

INFLUENCE OF SURFACE-ACTIVE SOLUTES ON MARANGONI INSTABILITY IN LIQUID-LIQUID SYSTEMS*

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The onset of Marangoni instability in partially miscible liquid-liquid systems, such as organic-aqueous systems, is studied in the presence of surface-active solutes. Marangoni convection may be induced by interfacial tension gradients, due to the heat of solution released or absorbed on the interface between the liquids and to the interfacial solute gradients. A linear stability analysis is carried out to predict marginal instability for solutes decreasing or increasing the interfacial tension.

1. Introduction. Marangoni convection is often observed during the transfer of a surface-active solute across an interface between two *immiscible* liquids, i.e. in ternary systems (see [1] and references therein). The instability is driven by tangential forces induced by interfacial tension gradients, due to local variations in the interfacial concentration of the solute.

When the liquids are partially *miscible*, mass transfer may also be accompanied by Marangoni convection, even in the absence of surface-active agents, due to temperature fluctuations produced by the heat of solution that absorbs or releases at the interface between both liquids [2]. Thermal Marangoni instability in binary liquid-liquid systems was considered in [2–3] where the stability criteria were derived. The effect of surface-active solutes on Marangoni convection in partially miscible liquid-liquid systems was investigated experimentally in [4] and theoretically in [5–6]. The presence of surface-tension-*decreasing*-solute was considered in [5] while the case of surface-tension-*increasing*-solute was studied in [6].

In the present paper, basing on the solutions of the stability problem obtained in [5–6], we summarize and compare the instability conditions for both types of solutes. We show their effects on the onset of Marangoni instability in partially miscible liquid-liquid systems.

2. Formulation of the stability problem. Consider a system of two semi-infinite layers of an organic liquid (upper phase 1) and water (lower phase 2) which are in contact along a plane horizontal interface. The organic liquid is initially pre-saturated with water and it dissolves in the aqueous phase. Since the mass dissolution process is much more

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slower than the heat transfer, for relatively long time there exists a very thin mixing zone between both liquids which can be modelled as a two-dimensional Newtonian surface. The aqueous phase contains a small amount of a surface-active solute which is soluble in the organic one and, therefore, it is transferring from phase 2 to phase 1 in direction opposite to the mass transfer. Solutes that decrease or increase the interfacial tension are considered.

The dissolution of one liquid in another may be accompanied by release or absorption of heat at the interface. Under external isothermal conditions, the released heat will be transferred from the interface into both bulks or in the opposite directions when the heat is absorbed. The heat fluxes cause temperature gradients along the interface resulting in variation of the interfacial tension. Due to the transfer of the surface-active solute across the interface, the interfacial excess-solute concentration Γ will vary along the interface and will differ from its initial value Γ^0 .

The interfacial tension of the liquid-liquid system depends on the interfacial temperature T_Σ and the interfacial excess-solute concentration by the linear expression

$$(1) \quad \sigma = \sigma_0 - \sigma_T (T_\Sigma - T_\Sigma^0) - \sigma_\Gamma (\Gamma - \Gamma^0), \quad \sigma_T = \left(-\frac{\partial \sigma}{\partial T} \right)_0, \quad \sigma_\Gamma = \left(-\frac{\partial \sigma}{\partial \Gamma} \right)_0,$$

where σ_T and σ_Γ are interfacial tension coefficients and T_Σ^0 is the reference temperature. Both coefficients assume positive and negative values. The coefficient $\sigma_T > 0$ for surface-tension-*decreasing*-solutes and $\sigma_T < 0$ for surface-tension-*increasing*-solutes. Considering very dilute solutions, the Gibbs adsorption isotherm is assumed to be valid at the interface, i.e. one has $\Gamma = \delta_2 S_{2\Sigma} - \delta_1 S_{1\Sigma}$, where δ_i are called Gibbs layer depths. These equations relate the interfacial excess-solute concentration to the bulk solute concentrations $S_{i\Sigma}$ ($i = 1, 2$) from both sides of the interface. According to the Gibbs theory, the concentration Γ has the same sign as σ_Γ . It also satisfies a solute balance equation along the interface.

The phase concentrations at the interface are assumed to be equilibrium ones which correspond to the interfacial temperature, i.e. $C_{i\Sigma} = R_i T_\Sigma$, where R_i are constants. The solute and heat fluxes at the interface satisfy the heat balance equation [2-3]

$$(2) \quad -k_2 \frac{\partial T_2}{\partial z} + Q_2 D_2^C \frac{\partial C_2}{\partial z} = -k_1 \frac{\partial T_1}{\partial z} + Q_1 D_1^C \frac{\partial C_1}{\partial z},$$

where k_i is the heat conductivity of phase i , D_2^C is the diffusivity of the organic liquid in water, Q_2 is the heat of solution of the organic liquid in water per mole of organic liquid, D_1^C and Q_1 are the corresponding diffusivity and heat of solution of water in the organic phase. The heats of solution Q_i are taken to be positive when heat is released and negative for heat absorption.

The linear stability theory is applied to the equations of motion, convective mass and solute diffusion, and energy. The details of the stability analysis are given in [5-6]. In the steady-state of the liquid-liquid system when the fluids are in rest, the temperature and the mass and solute concentrations are presented by linear functions of the vertical coordinate z (the axis z is directed from phase 2 to phase 1). The temperature gradients β_1^T and β_2^T have opposite signs depending on the heat process going on at the interface. When heat is liberated, the heat fluxes are directed from the interface to the bulks, so $\beta_1^T < 0$ and $\beta_2^T > 0$. In the case of heat absorption, the fluxes are directed to the interface and $\beta_1^T > 0$ and $\beta_2^T < 0$. The positive mass concentration gradient β_2^C is related to the

last quantities, due to the heat balance equation (2). The solute concentration gradients $(-\beta_1^S)$ and $(-\beta_2^S)$ are negative for transfer of solute from the aqueous to the organic phase, i.e. $\beta_i^S > 0$.

The solution of the hydrodynamic stability problem is searched in normal modes for the vertical components of the liquid velocities w_i , the mass concentrations C_i , the solute concentrations S_i , the liquid temperatures T_i ($i = 1, 2$), and the interfacial concentration Γ :

$$(3) \quad [w_i, C_i, S_i, T_i, \Gamma] = [\bar{W}_i(z), \bar{C}_i(z), \bar{S}_i(z), \bar{T}_i(z), \gamma] \exp [i(a_x x + a_y y) + \omega t] .$$

The unknown functions $\bar{W}_i(z)$, $\bar{C}_i(z)$, $\bar{S}_i(z)$, $\bar{T}_i(z)$ and the constant γ are amplitudes of an infinitesimal disturbance, t is the time, ω is a time growth constant and $a = \sqrt{a_x^2 + a_y^2}$ is a wavenumber. The growth constant is, in general, a complex number $\omega = \omega_R + i\omega_I$. The neutral (marginal) instability of the system to the disturbance is characterized by $\omega_R = 0$. When $\omega_R = 0$ implies that $\omega_I = 0$, then the marginal instability is stationary as the disturbance does not grow or decay. When $\omega = i\bar{\omega}$ is a pure imaginary number with a positive quantity $\bar{\omega}$ (called wave frequency), then the instability is oscillatory. Both cases of stationary and oscillatory instability are considered.

The stability problem is reduced to solving a system of linear equations for the amplitudes [6]:

$$(4) \quad \begin{aligned} & \left(\frac{d^2}{dz^2} - a^2 \right) \left(\frac{d^2}{dz^2} - a^2 - \omega \right) \bar{W}_i(z) = 0, \\ & \left[\frac{d^2}{dz^2} - (a^2 + r^2 \text{Pr}_2 \text{Le}_2^C \omega) \right] \bar{C}_1(z) = 0, \\ & \left[\frac{d^2}{dz^2} - (a^2 + \text{Pr}_2 \text{Le}_2^C \omega) \right] \bar{C}_2(z) = \text{Pr}_2 \text{Le}_2^C \bar{W}_2(z), \\ & \left[\frac{d^2}{dz^2} - (a^2 + r_S^2 \text{Sc}_2^S \omega) \right] \bar{S}_1(z) = r_S^2 \text{Sc}_2^S \bar{W}_1(z), \\ & \left[\frac{d^2}{dz^2} - (a^2 + \text{Sc}_2^S \omega) \right] \bar{S}_2(z) = -\text{Sc}_2^S \bar{W}_2(z), \\ & \left[\frac{d^2}{dz^2} - (a^2 + e^2 \text{Pr}_1 \omega) \right] \bar{T}_1(z) = -h^2 \text{Pr}_2 \frac{\beta}{1 + k\beta} \bar{W}_1(z), \\ & \left[\frac{d^2}{dz^2} - (a^2 + \text{Pr}_2 \omega) \right] \bar{T}_2(z) = \text{Pr}_2 \frac{1}{1 + k\beta} \bar{W}_2(z). \end{aligned}$$

Here, the following dimensionless parameters are introduced:

$$(5) \quad \begin{aligned} \text{Pr}_i &= \frac{\nu_i}{\kappa_i}, \quad \text{Le}_2^C = \frac{\kappa_2}{D_2^C}, \quad \text{Sc}_2^S = \frac{\nu_2}{D_2^S}, \quad e^2 = \frac{\nu_2}{\nu_1}, \quad h^2 = \frac{\kappa_2}{\kappa_1}, \\ r^2 &= \frac{D_2^C}{D_1^C}, \quad r_S^2 = \frac{D_2^S}{D_1^S}, \quad k = \frac{k_1}{k_2}, \quad \beta = -\frac{\beta_1^T}{\beta_2^T} > 0, \end{aligned}$$

where Pr_i is the Prandtl number for phase i , Le_2^C is the Lewis number for transfer of

organic liquid in aqueous phase, Sc_2^S is the Schmidt number for solute diffusion in water, $\nu_i = \mu_i/\rho_i$ is the kinematic viscosity, μ_i is the dynamic viscosity, ρ_i is the density, κ_i is the thermal diffusivity, e^2 is the kinematic viscosity ratio, h^2 is the heat diffusivity ratio, r^2 is the mass diffusivity ratio and r_S^2 is the solute diffusivity ratio.

The boundary conditions at the interface are (at $z = 0$)

$$\begin{aligned}
& \bar{W}_1(0) = \bar{W}_2(0) = 0, \quad D\bar{W}_1(0) = D\bar{W}_2(0), \\
& \mu(D^2 + a^2)\bar{W}_1(0) - (D^2 + a^2)\bar{W}_2(0) = a^2 \left(\frac{Ma_T}{Pr_2}\bar{T}_2(0) + \frac{Ma_S}{r_S^2 Sc_2^S} \gamma \right), \\
(6) \quad & \bar{C}_1(0) = \tilde{R}_1 \bar{T}_1(0), \quad \bar{C}_2(0) = \tilde{R}_2 \bar{T}_2(0), \quad \gamma = \frac{\delta r_S^2}{H} \bar{S}_1(0) = \frac{1}{H} \bar{S}_2(0), \\
& \bar{T}_1(0) = \bar{T}_2(0), \quad -D\bar{T}_2(0) + D\bar{C}_2(0) = -kD\bar{T}_1(0) + \frac{Q}{r^2} D\bar{C}_1(0), \\
& r_S^2 Sc_2^S \omega \gamma - DS_1(0) + r_S^2 DS_2(0) = 0.
\end{aligned}$$

The following dimensionless parameters are defined

$$\begin{aligned}
(7) \quad & Ma_S = \frac{\sigma_\Gamma S_{2\Sigma}^0 \delta_2^2}{\mu_2 D_2^S}, \quad Ma_T = \frac{\sigma_T Q_2 D_2^C \beta_2^C \delta_2^2}{\mu_2 \kappa_2 k_2}, \quad N_S = \frac{Ma_S}{Ma_T} = \frac{\sigma_\Gamma S_{2\Sigma}^0 \kappa_2 k_2}{\sigma_T Q_2 \beta_2^C D_2^C D_2^S}, \\
& H = \frac{\Gamma^0}{\beta_2^S \delta_2^2} = \frac{S_{2\Sigma}^0}{\beta_2^S \delta_2}, \quad \mu = \frac{\mu_1}{\mu_2}, \quad \delta = \frac{\delta_1}{\delta_2}, \quad \tilde{R}_i = \frac{Q_i D_i^C}{k_i} R_i.
\end{aligned}$$

Here, Ma_S and Ma_T are the solutal and thermal Marangoni numbers and N_S is their ratio. The solutal Marangoni number assumes positive and negative values depending on the sign of σ_Γ . The sign of the thermal Marangoni number Ma_T coincides with that of the product $\sigma_T Q_2$. The so-called adsorption number H is positive for $\sigma_\Gamma > 0$ and negative for $\sigma_\Gamma < 0$.

The solution of system (4) must vanish far from the interface, i.e.

$$(8) \quad \bar{W}_1, D\bar{W}_1, \bar{C}_1, \bar{S}_1, \bar{T}_1 \rightarrow 0 \text{ at } z \rightarrow \infty; \quad \bar{W}_2, D\bar{W}_2, \bar{C}_2, \bar{S}_2, \bar{T}_2 \rightarrow 0 \text{ at } z \rightarrow -\infty.$$

The problem (4), (6) and (8) consists of many physical parameters which vary for different liquids. Typical values of some parameters are: $Pr_2 = 6.15$ (for water), $Le_2^C = 150$, $Sc_2^S = 10^3$, $|N_S| = 10^7$, $|H| = 10^2$, $\beta = 0.8$, $k = 0.3$, $h^2 = 4$, $r^2 = 0.45$, $\mu = 0.5$ and $|\delta| = 0.9$. As the problem is an eigenvalue one, the solutions exist on some surfaces in the phase space (a, ϖ, Ma_S) , at given values of the other parameters. In the stationary case ($\varpi = 0$), the solutions exist on curves $Ma_S^{st} = Ma_S(a)$ named neutral stability curves.

3. Results. The characteristic equations for both cases of stationary and oscillatory instability were obtained and studied numerically in [5–6]. The numerical analysis shows that the instability conditions depend mainly on the solute activity (the sign of σ_Γ), on the heat of solution (the sign of $\sigma_T Q_2$), on the solute diffusivity ratio r_S^2 and on the kinematic viscosity ratio e^2 . The possible combinations of the last ratios corresponding to many liquid-liquid systems are: A1) $e^2 > r_S^2 > 1$, A2) $r_S^2 > e^2 > 1$, A3) $r_S^2 > 1 > e^2$, B1) $e^2 < r_S^2 < 1$, B2) $r_S^2 < e^2 < 1$, B3) $r_S^2 < 1 < e^2$, C1) $r_S^2 = 1 < e^2$ and C2) $e^2 < 1 = r_S^2$ [5–6]. Results were obtained for the following values: A) $r_s^2 = 1.2$ and e^2

equal to 2 (case *A1*), 1.1 (case *A2*) and 0.25 (case *A3*); *B*) $r_s^2 = 0.6$ and e^2 equal to 0.25 (case *B1*), 0.9 (case *B2*) and 2 (case *B3*); *C*) $r_s^2 = 1$ and $e^2 = 2$ (case *C1*) or $e^2 = 0.6$ (case *C2*). The wavenumber was ranged between 10^{-7} and 10.

Liquid-liquid systems with positive and negative product $\sigma_T Q_2$ are considered separately. In the stationary case, the neutral curves $Ma_S^{st} = Ma_S(a)$ turn out to be of two types. They consist of either two positive and negative branches, or one negative branch only. In the former case, the positive branch starts from zero and goes to infinity in a finite interval and, therefore, systems with *positive* Marangoni numbers are stationary unstable. The negative branch increases from minus infinity to some negative value (say, Ma_S^∞) as the wavenumber varies from zero to infinity. The asymptotic value Ma_S^∞ is the instability threshold and systems with *negative* Marangoni numbers are unstable for $Ma_S \leq Ma_S^\infty$. On the contrary, the negative branch of the second type starts from zero at $a = 0$ and decreases slowly approaching asymptotically Ma_S^∞ from above. The instability is expected to occur for $Ma_S^\infty \leq Ma_S < 0$.

Systems with $\sigma_T Q_2 > 0$						
Conditions on diffusivity and viscosity ratios	$\sigma_\Gamma > 0$			$\sigma_\Gamma < 0$		
	Stationary disturbances	Oscillatory disturbances	Marginal instability	Stationary disturbances	Oscillatory disturbances	Marginal instability
<i>A1</i> and <i>A2</i>	Stable	Unstable	Unstable	Unstable	Stable	Unstable
<i>A3</i>	Stable	Unstable	Unstable	Unstable	Stable or unstable	Unstable
<i>B1</i>	Unstable	Stable	Unstable	Stable	Stable or unstable	Stable or unstable
<i>B2</i> and <i>B3</i>	Unstable	Stable	Unstable	Stable	Stable	Stable
<i>C1</i>	Unstable	Unstable	Unstable	Stable	Stable	Stable
<i>C2</i>	Unstable	Stable	Unstable	Stable	Stable or unstable	Stable or unstable

Table 1. Instability conditions for systems with $\sigma_T Q_2 > 0$

In the case of oscillatory instability ($\omega = i\varpi$), the characteristic equation represents the solutal Marangoni number as a complex function $Ma_S^{os} = F_R(s; a) + i F_I(s; a)$ of a real positive variable $s \equiv \varpi/a^2$, at given a . As by definition the Marangoni number is a real number, we look for the roots s of the equation $F_I(s; a) = 0$ for fixed values of the wavenumber and the other physical parameters. There are some rare cases as case *C2* for systems with $\sigma_T Q_2 < 0$ in the presence of surface-tension-decreasing solutes, where the solution does not exist for physically reasonable values of the parameters involved, and the corresponding systems are stable to any oscillatory disturbance.

Results for both cases of stationary and oscillatory disturbances as well as for the general marginal instability are shown in Tables 1 and 2. In cases *A1* and *A2*, the conditions for stationary and oscillatory instability depend on the sign of σ_Γ only, independently of the sign of $\sigma_T Q_2$, but marginal instability can finally occur in all cases. Systems with $\sigma_T Q_2 > 0$ are predicted to be unstable for all combinations of the diffusivity and

Systems with $\sigma_T Q_2 > 0$						
Conditions on diffusivity and viscosity ratios	$\sigma_\Gamma > 0$			$\sigma_\Gamma < 0$		
	Stationary disturbances	Oscillatory disturbances	Marginal instability	Stationary disturbances	Oscillatory disturbances	Marginal instability
<i>A1</i> and <i>A2</i>	Stable	Unstable	Unstable	Unstable	Stable	Unstable
<i>A3</i>	Stable	Stable	Stable	Unstable	Unstable	Unstable
<i>B1</i>	Unstable	Stable	Unstable	Stable	Stable or unstable	Stable or unstable
<i>B2</i>	Unstable	Stable	Unstable	Stable	Stable or unstable	Stable or unstable
<i>B3</i>	Unstable	Stable	Unstable	Stable	Stable	Stable
<i>C1</i>	Stable	Unstable	Unstable	Unstable	Stable	Unstable
<i>C2</i>	Stable	Stable	Stable	Unstable	Unstable	Unstable

Table 2. Instability conditions for systems with $\sigma_T Q_2 < 0$

viscosity ratios when surface-tension-*decreasing* solutes ($\sigma_\Gamma > 0$) are present (Table 1). For surface-tension-*increasing* solutes ($\sigma_\Gamma < 0$), the systems are unstable for $r_S^2 > 1$, nevertheless what is the solute diffusivity ratio (all cases *A*). When $r_S^2 \leq 1$, then they are stable if the viscosity ratio is *larger* than the solute diffusivity one (cases *B2*, *B3* and *C1*) and could be stable or unstable when the viscosity ratio is *smaller* (in cases *B1* and *C2*).

Systems with $\sigma_T Q_2 < 0$ (Table 2), in the presence of surface-tension-*decreasing* solutes, are unstable in all cases, except for cases *A3* and *C2* where $r_S^2 \geq 1 > e^2$. If surface-tension-*increasing* solutes are present, then the systems are predicted to be unstable for $r_S^2 \geq 1$, independently of the solute diffusivity ratio (cases *A1*, *A2*, *A3*, *C1* and *C2*). They are stable for $r_S^2 < 1 < e^2$ (case *B3*) and can be stable or unstable for cases *B1* and *B2* when both ratios are less than one.

The theoretical result and experimental observation are in good agreement for the isobutanol-water system, but there is disagreement for the ethylacetate-water system [5].

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ВЛИЯНИЕ НА ПОВЪРХНОСТНО-АКТИВНИ ВЕЩЕСТВА ВЪРХУ МАРАНГОНИЕВАТА НЕУСТОЙЧИВОСТ В ТЕЧНО-ТЕЧНИ СИСТЕМИ

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Изучава се възникването на Марангониева неустойчивост в частично смесващи се течно-течни системи, като например органична течност и вода, при наличието на повърхностно-активно вещество. Марангониевата неустойчивост се индуцира от градиента на повърхностното напрежение вследствие на изменение на повърхностната температура, породено от отделената или погълнатата топлина на разтваряне върху междуфазовата повърхност и от изменението на концентрацията на веществото по нея. Проведен е анализ на линейната устойчивост за предсказване на неутралната неустойчивост за вещества намаляващи или повишаващи повърхностното напрежение.