

Spontaneous oscillations due to solutal Marangoni instability: air/water interface

Review Article

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Abstract: Systems far from equilibrium are able to self-organize and often demonstrate the formation of a large variety of dissipative structures. In systems with free liquid interfaces, self-organization is frequently associated with Marangoni instability. The development of solutal Marangoni instability can have specific features depending on the properties of adsorbed surfactant monolayer. Here we discuss a general approach to describe solutal Marangoni instability and review in details the recent experimental and theoretical results for a system where the specific properties of adsorbed layers are crucial for the observed dynamic regimes. In this system, Marangoni instability is a result of surfactant transfer from a small droplet located in the bulk of water to air/water interface. Various dynamic regimes, such as quasi-steady convection with a monotonous decrease of surface tension, spontaneous oscillations of surface tension, or their combination, are predicted by numerical simulations and observed experimentally. The particular dynamic regime and oscillation characteristics depend on the surfactant properties and the system aspect ratio.

Keywords: System far from equilibrium • Surfactant • Adsorption layer • Non-linear oscillations of surface tension • Marangoni effect
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1. Introduction

Systems far from equilibrium are omnipresent in the world. In fact, every living cell belongs to them. Examples can be found not only in nature, but also in society [1]. The most impressive feature of such systems is their ability to self-organize through the formation of dissipative structures [2]. Belousov-Zhabotinsky reaction is one of the best known examples of self-organization in chemistry [3]. In systems with free liquid interface self-organization phenomena, such as famous Benard cells, are often driven by gradients of interfacial tension (Marangoni effect) [4-6]. Self-organization in this case reveals itself as a convective instability, *i.e.*, spontaneous transition from a motionless state to a convective regime.

Marangoni effect and Marangoni instability are discussed in details below, in the section *General hydrodynamic approach*. Here it should be only noted, that the changes in the interfacial tension can occur due to the changes in temperature and/or in the interfacial composition. Therefore, dissipative structures appear

under heat or surfactant transfer in the systems with a free liquid interface. Temperature and composition can also have a combined effect, for example, when chemical reactions with a considerable thermal effect occur at the interface [7] or when there is essential heat of dissolution [8-10]. The convective instabilities enhance considerably the heat and mass transfer [11]. Therefore, they are important in many industrial applications, for example in the crystal growth from melts, liquid extraction *etc.* Marangoni instability can develop also during the measurements of the dynamic interfacial tension, thus affecting the measurement results [12]. It is an impressive example of the direct transformation of chemical energy into mechanical motion and in this respect it is a promising tool for the development of microfluidic devices. For an oscillatory instability, the oscillation characteristics depend considerably on the surfactant used. Therefore, oscillatory systems could be employed in artificial taste and drug sensors [13]. Except for the practical interest, the self-organization phenomena have fundamental significance, being a bridge between the artificial

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systems and living organisms and also providing better understanding of the regularities of the adsorption on dynamic interfaces. Thus, detailed understanding of the development of Marangoni instability in the real systems and the methods enabling the control of dynamic regimes are of great fundamental and practical importance.

The development of Marangoni instability in the systems with surfactant transfer can differ considerably from those with only heat transfer, because the interface with the adsorbed layer of a surfactant is in fact a separate phase with its own properties coupled tightly with the properties of the adjacent liquid bulk. In contradistinction to heat, surfactants can accumulate at the interface. That means that the surfactant fluxes to and out of the interface are as a rule not equal to each other as the heat fluxes are (in the absence of thermal sources and sinks at the interface). Moreover, the surfactant already present at the interface has a damping effect on the development of instability [14]. Therefore, if the initial surface coverage is high enough, instability never develops in the system.

While in many applications the liquid in bulk can be considered as incompressible one, the interface is compressible ($\text{div}_s(\mathbf{v}) = -\frac{\partial v_z}{\partial z} \neq 0$, with div_s being the surface divergence, $\mathbf{v}$ – the velocity vector, and z – the co-ordinate normal to the interface). Therefore, the interfacial concentration can change not only due to the surfactant fluxes from/to the bulk, but also due to the longitudinal deformations of the interface: the interfacial concentration increases by the contraction of the interface and decreases by its expansion. For the soluble surfactants considered here, the changes in the interfacial concentration and therefore, in the interfacial tension, depend not only on the deformation itself but also on the rate of deformation. In this respect, the interfacial layer of a surfactant is characterized by certain viscoelastic properties, in particular dilational viscoelasticity [15], which is also of a great importance for the development of instability.

It is noteworthy that in some cases it remains unclear whether Marangoni instability or other mechanisms are responsible for the self-organization processes accompanying the surfactant transfer through a liquid interface. The review of corresponding experimental results and some proposed mechanisms is presented in [24]. Most recently, the mechanisms considering the autocatalytic adsorption [25] or interfacial phase transitions [26] as a key point for the development of spontaneous oscillations have been proposed. In these studies, the observed Marangoni convection is considered as a secondary process caused by the inhomogeneity of interfacial concentration. At the same time some other recent studies [27,28] have shown

that in very similar systems, the self-organization can be explained in the frameworks of Marangoni instability, whereas the system chemistry can be crucial in providing the necessary conditions for the development of instability.

This review is devoted to the detailed analysis of the interplay between hydrodynamics and system chemistry in the self-organization phenomena caused by a surfactant transfer and adsorption. Here we consider the simplest system demonstrating the spontaneous oscillations of the surface tension, namely the system with a surfactant droplet dissolving under the water/air interface. It represents the simplest system, because the phenomenon can be observed in the presence of only one solute, without partitioning and transfer through the interface. For this system, it is easy to establish the oscillation mechanisms and to analyze the effect of specific properties of the surfactants and their adsorption layers.

The paper is organized as follows. In the section *General hydrodynamic approach* we consider the mechanism of the solutal Marangoni instability and the criteria based on the linear stability analysis enabling the instability prediction. In the section *Non-linear oscillations at the air/water interface* we consider in details the solutal Marangoni instability developing at the air/water interface due to dissolution of a droplet of a sparingly soluble surfactant in the aqueous bulk. The following will be discussed: i) available experimental results displaying that instability can result in different dynamic regimes depending on the surfactant properties and system geometry (the subsection *Experimental results*); ii) mathematical model used for direct numerical simulations of the behaviour of the system corresponding to that studied experimentally (the subsection *Mathematical model*); iii) the oscillation mechanism and the reasons for appearance of different dynamic regimes (the subsection *Oscillations mechanism*), and iv) the methods enabling control of the dynamic regimes and the oscillations period and amplitude (the subsection *Control of the dynamic regimes and oscillations characteristics*). In the two last subsections the comparison with experimental data is provided. The most important points are summarized in *Conclusions*.

2. General hydrodynamic approach

Marangoni effect consists in the development of bulk convection in a liquid due to the inhomogeneity of the interfacial tension. If an excess of surfactant is created somewhere on the liquid interface, the interfacial motion

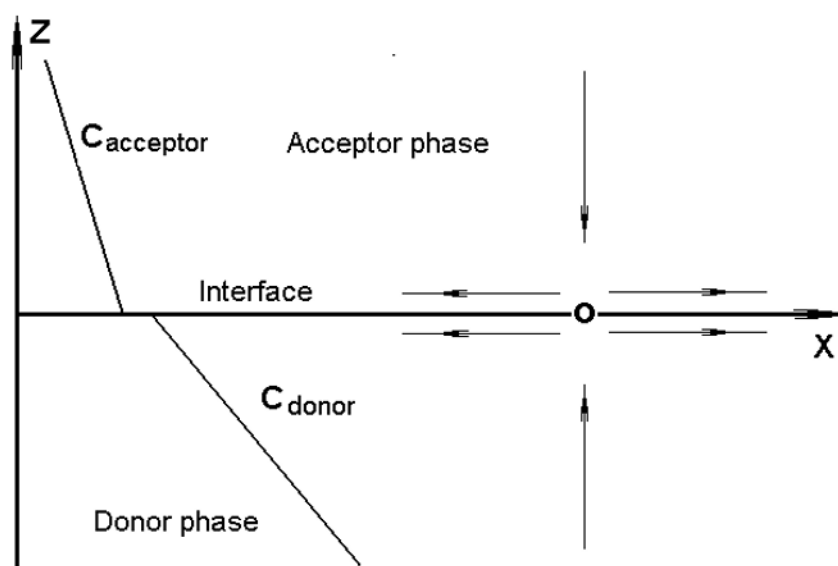


Figure 1. Mechanism of the solutal Marangoni instability.

begins from the point of lower interfacial tension (larger surfactant concentration) to the surrounding regions with higher interfacial tension (smaller surfactant concentration). This motion extends into the bulk due to the viscous transfer of momentum. The intensity of convection is determined by the gradient of interfacial tension. The larger amount of surfactant is put onto the interface the more intensive convection occurs. Marangoni effect assists establishing the homogeneous surfactant distribution over the interface. Therefore, Marangoni convection weakens and terminates very quickly provided there is no continuous supply of the surfactant to the point of interest on the interface.

The situation changes drastically if there is a source of the surfactant inside the system and Marangoni convection promotes additional supply of the surfactant to the point of interest, *i.e.*, there is a feedback between the intensity of convection and the gradient of interfacial tension. In this case, the velocity of convective motion spontaneously increases with time very quickly, indicating the development of Marangoni instability. The velocity grows until the dissipation of energy (proportional to v^2) reaches the release of free energy in the system (accumulated due to the difference in chemical potentials of the components in different parts of the system). Thereafter, the quasi-steady convection takes place, with the velocity slowly decreasing with time. The velocity decrease is a consequence of a decrease in the free energy due to the equilibration of chemical potentials over the system.

An example of the feedback system is presented in Fig. 1. Here a surfactant is transferred from the donor liquid phase to the acceptor liquid phase, as indicated

by the concentration gradients C_{donor} and C_{acceptor} . Initially the liquid is motionless and the surfactant transfer occurs due to the diffusion only. In any real system there are fluctuations of the local concentration at the interface as a result of the chaotic thermal motion. Let us assume that such a fluctuation, characterized by a higher surfactant concentration occurs in the point "o" at the interface. In this case, the liquid at the interface begins to flow from the point "o", shown by the arrows in Fig. 1, because the interfacial tension in this point is lower than that in its neighborhood. The bulk liquid is also involved in the convective motion due to the viscous stresses. According to the continuity conditions, the liquid should be supplied to the interfacial point "o" from the both bulk phases, as shown in Fig. 1. It brings to this point more diluted solution from the acceptor phase and more concentrated solution from the donor phase. Besides, the concentration in the point "o" will decrease because of the local expansion of the interface.

The further scenario depends exclusively on the properties of the liquid phases involved. If the supply of the surfactant to the point "o" from the donor phase exceeds its losses due to expansion of the interface and due to the supply of the diluted solution from the acceptor phase then there is a positive feedback in the system resulting in an increase of the interfacial concentration in the point "o" and in intensification of convection. In the opposite case instability does not develop and diffusion remains the only means of the surfactant transfer in the system. The amount of the surfactant getting the point "o" depends on both the ratio of the convective velocities in the bulk phases in the normal to the interface direction, *i.e.*, on the ratio of the

bulk viscosities, and the ratio of the surfactant diffusion coefficients. If the viscosity of the donor phase is higher than that of the acceptor phase, the bulk velocity in the donor phase is also higher, promoting the instability. If the surfactant diffusion coefficient in the donor phase is higher than that in the acceptor phase, the surfactant dissipates more quickly from the normal flux in the donor phase, suppressing the development of instability.

A rigorous quantitative theoretical study on the solutal Marangoni instability by the surfactant transfer through a planar liquid interface was performed for the first time by Sternling and Scriven [16]. They obtained instability criteria based on the linear stability analysis, *i.e.*, in the approximation of very small variations in concentrations and velocities, when the non-linear terms in Navier-Stokes equation and convective diffusion equation can be neglected. They have found that in accordance with the qualitative discussion above, the system is stable against any small disturbance if the surfactant diffusion coefficient in the donor phase is higher than that in the acceptor phase, while the viscosity of the donor phase is smaller than that of the acceptor phase. In all other cases, the instability can develop in the system either as a stationary convection or as oscillations.

The model considered in [16] has certain limitations: in [16] it is assumed that the liquid layers are semi-infinite, the interface does not deform in the normal direction, the surfactant does not adsorb on the interface and there is no surfactant transfer inside the interfacial layer. These limitations have been overcome in the subsequent studies. In [17-19], a more rigorous model was considered, taking into account the surface deformation, the adsorption of the surfactant and its transfer inside the interface by using more accurate equations for the interfacial momentum and mass balance. In the framework of this model it was shown that neglecting the normal deformations of the interface used in [16] is quite correct for the Marangoni instability producing the longitudinal motion. At the same time, the instability criteria were modified. According to [19], in the long wave approximation, a liquid layer is always unstable under the conditions of surfactant transfer. The steady convection is expected at

$$\frac{D_d v_a}{D_a v_d} < 1 \quad (1)$$

where D_d and D_a are the diffusion coefficients, and v_d and v_a are the kinematic viscosities in the donor and the acceptor phase, respectively, whereas oscillations are expected in the opposite case

$$\frac{D_d v_a}{D_a v_d} > 1 \quad (2)$$

It should be noted that the criteria in Eqs. 1 and 2 are necessary conditions but not sufficient for the instability development. If one of those criteria is fulfilled, the instability sets up only if the normal concentration gradient at the interface is large enough [18]. The critical gradient depends on the surfactant properties and the viscosities of the liquid phases. Those dependencies are included in a characteristic dimensionless group called Marangoni number

$$Ma = \frac{d\gamma}{dc} \frac{dc}{dz} \frac{d^2}{\rho \nu D} \quad (3)$$

where γ is the interfacial tension, c is the surfactant concentration, ρ is the liquid density, d is the characteristic length scale. The instability develops only if the difference of the Marangoni numbers in the donor and the acceptor phase exceed a threshold value.

The effect of the limited depth of the liquid layer was considered in [20,21]. The model used in [20] is similar to that employed in the treatment of the thermal Marangoni problem, *i.e.*, the effects of the surfactant adsorption and its transfer inside the interfacial layer are not taken into account. The model used in [21] employs a more accurate mass balance equation similar to [17-19], but it considers only the criteria for the non-oscillatory instability. The main conclusion of both studies – the depth of the liquid layers involved in the surfactant transfer is crucial for the instability development and for its type. For example, according to [20,21] the system can demonstrate non-oscillatory Marangoni instability by the transfer in both directions, $1 \rightarrow 2$ and $2 \rightarrow 1$ if $D_1/D_2 < 1$ and $h_1/h_2 > 1$ (h being the depth of the liquid layer). As discussed above, such situation is impossible for semi-infinite liquid layers. Here, semi-infinite means that the liquid layer depth is much larger than the characteristic length scale. The value

$$d = \sqrt{\frac{\Gamma_0}{dc/dz}}$$

(Γ_0 being the initial value of surfactant adsorption) is proposed in [20] as a characteristic length scale for the diffusion controlled adsorption kinetics.

The results in [16-20] are obtained assuming the diffusion limited adsorption kinetics. It is generally accepted that diffusion is the limiting step in the adsorption kinetics of most surfactants from their solutions. However, for example for proteins and polymers adsorbed from solution, as well as for surfactants adsorbed from the gas phase, the adsorption rate can be a time limiting step. The effect of adsorption/desorption limited kinetics on the development of Marangoni instability is considered in [21,22]. The most general conclusions are: i) the system is stable if the adsorption/desorption is the limiting step

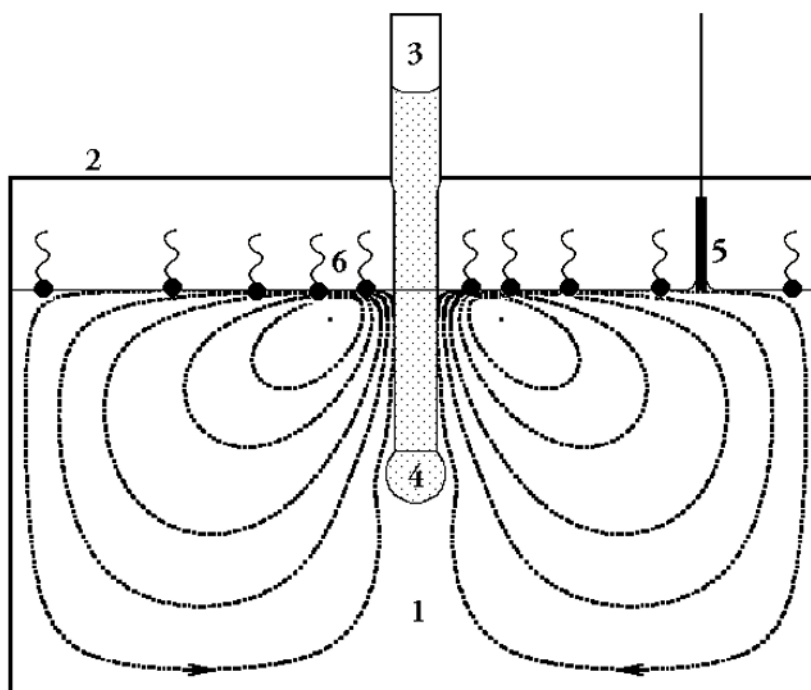


Figure 2. Schematic representation of the system producing spontaneous oscillations: 1 – cylindrical vessel filled with water, 2 – covering plate, 3 – capillary, 4 – surfactant droplet, 5 – Wilhelmy plate, 6 – air/water interface with adsorbed surfactant.

in the both fluid phases; ii) by the transfer from a phase with adsorption controlled kinetics to the phase with diffusion controlled kinetics the oscillatory instability is possible, whereas the steady convection is expected for the opposite transfer direction. The instability criteria for spherical interfaces are more complicated than those for the planar interfaces and they are discussed in [23].

In summary, it can be stated that the theory of solutal Marangoni instability is elaborated thoroughly in the framework of the linear stability analysis. The mechanism of the instability development during the initial stage is quite clear and the criteria are derived to enable the instability prediction. A detailed discussion on the instability criteria is presented in a recent review [24]. Very often, the criteria derived in the framework of the linear stability analysis work quite well. For example, as discussed above, oscillatory instability is expected by the adsorption of a surfactant from the gas phase and its transfer into the liquid phase. Indeed, a large variety of oscillatory patterns was observed in the corresponding systems [29,30]. However, in many cases applying the available criteria to the real systems is not straightforward because a precise and detailed analysis of all acting factors is necessary. In addition, the criteria based on the linear stability analysis are related only to the initial stages of the instability development. By the increase of the convective velocity the transition to a non-linear

regime occurs, where new stabilizing and destabilizing factors can appear. The theoretical consideration shows that certain changes in the dynamic behavior are expected already in the weak non-linear regimes [31]. In particular, the shape of the convective patterns changes by increasing the Marangoni number. Below we consider in details a system where the non-linear effects and the properties of the adsorbed surfactant layer are crucial for the understanding and controlling the system behavior.

3. Non-linear oscillations at the air/water interface

3.1. Experimental results

As it was mentioned in the previous section, according to the available instability criteria based on the linear stability analysis, the oscillatory instability is expected by the surfactant transfer from a gas to a liquid phase, whereas steady convection should occur by the opposite direction of the transfer. In contradiction to these predictions, a simple system was discovered demonstrating spontaneous oscillations by the transfer of a surfactant from the liquid bulk to gas/liquid interface [32]. This system is schematically presented in Fig. 2. It consists of a cylindrical glass vessel

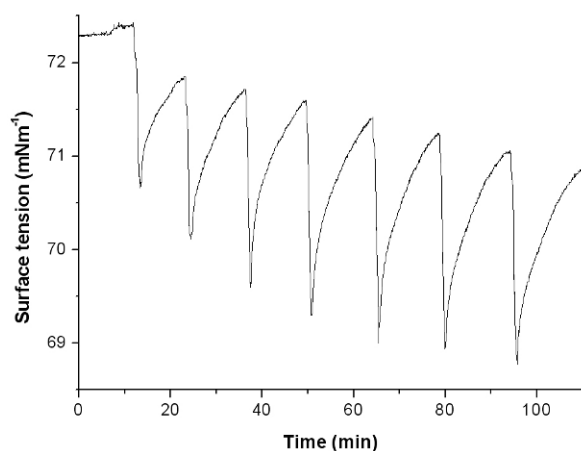


Figure 3. Spontaneous oscillations of the surface tension produced by the dissolution of a droplet of diethyl phthalate. The vessel diameter $d=45$ mm, the capillary immersion depth $h=6.2$ mm (reprinted from [33], with permission from American Chemical Society).

(1 in Fig. 2) filled with ultrapure deionised water. After filling, the vessel is covered (2 in Fig. 2) to prevent the thermal convection due to water and surfactant evaporation.

A glass capillary (a Pasteur pipette, 3 in Fig. 2) with an orifice of about 1 mm is inserted in water to a desired depth. A freshly annealed platinum Wilhelmy plate connected to an electronic balance is put onto the surface and the measurement of the dynamic surface tension is performed during 1-2 hours to make certain that the surface tension is constant and that there are no surface active contaminations in the system. A droplet of a sparingly soluble surfactant is formed at the capillary tip by adding of small portions of the surfactant inside the capillary with a micro-litre syringe and the surface tension measurement is restarted. Dissolution of the surfactant from the droplet and its adsorption at the air/water surface results in variation of the surface tension causing spontaneous convection in the system.

The surfactants used in the experimental studies were diethyl phthalate [32], aliphatic alcohols [33-36] and fatty acids [37-39]. The surface tension remains constant during an induction period after the droplet dissolution starts, followed by an abrupt decrease indicating the development of Marangoni instability. The confirmation that the decrease of the surface tension is a result of convective instability was obtained by flow visualisation. Talcum particles located on the surface began to move very quickly from the capillary to the vessel wall synchronously with the drop of the surface tension. After that three different scenarios have been observed as follows.

The first regime is an oscillatory one (Fig. 3). At this regime the surface motion terminates very quickly (at

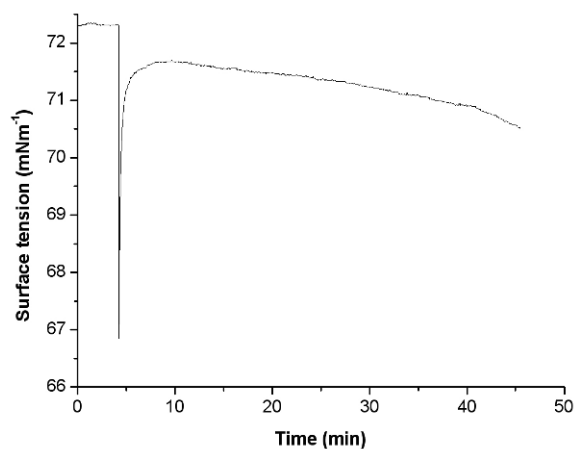


Figure 4. Single oscillation of the surface tension followed by the quasi-stationary regime. Dissolution of an octanol droplet in the vessel with diameter $d=48$ mm, the capillary immersion depth $h=5.3$ mm (reprinted from [33], with permission from American Chemical Society).

the time of the order of a second) and then the tracer particles move very slowly from the wall to the capillary on the interface becoming practically motionless in the bulk. The surface tension begins to increase very slowly and reaches eventually the value very close to that it had before the instability onset. This slow stage in the system evolution lasts much longer than the previous quick stage, from a minute to tens of minutes depending on the surfactant properties. After that, a convective instability accompanied by a very quick surface motion and rapid decrease of the surface tension occurs again, *i.e.*, the system with the surfactant droplet dissolving under the air/water interface demonstrates the development of spontaneous non-linear oscillations, as shown in Fig. 3.

In another scenario, the convection does not terminate but becomes much slower after a short fast stage, *i.e.*, this is a regime of quasi-steady convection predicted by the linear stability analysis for the transfer of the surfactant from a liquid phase to the gas/liquid interface. This regime is characterized by an increase of the surface tension followed by its gradual decrease (Fig. 4).

The third possible regime is a combination of the first two. In certain cases the slow decrease of the surface tension, characteristic for the regime of quasi-steady convection, terminates spontaneously, the surface tension increases a little bit, and after that the oscillatory regime develops as depicted in Fig. 5. The system behaviour depends essentially on the system geometry and on the surfactant used. Transition from the oscillatory regime to the regime of quasi-steady convection occurs either by a decrease of the capillary immersion depth or by an increase of the vessel diameter [34]. Noteworthy,

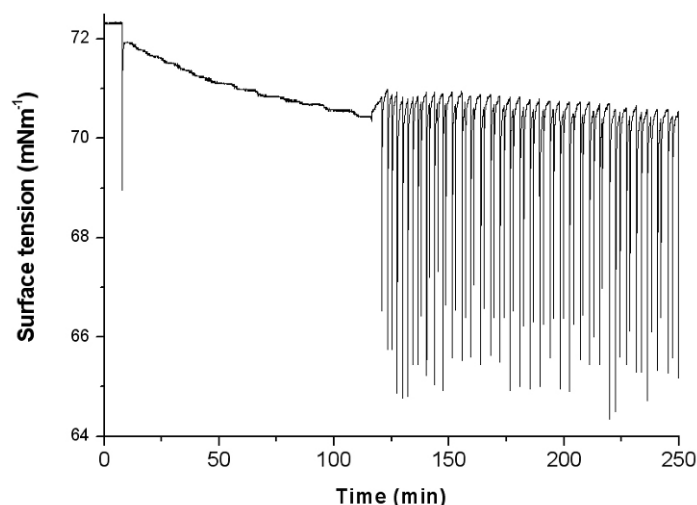


Figure 5. Combined regime produced by the dissolution of an octanoic acid droplet in 0.01 M phosphate buffer, pH=4.8. The vessel diameter $d=44$ mm, the capillary immersion depth $h=1$ mm.

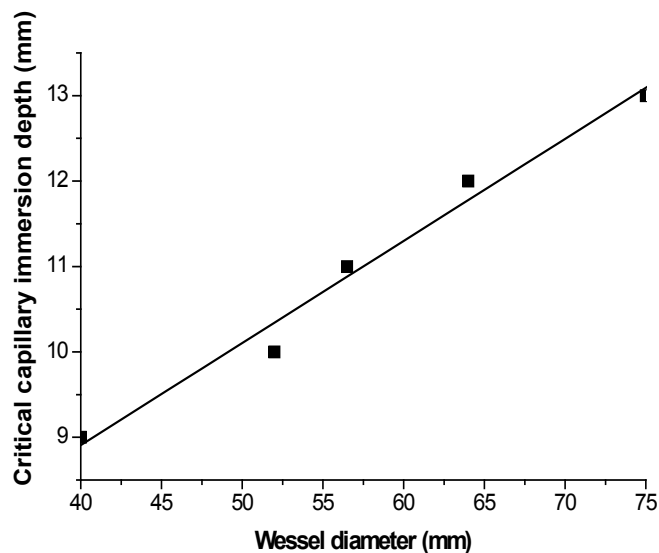


Figure 6. Dependence of the critical capillary immersion depth corresponding to the transition from the oscillatory regime to the regime of steady convection on the vessel diameter. A heptanol droplet under the air/water surface (reprinted from [34], with permission from Elsevier).

that the dependence of the critical immersion depth, corresponding to this transition, on the vessel diameter is practically linear, as shown in Fig. 6.

The effect of the surfactant properties was investigated in [33] for a series of aliphatic alcohols. For aliphatic alcohols the density and the surface activity decrease with the decrease of the alkyl chain length whereas the solubility in water increases. It was shown in [33] that the induction period as well as the oscillation period decreases with the decrease of the chain length (Fig. 7). The critical capillary immersion depth (by a constant vessel diameter) increases with the decrease of the chain length. Comparison of the oscillations produced by aliphatic alcohols and the respective fatty

acids [37] has shown that the buoyancy force owing to the concentration dependence of the solution density also affects considerably the oscillation characteristics. To explain the oscillation mechanism, the appearance of different regimes, and the dependence of the regime established as well as the oscillation characteristics on the surfactant properties and the system geometry, a comprehensive numerical study was performed as discussed below.

3.2. Mathematical model

The mathematical model used for the studies on solutal Marangoni instability in the experimental system discussed above is based on the set of partial differential

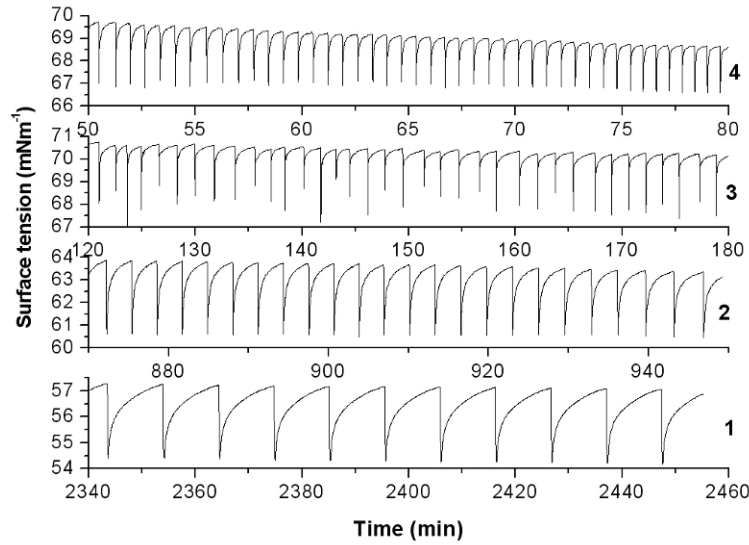


Figure 7. Oscillations of the surface tension produced by various aliphatic alcohols: 1 – octanol, $d=45$ mm, $h=6.1$ mm; 2 – heptanol, $d=57$ mm, $h=10.9$ mm; 3 – hexanol, $d=57$ mm, $h=13.3$ mm; 4 – pentanol, $d=37$ mm, $h=13.7$ mm.

equations including Navier-Stokes, continuity and convective diffusion equations. The liquid is assumed to be Newtonian, incompressible one being in contact with a passive gas. The Boussinesq approximation is accepted, *i.e.*, the dependence of the solution density on surfactant concentration is taken into account only in the buoyancy term. The geometry of the system corresponds to that presented in Fig. 2. Taking into account the cylindrical symmetry of the system and the experimental observations indicating predominantly radial character of the surface convection, the governing equations are written in a cylindrical co-ordinate system and the dependence on the angular co-ordinate is neglected. In this case, the equations can be rewritten in the terms of vorticity ω and stream function Ψ defined as

$$\omega = \frac{\partial v_r}{\partial z} - \frac{\partial v_z}{\partial r} \quad (4)$$

$$v_r = \frac{1}{r} \frac{\partial \Psi}{\partial z}, v_z = -\frac{1}{r} \frac{\partial \Psi}{\partial r} \quad (5)$$

Scaling time, length, velocity, concentration, stream function and vorticity with $L^2 D^{-1}$, L , DL^{-1} , c_0 , LD , DL^{-2} , respectively, the dimensionless forms of the governing equations read [40]:

$$\begin{aligned} & \frac{\partial \omega}{\partial t} + \frac{\partial(v_r \omega)}{\partial r} + \frac{\partial(v_z \omega)}{\partial z} - \\ & - Sc \left(\frac{\partial^2 \omega}{\partial r^2} + \frac{\partial^2 \omega}{\partial z^2} + \frac{1}{r} \frac{\partial \omega}{\partial r} - \frac{\omega}{r^2} \right) + Ra \cdot Sc \frac{\partial c}{\partial r} = 0 \end{aligned} \quad (6)$$

$$\frac{\partial^2 \Psi}{\partial r^2} + \frac{\partial^2 \Psi}{\partial z^2} - \frac{1}{r} \frac{\partial \Psi}{\partial r} - \omega r = 0 \quad (7)$$

$$\frac{\partial c}{\partial t} + \frac{\partial(v_r c)}{\partial r} + \frac{\partial(v_z c)}{\partial z} + \frac{v_r c}{r} - \left(\frac{\partial^2 c}{\partial r^2} + \frac{\partial^2 c}{\partial z^2} + \frac{1}{r} \frac{\partial c}{\partial r} \right) = 0 \quad (8)$$

where L is the characteristic length scale corresponding to the depth of the liquid layer, D is the bulk diffusion coefficient of the surfactant, c_0 is the surfactant solubility, t is the time, r is the radial coordinate, z is the co-ordinate normal to the surface, downward directed with $z=0$ at the surface, v_r and v_z are the velocity components in radial and normal to the surface directions respectively,

$$Sc = \frac{\nu}{D}$$

is the Schmidt number,

$$Ra = \frac{g c_0 L^3}{\rho_0 \nu D} \frac{\partial \rho}{\partial c}$$

is the Rayleigh number, ν is the kinematic viscosity of the liquid,

$$\rho = \rho_0 - \left(\frac{c}{c_0} \right) (\rho_0 - \rho_s)$$

is the solution density, ρ_0 is the solvent density, ρ_s is the density of the saturated surfactant solution, g is the acceleration due to gravity, and c is the surfactant concentration.

It is assumed that initially the liquid is motionless and the surfactant concentration is zero everywhere except in the droplet. The changes in droplet size due to dissolution as well as any thermal effects are neglected. The droplet is assumed to be spherical. The dimensionless surfactant concentration at the droplet

interface does not change with time and is equal to unity. No-slip boundary conditions are used for the vessel wall and bottom, for the capillary wall and for the droplet surface. The gas-liquid interface is supposed to be plain and non-deformable. The evaporation from the surface and the intrinsic surface viscosity are neglected. Diffusion controlled adsorption kinetics is assumed with the local equilibrium between the surface concentration, Γ , and the subsurface concentration, $c_s=c(z=0)$, described by the Langmuir isotherm:

$$\Gamma = \frac{c_s}{1 + K_L c_0 c_s} \quad (9)$$

where Γ is the dimensionless Gibbs adsorption scaled by $c_0 K_L \Gamma_m$, K_L and Γ_m are the parameters of the Langmuir isotherm.

The surface tension can be found in this case from Szyszkowsky-Langmuir equation which in the dimensional form reads:

$$\gamma = \gamma_0 + RT\Gamma_m \ln \left(1 - \frac{\Gamma}{\Gamma_m} \right) \quad (10)$$

where γ is the equilibrium surface tension of the solution, γ_0 is the surface tension of the solvent, R is the gas constant and T is the temperature.

The surface mass balance is described by the equation:

$$\frac{\partial \Gamma}{\partial t} + \frac{\partial(\Gamma v_r)}{\partial r} + \frac{\Gamma v_r}{r} - \frac{D_s}{D} \left(\frac{\partial^2 \Gamma}{\partial r^2} + \frac{1}{r} \frac{\partial \Gamma}{\partial r} \right) - N_E \left(\frac{\partial c}{\partial z} \right) = 0 \quad \text{at } z=0 \quad (11)$$

where

$$N_E = \frac{L}{K_L \Gamma_m},$$

is the exchange number that determines the effect of the surfactant exchange between the surface and the bulk ($N_E \rightarrow 0$ corresponds to the limiting case of insoluble monolayer), D_s is the surface diffusion coefficient.

The boundary condition for the vortex on the surface is obtained from the tangential stress balance using the Szyszkowsky-Langmuir equation as:

$$\omega = Ma \frac{1}{(1 - K_L c_0 \Gamma)} \frac{\partial \Gamma}{\partial r} \quad \text{at } z=0 \quad (12)$$

where

$$Ma = \frac{RT c_0 K_L \Gamma_m L}{\mu D} \quad (13)$$

is the Marangoni number. Comparison of Eqs. 13 and 3 shows that Marangoni number defined by Eq. 13 is the global one, characterising the system as a whole.

According to general definition, Eq. 3, Marangoni number should include the concentration gradient in the normal to the surface direction, and it is a number, *i.e.*, a constant, only for the systems with a linear concentration gradient, which does not change with time. In the system under consideration, the concentration gradients change in space and time. Therefore, the instability development should depend on the local Marangoni number near the interface [32]. This, however, depends on the global Marangoni number, Eq. 3.

An explicit finite difference method was used for the numerical simulations. Eq. 7 was solved by Gauss-Seidel iterative method. For Eqs. 6 and 8 two-point forward difference approximation is used for the time derivatives, three-point centered differences are used for the diffusion terms, and modified upwind differences are used for the convective terms [41].

3.3. Oscillations mechanism

To understand the dynamic regimes accompanying the dissolution of a surfactant droplet under the air/water interface, let us consider first the case when the solution density is independent of concentration, *i.e.*, the case without the buoyancy force. Here the last term in the left hand side of the Eq. 3 is equal to zero. Already in this simplest case the numerical simulations predict the appearance of the dynamic regimes observed experimentally. According to the simulations, the transition from the oscillatory regime to the regime of quasi-steady convection should occur either by a decrease of the capillary immersion depth or by an increase of the vessel diameter [42], in full agreement with the experiment. Also the numerical simulations show [43] that the oscillations of the surface tension and the surface velocity are fully synchronized with each other and every abrupt decrease of the surface tension in this system corresponds to the development of convective instability, as seen in Figs. 8 and 9.

The results presented in Figs. 8 and 9 are obtained for the surfactant properties similar to those for hexanol, namely $D_s=D=7.81 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, $c_0=58 \text{ mol m}^{-3}$, $\Gamma_m=6.2 \times 10^{-6} \text{ mol m}^{-2}$, $K_L=0.23 \text{ m}^3 \text{ mol}^{-1}$, but neglecting the buoyancy force. At larger capillary immersion depth ($h=8 \text{ mm}$), the oscillatory regime occurs. As a result of instability, the convective velocity increases very quickly, reaches a maximum and then decreases also quickly to zero and becoming even negative for a short time (Fig. 8b). During the gradual increase of the surface tension the velocity remains very close to zero. On the contrary, at smaller capillary immersion depth ($h=4$), the surface velocity does not decrease to zero, but remains on a detectable level of about 1 mm s^{-1} causing continuous decrease of the surface tension (Fig. 9b).

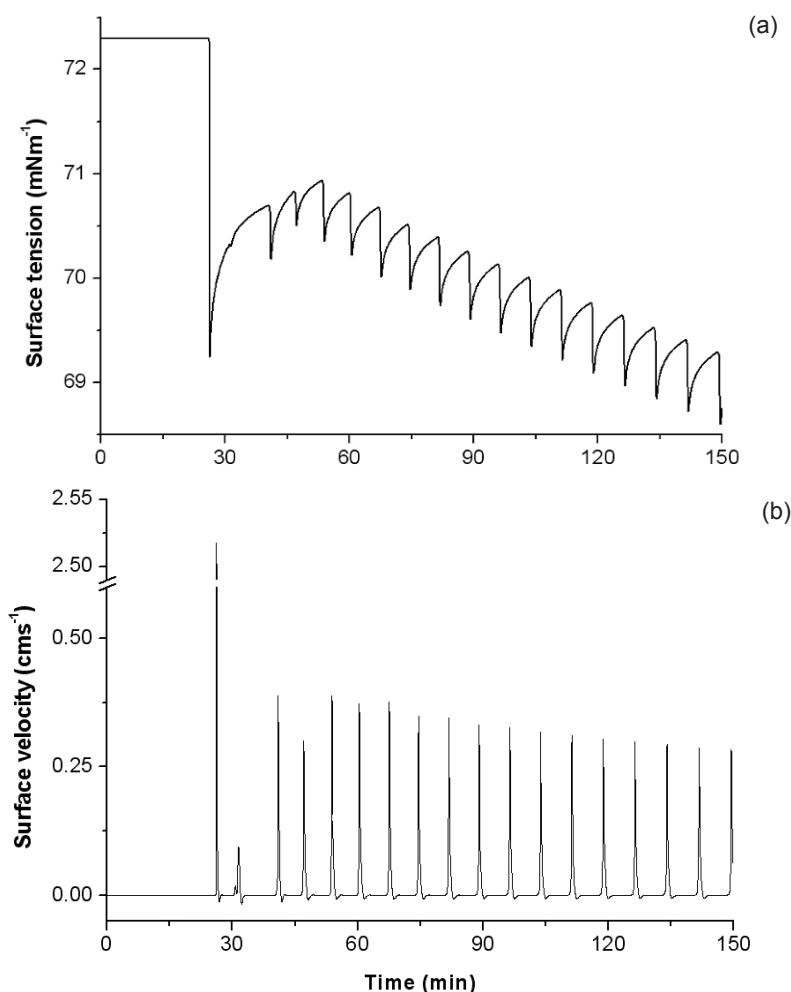


Figure 8. Results of numerical simulation on dissolution of a hexanol droplet under the air/water interface: vessel diameter $d=40$ mm, capillary immersion depth $h=8$ mm, buoyancy is neglected; a) surface tension vs time, b) surface velocity vs time (reprinted from [43], with permission from American Physical Society).

Thus, in this case the numerical simulations predict the development of the regime of quasi-steady convection. To understand the mechanisms underlying these two regimes, let us consider the processes in this system in more detail.

After a droplet is formed at the tip of the capillary, the surfactant begins to transfer from the droplet by diffusion. It is obvious from the system geometry that the distance from the droplet to the parts of the interface near the capillary is shorter than to the parts of the interface near the vessel wall. Therefore, after some noticeable amount of surfactant reaches the interface, the surface concentration gradient appears with the highest surface concentration (the lowest surface tension) in the capillary region and the lowest one (the highest surface tension) in the wall region. As a result, the Marangoni convection develops in the system with the streamline distribution shown in Fig. 2. It is clear from Fig. 2 that convection brings more concentrated solution from the droplet

to the surface in the capillary region, which results in further increase of the surface concentration gradient and the intensification of the convection in the system. Thus, there is a feedback in the system enabling the development of the Marangoni instability.

Initially, the convection velocity is very small and the diffusion mass transfer remains predominant in the system. Fig. 10a demonstrates that even after 26 min of the droplet dissolution, the concentration profiles remain rather close to the diffusional ones. Therefore initially the effect of the feedback is weak and the instability develops very slowly. This time interval belongs to the induction period, where the measured surface tension remains constant. Note that during this time the surfactant adsorbs on the interface, but the changes in the surface tension remain negligible, because relatively large adsorption values are required for the measurable changes in the surface tension. For example, the surface coverage has to be more than 1% of Γ_m

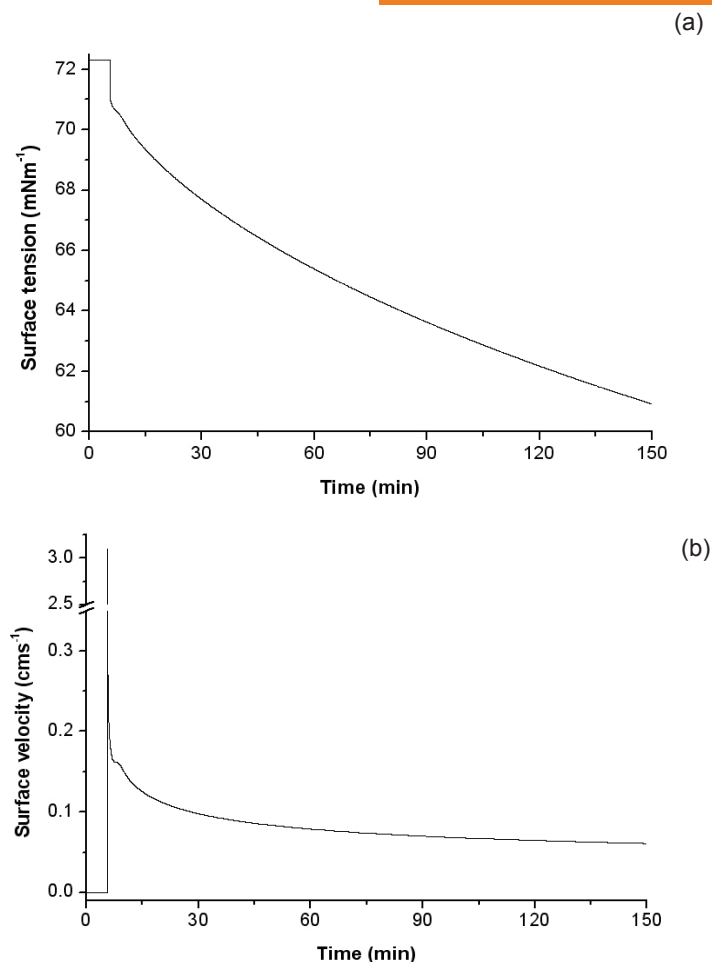


Figure 9. Results of numerical simulation on dissolution of a hexanol droplet under the air/water interface: vessel diameter $d=40$ mm, capillary immersion depth $h=4$ mm, buoyancy is neglected; a) Surface tension vs time, b) surface velocity vs time (reprinted from [43], with permission from American Physical Society).

to cause a change in the surface tension of 0.2 mN m^{-1} .

After the surfactant transfer due to Marangoni convection becomes comparable with that due to diffusion, the further growth of instability is very quick (Fig. 8b). The instability develops near the capillary, where the concentration gradients and hence the local Marangoni numbers are the highest [44]. Convection brings a large amount of surfactant to the interface in the capillary region and spreads it over the surface as shown in Fig. 10b. During a rather short time (about 20 s), the concentration profiles in the bulk change considerably due to convective transfer (Fig. 10b). The surface tension decreases abruptly at this moment, as shown in Fig. 8a.

It is instructive to follow the changes in the surface velocity during the short time interval corresponding to the first peak in Fig. 8b. They are presented in Fig. 11. The synchronous changes in the surface concentration are given in Fig. 12. The results in Fig. 12 are presented

in the terms of surface coverage, *i.e.*, the dimensional value of the Gibbs adsorption divided by Γ_m . This dimensionless group is included in the Szyszkowsky-Langmuir equation of state (Eq. 10).

The curves 1 in Figs. 11 and 12 correspond to the time of the instability growth. The surface velocity increases everywhere over the surface, but the concentration wave does not reach the container wall. When the surfactant wave reaches the container wall, the velocity gradient near the wall reaches the largest value (Fig. 11, curve 2) and therefore, very strong surface contraction occurs in the wall region. The surface contraction causes the increase of the surface concentration in the wall region and the reverse concentration gradient appears, as seen from the curve 2 in Fig. 12. At this point, the surface concentration is already large enough (Fig. 12, curve 2) to cause also a noticeable reverse gradient of the surface tension resulting in a decrease of the surface velocity near the wall, whereas in the middle part of the container the velocity still grows

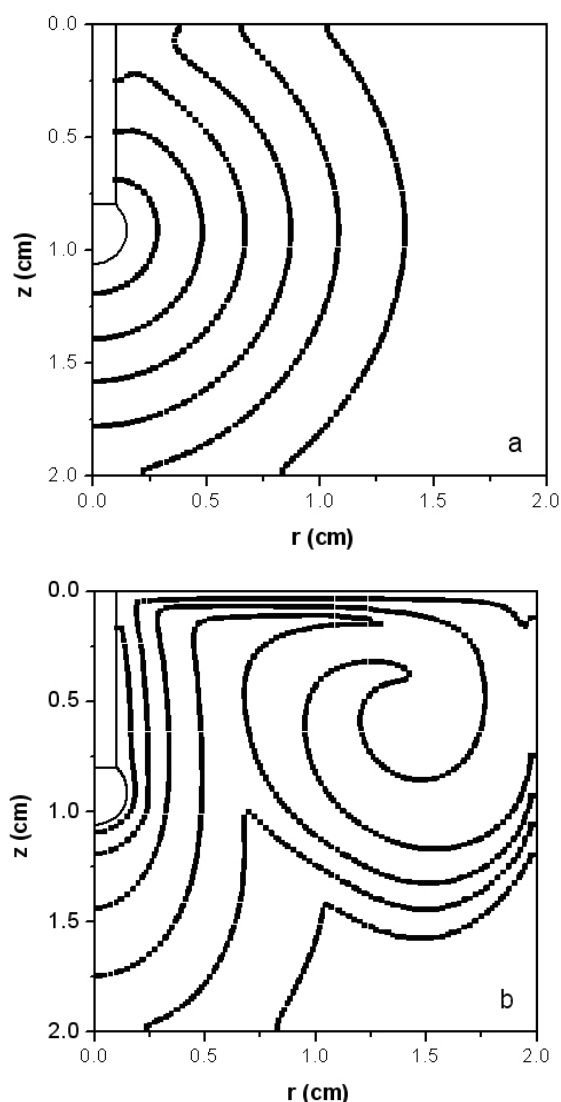


Figure 10. Numerical results on the concentration distribution by dissolution of a hexanol droplet under the air/water surface: a – $t=26$ min, b – $t=26$ min 20s (for the oscillatory regime shown in Fig. 8, (reprinted from [43], with permission from American Physical Society).

(Fig. 11, curve 3), being supported by the direct concentration gradient (Fig. 12, curve 3). The reverse concentration gradient, which is a manifestation of specific viscoelastic surface properties, develops over the larger part of the surface causing further decrease of the surface velocity.

In the capillary region the velocity gradient grows up to this time, resulting in a surface expansion. This expansion results in a lower surface concentration as compared with a non-deformable surface. At first the surfactant flux from the bulk to the surface is sufficient to provide the growth of the surface concentration all over the system and even the growth of the concentration

gradient in the capillary region. But after 26 min 13 s the velocity decrease due to the reverse concentration gradient leads to a decrease in the surfactant flux to the interface in the capillary region and the amount of the surfactant supplied to the interface becomes insufficient to support the direct concentration gradient. Therefore, despite the growth of the surface concentration everywhere on the surface, the surface concentration gradient being a driving force of the instability development decreases (Fig. 12 curve 4). The reverse concentration gradient becomes also smaller, but still exists and contributes to the suppressing of the convective motion as well.

According to the feedback described above, the decrease of the surface concentration gradient causes a decrease of the surface velocity (Fig. 11 curve 4). During certain time the surface concentration continues to grow (Fig. 12 curve 5), but the surface concentration gradient and the surface velocity decrease (Fig. 11 curve 5). During the fast convective stage the surfactant is supplied to the surface in a relatively small region near the capillary, spreading then over the surface. As a consequence, on the most part of the surface, the concentration in the bulk under the surface becomes lower than in the subsurface and, therefore, the diffusion transfer occurs from the subsurface to the adjacent bulk. When the convection is strong enough, the loss of the surfactant due to those diffusion fluxes is compensated by the surface convective fluxes. But when the velocity becomes too small to compensate the loss of the adsorbed surfactant, the surface concentration begins to decrease (Fig. 12 curve 6).

The instability growth slows down and starts to fade due to both the contraction of the surface in the wall region and the expansion of the surface in the capillary region where the surfactant is supplied to the interface. It should be, however, stressed that only the contraction in the wall region and the strength of the reverse gradient of the surface tension are crucial for the final dynamic regime established after the fast convective stage. If the reverse gradient of the surface tension is strong enough, it causes the movement of the liquid near the wall in the opposite direction, from the wall to the capillary (Fig. 13a), and the reverse convective roll extends over the surface (Fig. 13b). It is seen from Fig. 13b, that this reverse convective roll breaks up the surfactant supply to the surface in the capillary region. This means that in the considered case, the instability fully terminates and the system returns back to the slow diffusion stage of its evolution. As it was already mentioned, at this period of time the surfactant desorbs from the surface to come into equilibrium with the adjacent bulk. After the equilibrium between the subsurface and the adjacent

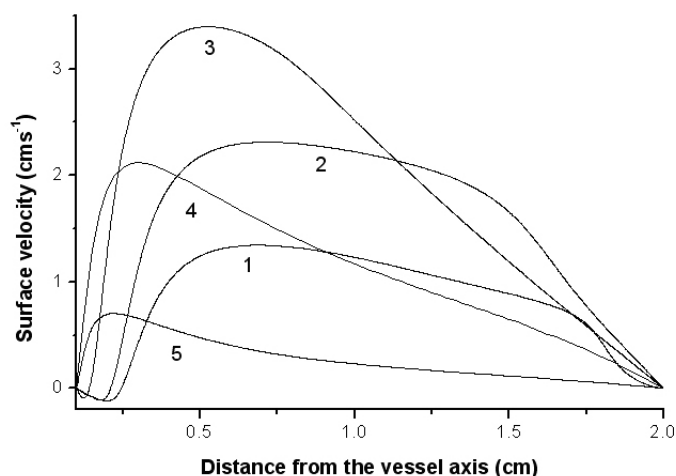


Figure 11. Numerical results on the radial distribution of the surface velocity by dissolution of a hexanol droplet under the air/water surface: 1 – $t=26$ min 11 s, 2 – $t=26$ min 12 s, 3 – $t=26$ min 13 s, 4 – $t=26$ min 14 s, 5 – $t=26$ min 20 s (for the oscillatory regime shown in Fig. 8, reprinted from [43], with permission from American Physical Society).

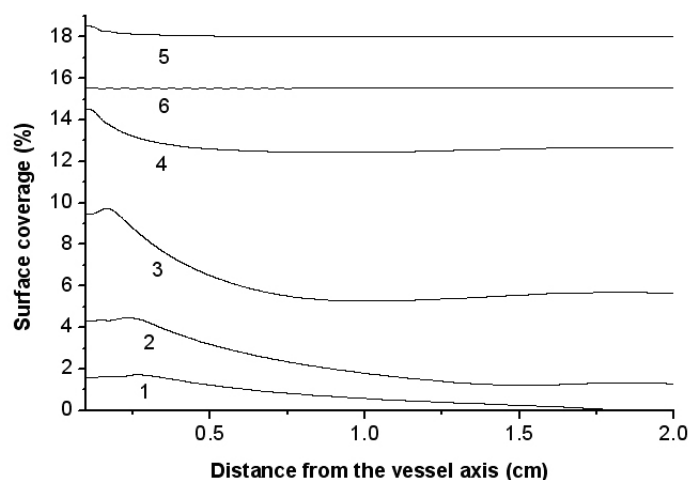


Figure 12. Numerical results on the radial distribution of the surface concentration by dissolution of a hexanol droplet under the air/water surface: 1 – $t=26$ min 11 s, 2 – $t=26$ min 12 s, 3 – $t=26$ min 13 s, 4 – $t=26$ min 14 s, 5 – $t=26$ min 20 s, 6 – $t=27$ min (for the oscillatory regime shown in Fig. 8).

bulk is reestablished, the instability develops again and the next oscillation begins. Thus, if the reverse gradient of the surface tension is strong enough, it causes the formation of the reverse convective roll, fully terminating the instability. This is a necessary condition for establishing of the oscillatory regime.

If the reverse gradient of the surface tension is weak, the reverse roll does not appear or it has not enough power to extend over the whole surface. In this case the convective flux to the interface remains in the capillary region and the convection stabilizes on the level where the release of the free energy in the system balances the mechanical dissipation. The regime of the quasi-steady convection establishes in the system. The relation between the maximum velocity reached

in the system during the instability development and the reverse gradient of the surface tension depends essentially on the system geometry. For a system which is infinite in the radial direction, the oscillatory regime does not appear at all, and only the regime with the quasi-steady convection takes place [45]. For the vessel of a finite radius, the regime is determined by the ratio of the capillary immersion depth to the vessel radius. According to the results of numerical simulations [42], both the increase of the vessel radius and the decrease of the capillary immersion depth result in an increase of the tangential gradients of the surface concentration, in a faster growth of the surface velocity, and thus, in a larger value of the maximum surface velocity. Obviously, the larger the maximum surface velocity,

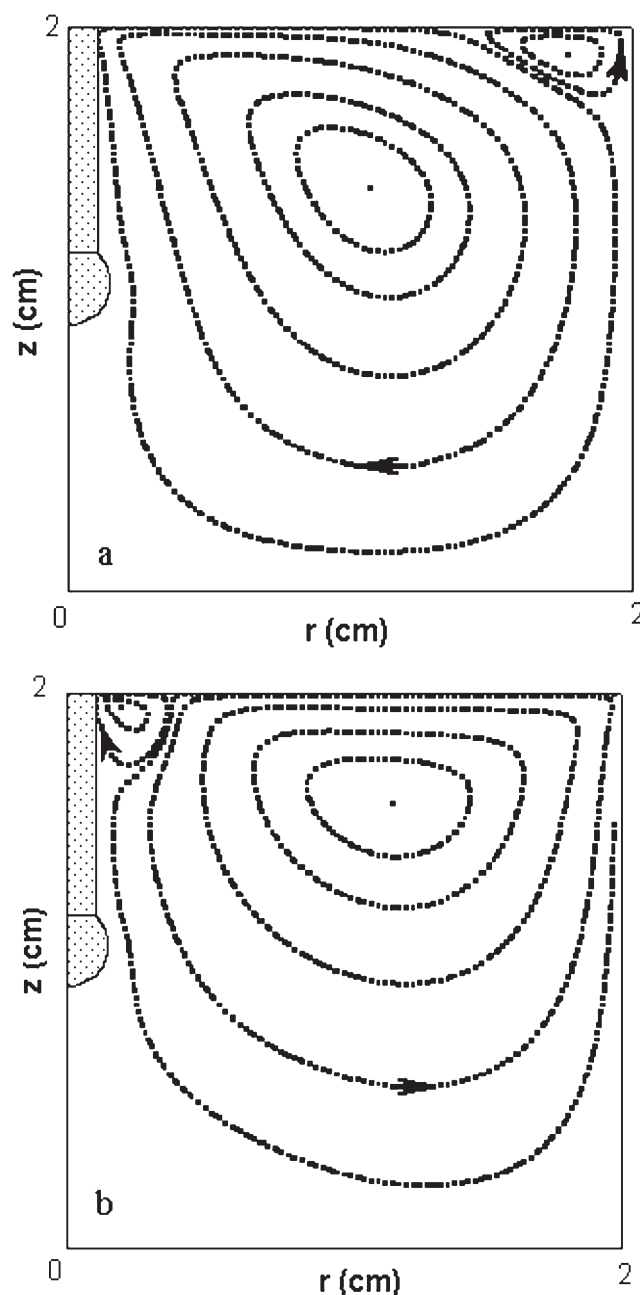


Figure 13. The reverse convective roll causing the return to the slow diffusion stage in oscillatory regime (numerical results, reprinted from [44], with permission from American Physical Society, see text for details).

the stronger the surface contraction, and therefore, larger reverse concentration gradient is expected. But of course, this relation is non-linear. According to [42], the reverse concentration gradient (and the surface tension gradient) increases slower than the surface velocity. Therefore, at certain critical value of the surface velocity, *i.e.*, at certain critical aspect ratio (the ratio of the capillary immersion depth to the vessel diameter), the oscillatory regime should be replaced by the regime

of quasi-steady convection. This numerical result is in full agreement with the experimental data [34].

The critical aspect ratio and the oscillation characteristics depend considerably on the properties of the surfactant used. For example, according to the results of numerical simulations, the increase of both the surfactant solubility and its surface activity should result in an increase of the oscillation amplitude. The increased surfactant solubility results in a shorter

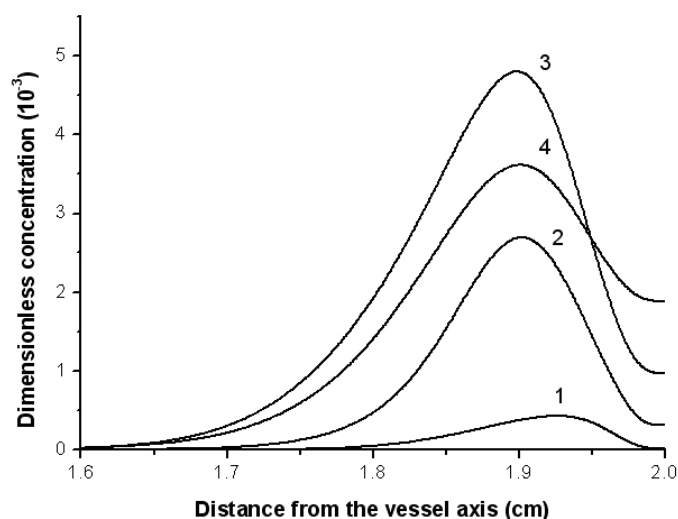


Figure 14. Numerical results on the distribution of the surfactant concentration in the bulk, 3 mm below the surface: 1 – $t=t^* + 2$ s, 2 – $t=t^* + 17$ s, 3 – $t=t^* + 55$ s, 4 – $t=t^* + 2$ min 19 s, t^* – the time when the surface velocity has a maximum. The surfactant properties: $\Gamma_m = 6.6 \times 10^{-6}$ mol m $^{-2}$, $K_L = 3.23$ m 3 mol $^{-1}$, $c_0 = 3.4$ mol m $^{-3}$, $\rho_0 \rho_s = 10^{-5}$ g cm $^{-3}$. The capillary immersion depth $h = 8$ mm (reprinted with permission from [40], copyright (2005) American Chemical Society).

oscillation period, whereas the higher surface activity increases it [44]. Considering aliphatic alcohols, for which the solubility decreases with the increase of the chain length, whereas the surface activity increases, one can expect that the oscillation amplitude does not change essentially in this series because of the opposite effects of the solubility and surface activity, but the oscillation period should decrease with the decrease of chain length. This prediction is in a good agreement with the experimental data presented in Fig. 7.

The dependence of the solution density on surfactant concentration was neglected in the foregoing consideration. However, this property also affects considerably the system dynamics, as shown in [40]. The difference in the solution densities at different concentrations causes the buoyancy convection. If the solution density decreases with the increase in the concentration, as in the series of aliphatic alcohols, then the direction of the buoyancy convection coincides with that presented in Fig. 2. Buoyancy intensifies considerably the surfactant transfer in the system with respect to the pure diffusional case. As a result, the induction period and the period of oscillation decrease with the increase of buoyancy, whereas the changes in the oscillation amplitude are insignificant [40]. The changes in the oscillation period observed experimentally in the series of aliphatic alcohols are to a large extent due to buoyancy, because the density of the saturated solution decreases considerably with the decrease of the chain length. The critical aspect ratio designating the transition from the oscillatory regime to the regime of quasi-steady convection increases with the increase

of the buoyancy force.

It is noteworthy that the buoyancy contributes also to the instability termination. The reverse concentration gradient appears also in the bulk solution near the wall, because after the surface contraction an excess of the surfactant desorbs and distributes in the bulk. Fig. 14 demonstrates that this reverse concentration gradient in the bulk solution preserves during a rather long time. It results in the buoyancy force which promotes the liquid in the bulk near the wall to move upwards, and therefore, the liquid on the surface to move in the direction from the wall to the capillary, *i.e.*, in the same direction as the reverse gradient of the surface tension does. Thus, the change in the density difference between the solvent and the surfactant solution is also one of ways to control the dynamic regimes and the oscillation characteristics in the systems with a dissolving surfactant droplet.

3.4. Control of the dynamic regimes and oscillations characteristics

The oscillations produced by the dissolution of a surfactant droplet under the liquid surface are an impressive example of a motor based on a direct transformation of chemical energy to the energy of mechanical motion. By using a small amount of a surfactant, of several microliters only, the regular oscillations in the liquid can be sustained for many hours. For example, the oscillations in the system with an octanol droplet have been observed during 72 hours [33]. The intensity and periodicity of the motion can be regulated using different surfactants and changing the system geometry. Understanding the oscillation

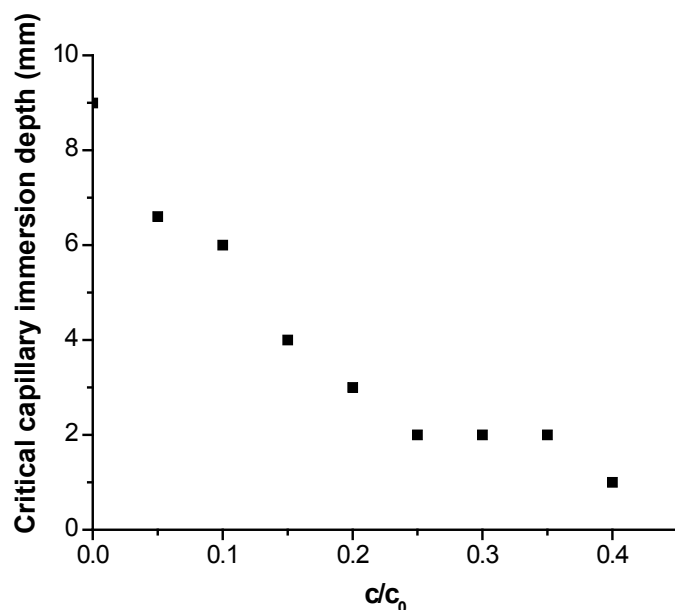


Figure 15. Dependence of the critical capillary immersion depth dividing the oscillatory regime and the regime of steady convection by the dissolution of a heptanol droplet on the initial concentration of heptanol in the liquid bulk; the vessel diameter 40 mm (reprinted from [36], with permission from Elsevier).

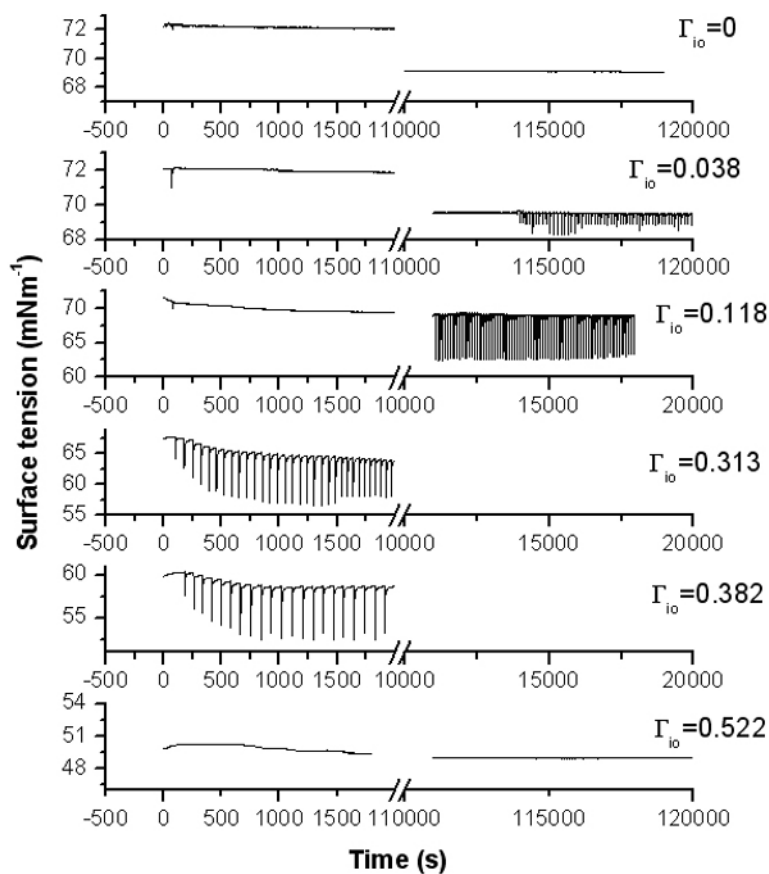


Figure 16. Dynamic regimes by dissolution of a heptanol droplet in the presence of a spread monolayer of DMPC (L- α -phosphatidylcholine, dimyristoyl), the initial surface coverage is shown on the curves, the vessel diameter $d=75$ mm, the capillary immersion depth $h=1$ mm (reprinted from [35], with permission from Elsevier).

mechanism enables proposing supplementary tools for the control of the oscillations.

As it was discussed above, the oscillation characteristics depend on the surfactant properties, in particular on the surface activity. For weak acid or weak base surfactants, the degree of dissociation depends on pH. Often dissociated and non-dissociated forms have very different surface activities. This is the case for fatty acids. For example, the surface activity of non-dissociated octanoic acid is about 100 times larger than that of dissociated form. At the same time the surface activity of a dissociated acid can be augmented by the increase of the ionic strength of the solution. Numerical [39] as well as experimental [38,39] studies of the fatty acid systems have shown that indeed by the increase of pH the oscillation amplitude decreases and at pH 7 the oscillations are not detectable any more. When keeping the same pH 7 and increasing the ionic strength of the solution by adding salt, the oscillation amplitude increases and well detectable oscillations are observed already at 0.5 M of 1:1 electrolyte.

Another way to control the dynamic regimes by the dissolution of a surfactant droplet is based on understanding of the mechanism of instability termination due to the reverse gradient of surface tension. According to Eq. 10, the dependence of the surface tension on the surface coverage is strongly non-linear and becomes steeper with increasing surface coverage. Therefore, the easiest way to increase the reverse gradient of the surface tension and to provide the oscillatory regime instead of the quasi-steady convection is to increase the initial value of the surface coverage. The numerical simulations have predicted such transition for two different cases: the initial presence of a soluble surfactant in the liquid bulk [36] and the initial presence of a spread monolayer of an insoluble surfactant on the interface [35]. The possibility of a combined regime was first predicted and observed in [35]. It occurs because the accumulation of the surfactant and the increase of the surface coverage cause a decrease in the critical aspect ratio and therefore, if the adsorption process continues during a long enough time, the actual capillary immersion depth becomes larger than the critical one for the given surface coverage.

In the system with a heptanol droplet, the essential decrease of the critical capillary immersion depth occurs at the initial presence of heptanol in the bulk phase with the concentration of about 10-20% of the solubility limit (Fig. 15) [36]. In the presence of a spread monolayer, the transition from the quasi-steady convection regime to the oscillatory regime occurs *via* the intermediate combined regime present in a broad range of the initial surface coverage (Fig. 16). When the surface coverage

becomes sufficiently large, of 52.2%, the oscillations are absent as the instability cannot develop under such conditions.

4. Conclusions

The systems with a surfactant droplet dissolving under an air/water interface undergo the Marangoni instability. The instability can develop as a quasi-steady convection or as a spontaneous non-linear oscillation. A combined regime can be also observed when the quasi-steady convection after certain time is replaced by the oscillatory regime. The particular dynamic regime and the oscillation characteristics (period, amplitude and induction period before the oscillation) depend on the surfactant properties and the aspect ratio of the system.

The numerical simulations using the mathematical model based on the first principles, namely the Navier-Stokes, continuity and convective diffusion equations with the appropriate boundary conditions, have shown that the oscillations are a result of periodically arising and terminating Marangoni instability. The local contraction of the adsorbed monolayer, causing the appearance of the elastic force that opposes the development of the instability, is the main reason for the instability termination.

The results of the numerical simulations are in a good agreement with the experimental data. In particular, it has been shown theoretically and experimentally that the dynamic regimes and the oscillation characteristics can be controlled by methods such as changing the pH and the ionic strength, as well as the addition of a surfactant in the bulk or on the surface.

The presented results give a clue for understanding the behavior of the more complicated systems, some of which will be considered in the forthcoming review. They also can be used in many practically important applications, such as in the studies of adsorption kinetics, stability of thin liquid films, foams and emulsions, liquid/liquid extraction, microfluidics *etc.*

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