prediction and experimental data (see Table 1).

5.2. Isobutanol–water

5.2.1. Transfer of isobutanol into water

In the case of transfer of isobutanol into water, the Marangoni number assumes negative values as the heat of solution ($Q_2 = 12100$ kJ/kmol) and the interfacial tension coefficient ($\gamma = -0.005 \times 10^{-3}$ N/m K) have different signs. Functions $F_1(s)$ and $F_2(s)$ are plotted in Figs. 5 and 6. Analysing the asymptotic behaviour of $F_2(s)$, it is found that the function remains negative for any, even very large, values of the independent variable, i.e. the mathematical problem has no real solution for finite s. It means that the transfer of isobutanol into water is a *stable* process. This conclusion is in contrast with Perez de Ortiz and Sawistowski's prediction of the appearance of oscillatory instabilities. This disagreement will be discussed later when the transfer in the opposite direction is considered.

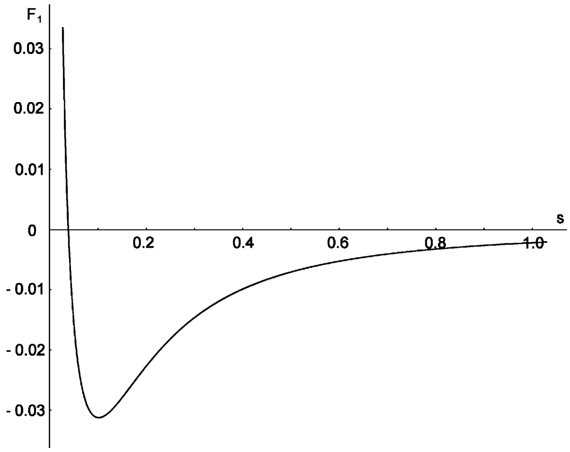

Fig. 5. Function F_1 for transfer of isobutanol into water.

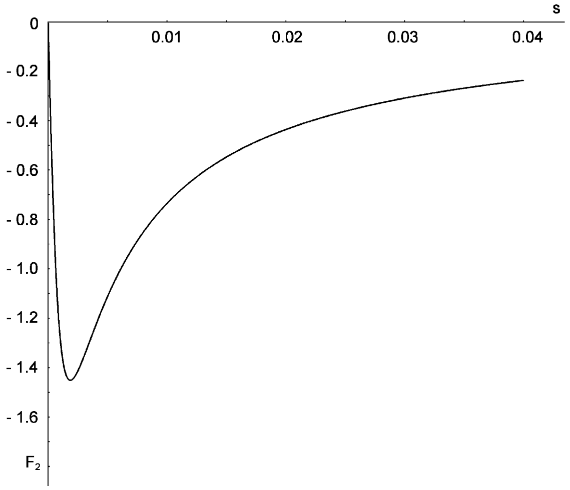

Fig. 6. Function F_2 for transfer of isobutanol into water.

5.2.2. Transfer of water into isobutanol

For the transfer of water into isobutanol the heat of solution is absorbed ($Q_2 = -1234$ kJ/kmol) and the Marangoni number is positive. Functions $F_1(s)$ and $F_2(s)$ have similar behaviour to the previous case, but now the value $F_1(0) = 5.285$ determines the Marangoni number $Ma_{\rm st} = 0.189$ for stationary instability. Hence, oscillatory instabilities are not expected to set in. This agrees with Perez de Ortiz and Sawistowski's result.

In summary, the present results for the onset of oscillatory instability are in agreement with Perez de Ortiz and Sawistowski's predictions for ethylacetate-water in both directions of transfer and for the transfer of water into isobutanol, while there is disagreement in the case of transfer of isobutanol into water.

Perez de Ortiz and Sawistowski [9] formulated the following stability criterion: 'Oscillatory instabilities will set in when mass transfer takes place out of the phase of higher viscosity', i.e. when $e^2 = \nu_2/\nu_1 < 1$ for the transfer of phase 1 into phase 2. This criterion was obtained from the analysis of the asymptotic behaviour of the imaginary part of the characteristic equation carried out in detail in [31]. There, it is concluded that the imaginary part has at least one root for a non-zero s if $e^2 = \nu_2/\nu_1 < 1$.

According to Perez de Ortiz and Sawistowski's criterion, in a given binary system, oscillatory instability can only occur in one direction of mass transfer, which depends on the magnitude of the viscosity ratio (see their predictions of oscillatory instability shown in Table 1). Since it is surprising that the onset of oscillatory instability in their work does not depend on other physical properties of the liquids, their stability criterion has been checked carefully and agreement has not been found with the present work. The study of the asymptotic behaviour of the characteristic equation (15), shows that the imaginary part of function $F(\mathrm{i}s)$ behaves as

$$F_2(s) \underset{s\to\infty}{\longrightarrow} \begin{cases} 0_+ & \text{if} \quad (e^2-1)S < 0, \\ 0_- & \text{if} \quad (e^2-1)S > 0, \end{cases} \tag{19}$$

where function S is given by

$$S = \frac{k\beta}{\mu}\left(\frac{1+\sqrt{Pr_2}}{\sqrt{Pr_2}}\right)\left(\frac{1+\mu e+\sqrt{Pr_2}}{e+h\sqrt{Pr_2}}\right) - \frac{\sqrt{Le_2}-1}{\sqrt{Le_2}+\mu h}. \tag{20}$$

When $(e^2-1)S < 0$, function $F_2(s)$ must cross the abscissa an odd number of times and approach it from above for large s. The calculations show that the function has only one non-zero root s_2, as, for example, in the case of transfer of ethylacetate into water (Fig. 4) where $(e^2 - 1)S = -0.469$. If $(e^2 - 1)S > 0$, the function $F_2(s)$ may cross the abscissa an even number of times or may not cross it at all. For the isobutanol-water system, the expression $(e^2 - 1)S$ is positive for transfer in both directions (equal to 0.362 for the transfer of isobutanol into water and 77.488 in the opposite direction) and the function $F_2(s)$ is negative for any $s > 0$. For this reason oscillatory instabilities will not appear in this system, despite the value of the viscosity ratio $e^2 = 0.226 < 1$ for the transfer of isobutanol into water.

The present results for the isobutanol–water system and those of Perez de Ortiz and Sawistowski [9] have been compared against experimental observations reported in the literature. In early experiments carried out by Ying and Sawistowski [8] instability of interfaces was not observed for the simultaneous transfer of isobutanol into water and water into isobutanol as well as for each separate direction. Later, Aguirre et al. [32] detected instabilities for the transfer of isobutanol into water only. Using a Schlieren/Mach-Zehnder integrated apparatus, Mendes-Tatsis and Agble [26] found that the transfer of isobutanol occurs across an *unstable* drop interface. Hence, Perez de Ortiz and Sawistowski's [9] prediction of oscillatory instabilities in the case of transfer of isobutanol into water is in agreement with the last experimental results while stationary instabilities expected to appear in the opposite direction of transfer have not been observed.

For the same isobutanol–water binary system the results obtained here are not in agreement with the experiments for transfer in each separate direction. A possible reason for this disagreement could be that any transient effects in the experiments that lead to onset of instability cannot be accounted for in the stability criteria, which have been developed for steady state conditions and therefore, the dependence of the static interfacial tension with temperature may be different from the dynamic interfacial tension one. For instance, if the experimental interfacial tension coefficient has the opposite sign from its steady state value, the stability criteria will change their meaning. In the case of the isobutanol–water system a positive value of the interfacial tension coefficient, instead of $\gamma = -0.005 \times 10^{-3}$ N/m K [9], gives a positive Marangoni number and the results for stationary instability will be opposite to the previously mentioned. Then, the transfer of water into isobutanol will be stable, while for the transfer in the opposite direction *stationary instability* will exist (the Marangoni number has the value $Ma_{\mathrm{st}} = 0.308$, at $a = 1$, corresponding to $F_1(0) = 3.251$). However, the change of the sign of γ will not alter the results for *oscillatory stability* for transfer in either direction, as the stability problem in this case has no real solution at all. It is concluded that the stability analysis presented is very sensitive to the sign of the interfacial tension coefficient.

5.3. Other binary systems

In Table 1 results are also shown for the other binary systems investigated. For the acetylacetone–water system, the present criterion predicts that oscillatory instabilities may appear in both directions of transfer while instabilities are experimentally observed for the transfer of acetylacetone into water only. Perez de Ortiz and Sawistowski's criteria also predict oscillatory instabilities for this direction of transfer, but there seems to be a misprint in their Table 4 [9]. According to their criterion, the system could only show oscillatory instabilities for the transfer of water into acetylacetone since the viscosity of water is higher than the viscosity of acetylacetone (see their Table 2 [9]) and not in the opposite direction.

The prediction for oscillatory instability in the case of transfer of methyl ethyl ketone (MEK) into water is not in agreement neither with Perez de Ortiz and Sawistowski's prediction of stability [9], nor with the experimental observations [8].

For the cyclohexanol–water system, which is observed to have an unstable interface for both directions of transfer, stationary instabilities are predicted to occur for the transfer from cyclohexanol into water, but the interface is predicted to be stable for transfer in the opposite direction. These results agree with those by Perez de Ortiz and Sawistowski [9] but there is disagreement for the oscillatory case for the transfer from cyclohexanol into water: the present work predicts the interface to be stable while Perez de Ortiz and Sawistowski's results predict it to be unstable. For the oscillatory case in the opposite directions both criteria predict the interface to be stable.

For the case of transfer of hexane into aniline, the system is predicted to be oscillatory stable, but has been observed to be unstable experimentally. The existence of gravitational instabilities in this case [9] may be one of the reasons for this disagreement. The transfer in the opposite direction is predicted unstable, which is in agreement with the experimental results, but although the function $(e^2 - 1)S = -0.183$ is negative the crossing point for $F_2(s)$ has not been found for very large values of s.

6. Conclusions

Linear stability theory has been used to predict Marangoni convection in partially miscible liquid–liquid systems. The onset of instabilities is due to the heat of solution released or absorbed at the interface during the mass transfer process. Necessary conditions for the existence of stationary or oscillatory Marangoni instabilities are obtained for mass transfer in one direction only. The characteristic equation is derived in analytical form and studied numerically for the binary systems considered by Perez de Ortiz and Sawistowski [9]. It is shown that stationary and oscillatory instabilities cannot exist simultaneously. Perez de Ortiz and Sawistowski's predictions for the stationary instability of the systems are confirmed, but in the oscillatory case there are disagreements between the present study and their results for some systems. The present results are also compared against experimental observations. Full agreement is achieved for the ethylacetate–water system in both directions of transfer, for the transfer of acetylacetone and cyclohexanol into water and of aniline into hexane. The theoretical predictions are not in accordance with the experimental results for the isobutanol-water in both directions of transfer, and for the transfer of water into acetylacetone and cyclohexanol, of MEK into water and of hexane into aniline. Possible reasons for those disagreements are discussed. For further validation of the developed linear stability criteria, more experimental work needs to be carried out.

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