Spontaneous non-linear oscillations of interfacial tension at oil/water interface

Abstract: Three particular systems are considered where transfer of a surfactant across the interface between two immiscible liquids, water and oil, is accompanied by spontaneous oscillations of relaxation type with an abrupt decrease of interfacial tension followed by its gradual increase. These oscillations cannot be explained in the frameworks of linear stability analysis, because they are related to essentially non-linear effects. The oscillations characteristics depend on the properties of a surfactant (interfacial activity, solubility, partition coefficient, density difference between the surfactant solution and pure solvent), other solutes present in one or both liquid phases, and, usually, also on the system geometry. If the transferred surfactant is an ionic one, then, the oscillations of interfacial tension are synchronised with the oscillations of electric potential across the interface. The available hypothesis about oscillations mechanism are discussed, in particular, the model proposed recently for oscillations due to Marangoni instability by surfactant transfer from a point source located in one of the liquid bulk phases.

Keywords: self-organization, systems far from equilibrium, Marangoni instability, electrical potential oscillations, liquid membrane.

1 Introduction

Spontaneous oscillations arising by a surfactant transfer to or across the liquid interface are one of the impressive examples of self-organization in the systems far from equilibrium. Elucidation of the oscillations mechanism and the methods enabling control of oscillations appearance and characteristics are of great fundamental and practical importance, in particular, for liquid/liquid extraction, stability of foams and emulsions, correct measurement of dynamic surface tension, chemical motors for microfluidic devices, understanding the rhythmic processes in living organisms etc.

Usually, spontaneous development of oscillations or a steady convection accompanying surfactant transfer in systems far from equilibrium is related to the development of Marangoni instability and can be predicted using the criteria derived on the base of linear stability analysis [1-4]. The Marangoni instability is directly related to the Marangoni effect, which is the development of convective motion in the bulk of liquid due to an imposed gradient of interfacial tension. The gradient of interfacial tension can appear as a result of non-uniform distribution of temperature or a surfactant over the interface. If this gradient is supported during a set time on approximately the same level, one can observe a steady (or quasi-steady) convection. When the gradient disappears, convection terminates due to viscous dissipation. The imposed tangential gradient is not necessary for the onset of Marangoni instability. There are always fluctuations of concentration or temperature at the interface and therefore some weak chaotic convection on a microscopic level. The instability develops if these fluctuations amplify themselves to a macroscopic scale by bringing to the point of lower surface tension more warm liquid or more concentrated surfactant solution. It should be stressed, therefore, that the Marangoni effect requires the existence of an imposed tangential gradient of concentration or temperature at the interface and therefore some weak chaotic convection on a microscopic level. The instability develops if these fluctuations amplify themselves to a macroscopic scale by bringing to the point of lower surface tension more warm liquid or more concentrated surfactant solution. It should be stressed, therefore, that the Marangoni effect requires the existence of an imposed tangential gradient of concentration or temperature at the interface, whereas Marangoni instability can develop without it, since during the instability development, this macroscopic tangential gradient appears spontaneously due to the existence of a normal gradient.

The instability criteria and the mechanism of the solutal Marangoni instability are discussed shortly in the recent review [5] where the oscillations generated at air/water interface due to transfer of a surfactant from a small source located within the bulk have been considered both from theoretical and experimental points of view.
The system discussed in [5] is of interest because with the same surfactant it can demonstrate either a quasi-steady behavior or oscillations (depending, in particular, on the system geometry or on the initial presence of a surfactant within the bulk or on the interface), whereas linear stability analysis predicts only steady convection under such circumstances. This contradiction arises because the established dynamic regimes observed in experiments depend on specific properties of the adsorbed surfactant layer as well as on some non-linear effects, and, therefore, cannot be predicted in the frameworks of linear stability analysis.

Below, we consider three particular systems also demonstrating spontaneous oscillations, but at liquid/liquid interface. The first one is similar to that considered in [5], but with a liquid as a second fluid phase instead of air. This system is very simple from the chemical point of view, because oscillations can be generated with only one solute transferred and without any chemical reactions. The second system considered consists also of two liquid layers, but with a surfactant initially being uniformly distributed in one of the liquid phases with partition in favor of another liquid phase. This system typically contains a non-surface active solute in the second liquid phase, with partition equilibrium in favor of the first liquid. The transfer of both solutes occurs simultaneously with possible chemical reaction between them in the interfacial region. Therefore, this system is more complicated chemically as compared to the first one, and in this case, the role of surface chemistry in the system dynamics is not as straightforward. The third one is the liquid membrane system, where surfactant is transferred from a donor phase to an acceptor phase through a liquid membrane. This system is even more complicated from a chemical point of view, because usually a variety of solutes are added to each of three liquid phases.

For the second and third systems, there is no generally accepted mechanism of oscillations. Therefore, we will discuss the experimental and numerical data and the available hypothesis concerning the oscillations mechanism in these systems. Similarity of the processes in all three systems is clearly displayed. At the same time, instability development and oscillations characteristics are strongly dependent on possible chemical reactions in such systems. Some studies on the oscillations in the mentioned systems have been discussed earlier in [6]. The present review is focused on the more recent results, but for the sake of connectedness, the most important results included in [6] are considered as well.

2 Oscillations due to surfactant supply from a point source in the bulk

The first system displaying non-linear spontaneous oscillations at the liquid/liquid interface is presented in Fig. 1 [7,8]. It consists of two immiscible liquid layers, for example water as the lower phase, and an alkane as the upper phase, gently placed one over the other in a cylindrical cell. The surfactant source is a small droplet of a sparingly soluble surfactant formed at the capillary tip in the aqueous phase. A freshly annealed platinum Wilhelmy plate connected to an electronic balance is used for the measurement of interfacial tension.

The direct numerical simulations performed with a mathematical model, similar to that discussed in [5] and based on the Navier-Stokes, continuity and convective diffusion equations with appropriate boundary conditions have shown [7] that the dynamic behaviour of this system is governed by the mechanisms very similar to those considered in [5] for the air/water interface. These mechanisms can be shortly explained as follows.

After the droplet is formed at the tip of the capillary, the surfactant dissolves from the droplet and transfers over the system due to diffusion and buoyancy driven convection. The intensity of convection depends on the density difference between pure water and the surfactant
solution. If the solution density is lower than the density of water, then, the buoyancy driven convection is directed upwards near the capillary, and the streamline distribution is that shown in Fig. 1 (lower phase). Due to viscosity, the movement is transferred into the upper liquid phase (oil). The streamline distribution in the upper phase is also shown in Fig. 1. The driving force of buoyancy convection is the density difference between the concentrated surfactant solution near the droplet and the diluted solution far from the droplet. However, convection mixes the solution; therefore, after set time, the buoyancy driven convection begins to slow down which is confirmed by the numerical simulations for air/water interface [9].

As it is clear from Fig. 1, both diffusion and buoyancy driven convection in the water phase bring more surfactant to the capillary region than to more distant parts of the interface. Therefore, after a set time, when the surfactant reaches the interface, the concentration gradient and, as a consequence, the surface tension gradient occurs on the interface causing interfacial convection, named Marangoni convection. This convection is directed from the capillary to the wall, i.e., the Marangoni convection has the same direction as buoyancy convection and enhances it. Certain amount of surfactant desorbs from the interface into the oil phase according to the partition equilibrium. Therefore, the larger the surfactant partition coefficient between the oil and water, the smaller the interfacial concentration gradient and, so, slower Marangoni convection. Note: according to the streamline distribution shown in Fig. 1, the convection in the upper phase brings to the capillary region more diluted solution from the bulk. Therefore, the intensity of the Marangoni convection is determined also by the viscosity and the surfactant diffusion coefficient in the oil.

Dissolution of the surfactant in the oil phase changes its density, and the buoyancy force appears in this phase as well. It can support or suppress Marangoni convection depending on the sign of the density changes. However, the effect of buoyancy in the oil phase is usually rather weak because of the relatively small bulk concentration gradients. Numerical simulations have shown that the effect of buoyancy in the oil phase can be neglected if the density difference between the pure oil and saturated surfactant solution is less than $10^{-3}$ g cm$^{-3}$. At the same time, the buoyancy driven convection in the water phase has a considerable impact on the system behaviour already at the density difference of $10^{-6}$ g cm$^{-3}$ [7].

For the Marangoni convection, there is a feedback in the system enabling its growth due to development of Marangoni instability: convection brings more surfactant to the interface in the capillary region, increasing in this way the gradient of interfacial tension which results in a further increase of the Marangoni flow. Initially, the Marangoni convection is weak and the surfactant transfer by this mechanism is negligible but increases with time. The effect of the feedback becomes essential after the contribution of Marangoni convection in the surfactant transfer becomes comparable with the transfer due to diffusion and buoyancy driven convection. Therefore, the instability develops after set induction period and results in a considerable intensification of convection in the system bringing a large amount of surfactant and spreading it over the interface. The interfacial tension decreases abruptly at this moment, as it is shown in Figs. 2 and 3.

When the wave spreading the surfactant over the interface reaches the wall of the cell, the surfactant cannot penetrate through the wall and should remain there. It cannot leave the interface instantaneously as desorption is controlled by the diffusion in normal to the interface direction and is slower than the surfactant spreading at the interface. Therefore, the excess of the surfactant accumulates in the wall region resulting in a reverse gradient of the interfacial tension suppressing convection. However, due to inertia, convection does not stop immediately but slows down with the gradually increasing reverse gradient.

Dissolution of the surfactant into the water bulk causes the reverse buoyancy force near the wall. Corresponding buoyancy force in the oil phase should also be taken into account. Its value and direction depends on the density difference between pure oil and surfactant solution.

If the reverse gradient of the interfacial tension and buoyancy are not strong enough to cease the convection, then, a regime of quasi-stationary convection establishes with a gradual monotonic decrease of the interfacial tension after a single oscillation (curves 1 and 2 in Fig. 2). Note: however, after a sufficient amount of surfactant has accumulated in the interface, an oscillatory regime can spontaneously replace the regime of steady convection, as discussed in details in [10,11].

When the reverse gradients are strong enough, the convection terminates completely. This occurs as the reverse convective roll spreads from the wall region over the whole system (Fig. 4). The velocity in this roll is very low, but it is directed opposite to the initial roll shown in Fig. 1. When the reverse roll captures all the system (Fig. 4c) and breaks up the surfactant supply from the droplet to the interface, instability terminates. At this time, surfactant desorbs from the interface to re-establish equilibrium with the adjacent bulk phases. The interfacial tension increases gradually (Fig. 3). After
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A set time, diffusion and buoyancy (now being weaker because of mixing) bring new portions of the surfactant to the interface in the capillary region. This results in development of a new convective roll with interfacial flow directed from the capillary to the wall, initially near the capillary. The reverse roll shrinks then (Fig. 4d) and eventually disappears. The Marangoni instability develops again giving rise to the next oscillation. The regime with repeated oscillations establishes in the system.

According to numerical simulations [7] confirmed by the experimental study [7,8], the dynamic regime accompanying the droplet dissolution under liquid/liquid interface depends on the surfactant properties and the capillary immersion depth (at constant vessel diameter) similar to air/water interface. The experimental examples for the series of aliphatic alcohols are given in Fig. 2. Here the upper liquid phase was heptane. It is seen that dissolution of octanol and heptanol droplets result in oscillatory regime; whereas, for hexanol and pentanol, a combined regime takes place: first a regime of quasi-steady convection develops with monotonous decrease of the interfacial tension, which is replaced later by the oscillatory regime. The comparison of curves 1 and 2 in Fig. 2 shows that during the regime of quasi-steady convection, the interfacial tension decreases faster in the case of pentanol droplet. As the surface activity of pentanol is lower than that of hexanol, it is obvious that the convection is more intensive in the case of pentanol because much more surfactant is necessary to provide such changes in the interfacial tension.

When the amount of surfactant accumulated at the interface becomes large enough, the oscillatory regime establishes in the system [9,10]. As it was already discussed in [5] for air/water interface, the critical capillary immersion depth corresponding to the transition from the oscillatory regime to the regime of quasi-steady convection increases with the decrease of the chain length of alcohol. The same is true for the oil/water interface considered in [7,8]. Namely, for the system presented in Fig. 2, the increase of the capillary immersion depth to h=14 mm results in transition to pure oscillatory regime for the hexanol droplet, whereas a combined regime is still observed for the pentanol droplet. Summarising, it should be stressed that the change of the regime can be observed for surfactants with any chain length, but it occurs at different capillary immersion depths. The threshold depth is larger for the shorter chain lengths.

The effect of the surfactant properties, considered earlier for air/water interface [9,12], is, on the whole, true for liquid/liquid interface as well [7,8]. So, an increase in the density difference between pure water and saturated surfactant solution results in a decrease of induction period as well as oscillation period. An increase of either surfactant solubility or surface activity results in an increase of the oscillation amplitude. An increase of surface activity causes an increase of oscillation period, whereas an increase of solubility acts in the opposite direction. The effect of activity is, however, more pronounced. That is why the oscillation period increases with an increase in the surface activity of surfactant provided that the product of solubility and activity remains constant. The latter is the case for the series of aliphatic alcohols. Therefore, in the series of aliphatic alcohols, according to the model proposed, oscillation periods should increase with the increase of the chain length because of i) the increase of activity and ii) the increase of the density difference between the pure water and the saturated surfactant solution. This conclusion is consistent with the experimental results presented in Fig. 2.

At the same time, new affecting parameters appear in liquid/liquid system, namely viscosity of the second liquid phase, diffusion coefficient of the surfactant in the second
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liquid, and the dependence of density of the second liquid on surfactant concentration. The effect of these parameters is also discussed in [7], where it was shown that the most important new parameter is the partition coefficient of the surfactant between oil and water. With an increase of the partition coefficient, the oscillation amplitude decreases; and at large enough values, the oscillations become non-detectable. The experimental validation of this theoretical prediction is given in Fig. 3. In Fig. 3a, there is a comparison of oscillations accompanying the dissolution of a pentanol droplet under heptane/water and air/water interfaces. The partition coefficient of pentanol between heptane and water is about 1, and the amplitude of oscillations on heptane/water interface is only slightly smaller than that on air/water interface. Fig. 3b shows the oscillations produced by an octanol droplet. The partition coefficient of octanol between heptane and water is about 40, and the amplitude of oscillations at the heptane/water interface is much smaller than that at the air/water interface.

Another configuration of the system with a surfactant source in bulk was proposed in [13-18]. Interfacial tension was measured by the quasi-elastic laser scattering method which enabled the measurement without any perturbation of the system. Experiments were performed in a quartz cell either cylindrical (of inner diameter 36 mm [15,16]) or with a square cross section (40×40 mm²) [17,18]. In [17,18], the inner wall of the cell was modified with 10% solution of octadecyltrichlorosilane in toluene to prevent meniscus formation. Oscillations were observed in both types of cell.

Figure 3: Spontaneous oscillations of the interfacial tension produced by a) pentanol droplet, b) octanol droplet: 1 – air/water interface, 2 – heptane/water interface. Reprinted with permission from [7]. Copyright 2005 American Chemical Society.

Figure 4: Streamlined distribution during the termination of the Marangoni instability at liquid/liquid interface (see text for details). Reprinted with permission from [7]. Copyright 2005 American Chemical Society.
A surfactant was supplied continuously with a prescribed rate through the tip of a syringe with an orifice of 0.3 mm. The employing of the continuous supply of the surfactant enabled the experiments with surfactants having high solubility in water, notably with micellar solutions. In particular, in experiments presented in [13-17], aqueous solutions of sodium alkyl sulphates were used as a surfactant source. A wide range of surfactants, cationic, anionic, zwitterionic and non-ionic have been studied in [18]. The syringe tip was placed into water, which was an upper liquid phase, whereas nitrobenzene was used as a lower liquid phase. The density of solutions of sodium alkyl sulphates is larger than the density of water [15]; therefore, the streamlines distribution for the buoyancy driven convection is similar to that shown in Fig. 1, i.e., the surfactant flow is directed toward the interface. The buoyancy convection is enhanced by the solution flux from the syringe having the same direction. Therefore, the surfactant transfer results in the formation of surfactant concentration gradient at the interface and the development of Marangoni convection directed from the point below the syringe tip to the vessel wall on the interface. The highest concentration of the surfactant is at the syringe tip. Therefore, there is the same feedback, as considered above, and Marangoni instability can develop as well. It is also obvious that for such a system geometry, the instability growth can be terminated by the mechanism discussed above.

Experimental study performed in [14-18] has shown that, similarly to the experiments with surfactant droplets, in the system with continuous supply of the surfactant solution through the syringe tip, interfacial tension remained constant during certain induction period. Then, spontaneous oscillations started with an abrupt decrease of the interfacial tension followed by its gradual increase. Visualisation with Eriochrome Black [17] has shown that the induction period corresponds to the time necessary for the surfactant to reach the interface. The abrupt decrease of interfacial tension was always accompanied by quick convective motions terminated when the interfacial tension began to increase. For ionic surfactants, the synchronous changes in the electrical potential between water and nitrobenzene were observed as shown in Fig. 5. It is interesting, that, when only a certain limited volume of surfactant solution was injected and after that the surfactant supply was stopped, only single oscillation was observed after the induction period [13]. Using a continuous supply of the surfactant during a long time [14-18], the following regularities were found.

When, keeping all other parameters constant, the distance between the tip of the syringe and the interface decreased, the regime with repeated oscillations was replaced with the regime with only one oscillation [15]. This result is in full agreement with the discussed above experimental and numerical results concerning the dissolution of a droplet [7]. If, keeping the distance between the tip of the syringe and the interface small, the rate of the surfactant supply decreased, then at a certain rate, the system returns again to the regime with repeated oscillations [15]. For example, for 10 mM solution of sodium dodecyl sulphate (SDS) at the supply rate 3 µL min\(^{-1}\) the repeated oscillations were observed at the distance between the syringe tip and the interface of h=8 mm; whereas, the only single oscillation (i.e., the regime of quasi-steady convection) was observed at h=2 mm. The repeated oscillations developed at h=2 mm if the supply rate decreased to 0.5 µL min\(^{-1}\). Comparison of oscillations obtained at h=2 with supply rates of 0.5 µL min\(^{-1}\) and 0.3 µL min\(^{-1}\) shows that a decrease of the supply rate results in an increase of the oscillation period and amplitude [15]. These results are also consistent with the model discussed above. The changes in the supply rate can be, as the first approximation, interpreted as changes in the buoyancy force or in the surfactant solubility for the case of the system with a dissolving droplet. According to the numerical simulations performed for water/air interface [9,12] and confirmed for the water/oil interface [7], a decrease of both buoyancy and surfactant solubility results in a decrease of the critical distance to the capillary, corresponding to the transition from oscillatory to quasi-stationary regime, as well as in an increase of the oscillation period in the oscillatory regime.

Figure 5: Synchronous spontaneous oscillations of interfacial tension and electrical potential between water and nitrobenzene accompanying the supply of SDS solution (10 mM) through the tip of a syringe situated at 8 mm from the water/nitrobenzene interface. The supply rate is 3 µL min\(^{-1}\). Reprinted with permission from [15]. Copyright 2004 Elsevier.
In the study reported in [16], the surfactant concentration in the injected solution, the flow rate, and the distance from the injection point to the interface were kept constant, 10 mM, 5 µL min⁻¹, and 2 mm, respectively. The varied parameter was the chain length of sodium alkyl sulphate, CₙH₂ₙ₊₁SO₄Na. The substances with n=6, 8, 10, 12 and 14 were used. In this series, the surface activity increases with the increase of the chain length. Experimental study performed in [16] has shown that repeated oscillations have been observed for the substances with n=6, 8 and 10, whereas, only a single oscillation was detected for n= 12 and 14. Visualisation of the interfacial flow with carbon powder located at the interface has shown that the abrupt decrease of the interfacial tension was accompanied by rapid surface convection directed from the cell axis to the wall. The simultaneous measurement of interfacial tension in the point under the syringe orifice and at the distance 15 mm from that point performed in [17] has shown that this motion is the result of the surface tension gradient. Convection was fully terminated after about 1 s in the case of repeated oscillations, whereas weak convection lasted a rather long time in the case of the single oscillation. This observation is in agreement with the results obtained for the system with a dissolving droplet. Visualisation experiments enabled the estimation of the maximum surface velocity during the first oscillation. It increased from 3.5 cm s⁻¹ for C₆H₁₄SO₄Na to 18.4 cm s⁻¹ for C₁₄H₂₉SO₄Na [16]. It is noteworthy that the direct causation between an increase of the maximum surface velocity and the transition from the regime with repeated oscillations to the regime with only single oscillation was discussed in [12]. According to [16], the oscillation period increases with the increase of the surfactant chain length, i.e., with the increase of surface activity, what is also consistent with the numerical results presented in [12].

The experiments discussed in [14-16] were performed in the presence of supporting electrolytes, 0.1 M tetra-n-butylammonium tetraphenylborate in nitrobenzene and 0.1 M LiCl in water enabling the measurements of electrical potential between the liquid phases. As the behavior of the electrical potential is synchronized with that of interfacial tension, the last characteristic was measured in [17,18]. According to [18], an increase in the electrolyte concentration resulted in an increase of oscillation amplitude for ionic surfactants, most probably due to the increase of surfactant activity. The measurements in [17] were performed with 10 mM SDS solution without supporting electrolytes, but the effect of one of those electrolytes, LiCl, on the oscillations characteristics was studied in detail. The decrease of LiCl concentration in the aqueous phase from 0.1 M to 0 resulted in a decrease of the oscillation period and amplitude, so in the absence of LiCl, the oscillation of interfacial tension was observed immediately under the syringe orifice, but no changes were detected at the distance 15 mm. The reason for such behavior is probably related to an essential increase in the solubility of surfactant in water and a decrease of its activity with a decrease of the electrolyte concentration. The changes in the activity and solubility compensate each other to some extent; therefore one can expect that the amount of surfactant adsorbed under the syringe tip depends only weakly on the electrolyte concentration. At the same time, desorption will be more intensive for smaller concentrations of electrolyte because of the increased solubility. It is, however, obvious that further study, experimental as well as theoretical, is necessary to understand clearly the effect of added electrolyte.

Additional study is necessary also to explain the effect of small amounts of tetra-N-butylammonium bromide added to nitrobenzene phase in the system with supporting electrolytes [14]. Tetra-N-butylammonium bromide dissociates in nitrobenzene on the tetra-N-butylammonium ion, already present here because of dissociation 0.1 M tetra-N-butylammonium tetraphenylborate, and Br⁻. As the maximum concentration of tetra-N-butylammonium bromide added is 10⁻⁶ M, the change in the concentration of the cation is negligible (in comparison to 0.1 M). Therefore, the effect can be related only to the anion Br⁻, soluble also in water. According to [14], addition of already ionized 10⁻⁶ M tetra-N-butylammonium bromide results in an acceleration of relaxation after the abrupt decrease of interfacial tension. At 10⁻⁴ M, the acceleration becomes more pronounced. The effect depends on the anion used and decreases in the series Cl⁻, Br⁻, I⁻.

Summarizing, spontaneous oscillations at liquid/liquid interface by surfactant supply from a point source situated in liquid bulk can be generated for two different system configurations: i) dissolution of a droplet of a sparingly soluble surfactant and ii) continuous supply of a surfactant solution through the tip of a syringe. The experimental results obtained in both configurations are in good agreement with each other and are consistent with the results of numerical simulations performed for the system i). The qualitative mechanism, proposed in [15,16], for oscillation in the system ii) in essential features agrees with the mechanism proposed in [7] for the system i). According to this mechanism, abrupt decrease of interfacial tension is the result of fast surfactant adsorption due to spontaneously arising Marangoni instability. Repeated oscillations appear in the case when instability terminates after a short time. If the surface velocity achieved during the instability development is
3 Oscillations by transfer across liquid membrane

The liquid membrane system (LM) [19] is well known in science and in industry, first of all as a separating tool enabling, for example, selective extraction of ions, including those of heavy metals, from low-concentrated solutions [20-22]. It consists of two aqueous liquid layers, one of them, named donor phase (source or feed phase), contains a mixture of solutes including that of the interest (analyte), whereas another one, being acceptor (receiver, strip, product) phase, is destined for collection of the analyte. The aqueous phases are interposed by a layer of immiscible organic solvent, being the liquid membrane itself. This organic phase usually contains a solute (carrier) selectively interacting with the solute of the interest from the aqueous donor phase. The carrier transfers the analyte to the membrane/acceptor interface and releases it into the acceptor phase.

Three main types of liquid membrane systems are known [19-21]. In the supported liquid membrane systems (SLM), the organic phase is located in the supporting porous medium. The emulsion liquid membrane system (ELM) is double water in oil in water emulsion. These liquid membrane systems, due to their high productivity, are mainly used in industry. The bulk liquid membrane system (BLM) is the simplest one in which two aqueous phases are separated by an organic layer without any support. Geometrically, such system can be realized by using U-shaped tube (Fig. 6a), upward or downward depending on the density of organic phase or by using a hollow tube inserted in the cylindrical vessel (Fig. 6b). This type of LM is suitable for physicochemical studies because its geometry simplifies considerably the theoretical description, but it is rarely used in industry because of relatively low productivity.

Spontaneous non-linear oscillations generated in bulk liquid membrane system were first discovered and studied by Yoshikawa and Matsubara [23,24]. Noteworthy, that in [23,24] and in the most subsequent studies the measured quantity was the electrical potential difference between the phases composing the liquid membrane system. However, as it will be discussed below, the changes in the electrical potential are synchronized with the changes in the interfacial tension at one of the interfaces involved.

Yoshikawa and Matsubara [23,24] used a 1.5 mM solution of picric acid in nitrobenzene placed at the bottom of U-shaped tube as a membrane, an aqueous solution of hexadecyl trimethyl ammonium bromide (CTAB) and either a short chain aliphatic alcohol (from the series from methanol to propanol) or benzyl alcohol as a donor phase, and aqueous solution of either 3 M NaCl, 3 M LiCl, 0.1 M potassium phosphate buffer or 0.1 M sucrose as an acceptor phase. In these experiments, the electrical potential difference between the donor and acceptor phases began to oscillate after an induction period of several minutes. The oscillations have the shape of the relaxation type, similar to that shown in Figs. 2, 3 and 5.

Noteworthy, the oscillations did not occur in the absence of either CTAB or alcohol, as well as by the replacement of the cationic surfactant CTAB by the anionic one, sodium hexadecyl sulfonate, with the same hydrophobic tail. Also, oscillations were not observed under stirring conditions. Oscillations have nearly the same amplitude 200-400 mV for all alcohols used. The amplitude was practically independent of the alcohol concentration; whereas, the oscillations period decreased with an increase of the alcohol concentration and its hydrophobicity. Oscillations observed in the presence of benzyl alcohol were inverted in comparison to those observed with aliphatic alcohols; the former have spikes toward the higher potentials, whereas the latter have spikes toward the lower potentials.

Already these first studies [23,24] have shown that the liquid membrane system is not only able to generate spontaneously oscillatory signals due to self-organization, but also that those oscillatory patterns depend on all the solutes involved. In this respect, the liquid membrane...
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system mimics the excitability of a biological system, e.g. biomembranes. Therefore, it was considered as a good candidate for the development of artificial sensors of tastes [25-28] or drugs [29,30].

Fig. 7 represents an example of the response of the liquid membrane system to various test substances, as obtained in [26]. In this study, the liquid membrane phase was octanol containing tetrabutylammonium chloride, the aqueous donor phase contained sodium dodecyl sulfate and ethanol, whereas the studied taste substances were dissolved in the aqueous acceptor phase. It is seen from Fig. 7, that a unique oscillation pattern corresponds to each taste substance. Those patterns differ in the initial level of the electrical potential, induction period before the oscillations onset, oscillation period and amplitude. Noteworthy: in [25], the taste substances were added to the donor phase, providing also in this case considerable effect on the oscillatory patterns.

Recently, the synchronization of the potential oscillations in two liquid membrane systems was reported [31] which demonstrates the potential applicability of those systems in mimicking the propagation of membrane potential pulses in living organisms.

The results of a very interesting experimental study are presented in [32], where the liquid membrane system with two surfactants, cationic (CTAB) and anionic (SDS), was considered. One of these surfactants was initially dissolved in one of the aqueous phases; whereas, the second one was dissolved in the membrane phase. Both systems, with either cationic or anionic surfactant in the aqueous phase, demonstrated oscillatory behavior, but the oscillation characteristics were very different. In the system i) containing SDS in the aqueous phase, oscillations started after a rather long induction period (>1000 s) and had relatively small amplitude (about 40 mV). Whereas, in the system ii) with CTAB in the aqueous phase, oscillations started without a noticeable induction period and had a much smaller period but larger amplitude (about 400 mV). The electrical potential was measured in this experiment between two aqueous phases, but, considering the values of induction period and oscillation amplitude, it can be assumed that in the system i), the oscillation has been localized at the membrane/acceptor interface, whereas in the system ii), it was generated at the donor/membrane interface (see discussion below).

A liquid membrane system with a surfactant dissolved only in the membrane phase and ethanol dissolved in the donor phase was studied in [33]. This work is interesting because of two reasons: i) the liquid phases have been placed in the straight glass tube, and ii) oscillations of the electrical potential have been obtained by using a non-

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**Figure 6:** Bulk liquid membrane system: (a) a downward U-shaped tube, (b) a hollow tube inserted in a vessel.

**Figure 7:** Oscillation patterns in the liquid membrane system in the presence of test substances in the acceptor phase: (A) without a taste substance, (B) 10 mM papaverine hydrochloride (bitterness), (C) 1 M maltose (sweetness), (D) 100 mM malic acid (sourness), (E) 100 mM magnesium chloride (saltiness), (F) 100 mM disodium guanosinate (umami). Reprinted with permission from [26]. Copyright 1998 Elsevier.
ionic surfactant, polyethylene glycol mono-4-nonylphenyl ether. It was assumed in [33] that the possibility of the electrical potential oscillations in this system is related to the contribution of the dipole moment of the non-ionic surfactant.

With the same solutes involved, oscillations depend on the membrane phase used. According to [34], in the liquid membrane system, containing CTAB in the donor phase and sucrose in the acceptor phase, oscillations through nitrobenzene membrane containing picric acid were well-shaped and rather regular with a large amplitude (300 mV). Oscillations started after the induction period of several minutes. By the replacement of nitrobenzene membrane with nitromethane membrane containing the same amount of picric acid, oscillations started without any induction period, they are less regular and have smaller amplitude with periodically large peaks. Those peaks are related to the formation of a new phase, which appears between the membrane and the acceptor phase [34,35]. By using an anionic surfactant, sodium oleate, in the donor phase, regular oscillations of rather small amplitude (30 mV) starting after an induction period were observed with nitromethane membrane, whereas there were no oscillations at all in the system with nitrobenzene membrane [34].

The latter examples show the chemical complicity of the liquid membrane oscillators and the importance of chemical interactions for the oscillatory patterns observed. Maybe this is the reason that, despite extensive experimental study of spontaneous oscillations generated in the liquid membrane systems including various organic liquids as the membrane phase and a broad range of solutes involved, a generally accepted mechanism of these oscillations is not elaborated until now. Nevertheless, some general regularities in the behavior of the oscillating liquid membrane systems and the preconditions for the appearance of oscillations are well established.

First of all, spontaneous oscillations appear only in the systems far from equilibrium. For example, in the discussed above liquid membrane system, presented in [23,24], the membrane phase, nitrobenzene, contained picric acid, soluble also in water with partition equilibrium being in favor of an aqueous phase, whereas partition equilibrium of CTAB dissolved initially in the aqueous donor phase is in favor of nitrobenzene. Therefore, after these liquid phases have been brought into contact, the transfer of solutes began, and the spontaneous oscillations are the result of this transfer.

The electrical potential difference between the aqueous donor and acception phases is the sum of five contributions: the potential differences in the bulk of liquids, donor, acceptor and membrane, as well as the potential differences across two liquid interfaces, donor/membrane and acceptor/membrane. The importance of each of those contributions across two liquid interfaces, donor/membrane and acceptor/membrane. The importance of each of those contributions was studied in detail in [36], where it was shown that the potential difference inside the aqueous bulks can be neglected and the potential difference in the bulk of the membrane phase can be neglected as well, if the volume of the membrane phase is large enough (7 mL for the study performed in [36]). With a smaller volume of membrane phase, there is some contribution from the bulk membrane phase in the total potential difference which decreases with time. Nevertheless, the main contributions give the potential differences across the interfaces. This conclusion is consistent with the theoretical analysis performed in [24].

It is also well established, that the oscillations of the electrical potential appear only if one of the solutes involved in the transfer is an ionic surfactant (CTAB in the above mentioned system). Therefore, it was assumed that the oscillations are related to the adsorption and desorption of the surfactant [24]. Indeed, the simultaneous monitoring of the electrical potential and interfacial tension has shown [37] that oscillations of the electrical potential are fully synchronized with the oscillations of interfacial tension (Fig. 8). It is seen from the data presented in Fig. 8 that the abrupt change in the electrical potential corresponds to the decrease of the interfacial tension, i.e., to the surfactant adsorption, whereas the gradual relaxation after that corresponds to the surfactant desorption. This is a common feature between the oscillations across a liquid membrane and the oscillations due to surfactant supply from a point source considered in the previous section.

In the first studies on spontaneous oscillations in liquid membrane systems, the electrical potential was measured between the donor and acceptor aqueous phases and the oscillations were called oscillations across the liquid membrane [23,26,29]. As the two-phase system, chemically identical to the donor/membrane system, demonstrated a similar oscillatory patterns [38], it was first accepted that the oscillations occur at the donor/membrane interface [24]. In [37], the electrical potential was measured between the aqueous phases, whereas the interfacial tension was measured at the donor/membrane interface; this study supported the conclusion made in [24]. However, in other studies [39,40] using a liquid membrane system with the geometry and chemistry rather close to those in [23,24,37], the oscillations were observed at the acceptor/membrane interface. Moreover, it was shown in [41] that the location of oscillations can be changed by changing concentrations of the solutes in
Spontaneous non-linear oscillations of interfacial tension at oil/water interface

It is interesting that according to [41] the oscillations at the acceptor/membrane interface are much more regular than those generated at the donor membrane interface.

Let us first consider the oscillations at the acceptor/membrane interface in more detail. The oscillations at the donor membrane interface will be considered in the next section together with the oscillations due to surfactant transfer in two-phase systems.

As it was already mentioned above, it is generally accepted that the oscillations through the liquid membrane are the result of abrupt adsorption of surfactant followed by its gradual desorption. The main question under discussion is the reason for the sudden adsorption of a large amount of surfactant. It is noteworthy that the adsorbed amount is obviously not in equilibrium with the adjacent bulk phases because the abrupt adsorption is followed by the gradual desorption.

There are two main approaches to answer this question. One of them [37,42,43] considers the solutional Marangoni instability [1-4] being the main driving force for the oscillations taking into account the evidence of spontaneous convection observed in liquid membrane systems (see [6] for details).

To prove the possibility of oscillations in a liquid membrane system without any complicated chemical mechanisms involved, a very simple liquid membrane system was considered in [42]. The geometry presented in Fig. 6b was employed. Pure aliphatic alcohols with a chain length of 5-7 carbon atoms were used as a donor phase, pure water was used as a membrane phase and pure dodecane was used as an acceptor phase. It is obvious that any chemical reactions are absent in this system. Nevertheless, it demonstrated regular oscillations of interfacial tension at the acceptor/membrane interface started after a set induction period (Fig. 9). The oscillation period depended essentially on the alcohol used and decreased with the shortening of the chain length.

Theoretical analysis of the behavior of a liquid membrane system where the only one surfactant is transferred from the donor to the acceptor through the liquid membrane phase in the absence of any chemical reactions, has been performed in [43] by direct numerical simulations. The mathematical model used in [43] was similar to the model discussed in the previous section when the droplet dissolved under the liquid interface, but adapted according to the liquid membrane geometry.

The full set of the non-stationary non-linear Navier-Stokes continuity and convective mass transfer equations was solved numerically in [43] for each of three phases involved (donor, membrane and acceptor phases). The buoyancy force due to dependence of the solution density on concentration was taken into account only for the membrane phase, as the preliminary analysis has shown that buoyancy can be neglected in the donor and acceptor phases. The surfactant was considered to be a nonionic one and the diffusion controlled adsorption kinetics was assumed. Local equilibrium was assumed between the surface concentration and the sublayer concentration described by the Langmuir isotherm. Local equilibrium of the surfactant distribution between the liquid phases at the interfaces was also assumed with the ratio of concentrations being equal to the equilibrium partition coefficient. Both donor/membrane and membrane/acceptor interfaces were supposed to be non-deformable. The boundary conditions imposed on those interfaces were the tangential stress balance employing the Szyszkowsky-Langmuir equation and the continuity of the tangential velocity component at the interface. It was also assumed that the donor/membrane interface is stable with respect to small fluctuations, i.e., no oscillation is generated at this interface. The oscillations generated at the donor/membrane interface are discussed in the next section.

Numerical simulations performed in [43] have confirmed that it is possible to obtain oscillations in a liquid membrane system where only one surfactant is transferred without any chemical reaction included. The oscillation mechanism is similar to that discussed in the previous section, i.e., the oscillations are the result of Marangoni instability periodically arising and terminating. The viscoelasticity of the adsorbed surfactant monolayer is the crucial property responsible for the
instability termination due to formation of the reverse interfacial tension gradient.

It should be stressed that the results are obtained in [43] based on the first principles and without any fitting parameters. They are in good agreement with the data presented in [42] where a very similar system was studied experimentally as well as with other experimental results. For example, according to [30], the oscillation at the membrane/acceptor interface started when the surfactant transferred from the donor phase reached this interface, and the potential drop was synchronized with a considerable convection in the membrane phase. This observation obviously indicates the onset of Marangoni instability.

Available experimental results on the dependence of the oscillation characteristics on the system geometry are also in good agreement with the results of numerical simulations. In particular, according to both the numerical simulations [43] and the experiments [36], the oscillation amplitude decreases with an increase of the distance from the donor/membrane interface to the membrane/acceptor interface, i.e., with an increase of the volume of the membrane.

The results of numerical simulations have shown [43] that the oscillation characteristics are determined by the surfactant activity, the partition coefficient and the concentration of monomers (or the critical micelle concentration, CMC). Therefore, it can be supposed that addition of various substances in each phase of a liquid membrane system can serve to optimize the CMC in the donor phase, the surfactant activity at the membrane/acceptor interface or the surfactant distribution coefficients between the membrane and the donor and/or acceptor phases to obtain oscillations with a sufficiently large amplitude to be detected in the experiment.

Experimentally, it is a well established fact that the oscillation characteristics can be controlled by the change of the surfactant properties by additives. For example, according to [40], addition of an alcohol into the donor phase of the liquid membrane system, containing hexadecyltrimethylammonium bromide in the donor phase and picric acid in the membrane phase, results in an increase of the oscillation amplitude. One of the modifications of the system properties by ethanol addition is the increase in solubility of both picric acid and the picrate containing ion pairs in the membrane phase [40]. Addition of butanol to the donor phase containing sodium oleate in another liquid membrane system [44] resulted not only in an increase of the oscillation amplitude, but also in an essential decrease of the induction period (from 1800 s to 100 s). Therefore, it can be assumed that the presence of butanol facilitated the transfer of the surfactant through the membrane phase, probably promoting convective motion in the membrane.

In [45], fitting of the experimental data for oscillations across the liquid membrane was performed in the framework of the model assuming that the surfactant is supplied to the interface membrane/acceptor very quickly during the abrupt change of the electrical potential (without identifying the mechanism), and then it desorbs and diffuses into the adjacent bulk during the slow relaxation stage. Comparison of the results for the acceptor phase being either pure water or aqueous solution of sodium chloride, has shown that the decrease of oscillation amplitude and the increase of oscillation period observed in the presence of sodium chloride can be explained by the increase of the surfactant activity at the membrane/acceptor interface [45]. However, it should be taken into account that the three surfactant properties mentioned above are coupled with each other, and the choice of optimal system composition can be a very complicated experimental task. Possible chemical reactions complicate the system behavior.
even more. Unfortunately, the model presented in [43] does not take this complicity into account, therefore, further development of the model coupled with detailed experimental study, taking into account real changes in solubility (CMC), partition coefficient and activity, is necessary.

As discussed above, theoretical and experimental study has shown that the oscillations at the membrane/acceptor interface can occur without any chemical reaction in the system, as a result of periodically arising and terminating Marangoni instability. It should be noted, however, that this is only one possibility. Another possibility is proposed in [35,40,44,46] where it is assumed that the oscillations can be of pure chemical origin. Note, the main steps of the oscillation process considered within both approaches are the same – diffusion of surfactant to the acceptor/membrane interface, abrupt adsorption of surfactant followed by its gradual desorption. But it is assumed in [35,40,44,46] that the quick adsorption can result from a very high adsorption constant or autocatalytic character of adsorption. Equations of chemical kinetics were written for all species present in various liquid membrane oscillators and then kinetic coefficients were determined from the best fitting of the experimental results. To validate the results obtained in [35,40,44,46], further study is necessary to confirm the mechanism proposed. In particular, it is desirable to prove independently the possibility of autocatalytic adsorption in the systems studied and to compare the kinetic coefficients obtained with those, found from other experiments, for example, from studying of dynamic surface tension or surface dilational rheology for the two-phase membrane/acceptor system. Recently, autocatalytic interfacial reaction affecting the development of Marangoni instability has been proved for a biphasic system, where miristoi chloride or miristic acid was initially dissolved in the organic phase and the aqueous phase contained potassium hydroxide (see the next section) [47].

4 Oscillations in biphasic system due to partition fluxes

Oscillations at the donor/membrane interface of a liquid membrane system are similar to those generated in the corresponding biphasic system. Historically, these oscillations have been discovered first and were studied systematically in 1970-1980 [48,49]. For the review of early works on the oscillations in biphasic systems, see [6]. The classical system demonstrating oscillations in biphasic configuration consists of a solution of picric acid in nitrobenzene overlaid by an aqueous solution of a long-chained alkyltrimethylammonium halogenide (ionic surfactant) such as CTAB. After two liquid phases are brought into contact, both solutes are out of partition equilibrium, therefore, mass transfer occurs in the system accompanied by a chemical reaction at the interface resulting in formation of alkyltrimethylammonium picrate being also a surfactant. Oscillations in this system start after set induction period. Their character depends, essentially, on the material of the container. According to [49], considerable transverse surface deformation was observed in a container made of glass, whereas, only longitudinal deformations occurred in a polyethylene beaker. According to [48,49], interfacial chemical reactions and their interactions with hydrodynamic processes in the system are crucial for the oscillation development. Importance of hydrodynamic processes is confirmed by the fact that the oscillations are absent under stirring.

The further work has shown that the oscillations can be generated in this system without any chemical reaction involved. Therefore, it can be assumed that in this system, Marangoni instability is the main driving force of oscillations. In [50], oscillations have been observed at water/dichloromethane interface by transfer of only one surface active solute, CTAB. It was noteworthy, that for the first time, oscillations have been observed by either transfer from water to dichloromethane or in the opposite direction. It is also interesting that, according to the flow visualization performed in [50], the abrupt decrease of interfacial tension was accompanied by considerable convection which terminated very quickly and no convection was observed during the stage of gradual increase of interfacial tension.

The effect of picric acid present in the organic phase (in the system with CTAB in aqueous phase) has been discussed in [51]. The partition of picric acid is in favor of water, but after the picrate ion (Pi-) enters the aqueous phase, it interacts with CTAB ion forming cetiltrimethyl ammonium picrate, CTAPI, which is practically insoluble in water and partitions back to the organic phase. Therefore, the presence of picric acid increases the surfactant concentration gradients in the system, and in this way, can facilitate the development of Marangoni instability [51].

Another biphasic system considered in [51], consists of tetraalkylammonium bromide solution in dichloromethane overlaid by aqueous solution of SDS. The oscillations were observed in this study by using either tetraethyl-, tetrpropyl- or tetrabutylammonium...
bromide, but they were not as regular as the system with CTAB. It should be stressed that SDS is not soluble in dichloromethane; therefore, initially, the only transferred solute is tetraalkylammonium bromide, and the oscillations are not observed in its absence. Tetraalkylammonium bromides used in this study have a rather low surface activity, and the transfer of those substances cannot be the oscillation reason, but the products of their reaction with SDS, tetraalkylammonium dodecylsulphates, TAADS, are surface active and soluble in both aqueous and organic phases. Therefore, it was assumed in [51] that only the transfer of the product of chemical reaction causes oscillations in this system. To prove this assumption, another non-reactive system containing only one solute, TAADS, was studied in [51]. Similar to CTAB, all three TAADSs generated oscillations by both transfer directions (either from organics to water or from water to organics). Thus, the results obtained in [50,51] have shown that chemical reactions are not a necessary condition for oscillation development.

The further confirmation of this conclusion was obtained in [52,53] where the oscillations of interfacial tension have been observed for the first time by the transfer of non-ionic surfactants, oxyethylated alcohols $C_8\text{EO}_4$ and $C_8\text{EO}_5$ from water to heptane. It is noteworthy that in this system, based on linear stability analysis [1,2], the Marangoni instability by the transfer of surfactant from water to heptane should reveal itself as a stationary convection, but not as oscillations [52].

The numerical simulations, performed based on the first principles (non-linear non-stationary Navier-Stokes equations, continuity and convective diffusion equations with appropriate boundary conditions) have shown [52,53] that, in accordance to linear stability analysis, Marangoni instability in biphasic system initially develops as a steady convection. Instability development brings a large amount of surfactant to the interface at the point where the upward flow is established (Point A in Fig. 10a) and spreads it over the interface causing an abrupt decrease of the interfacial tension. However, when the convective velocity becomes large enough, non-linear effects related to the local expansion (around the point A in Fig. 10b) and the local contraction of the liquid interface (near the walls in Fig. 10b) result in formation of retarding concentration gradients and in instability termination. Note: the transition from the surfactant distribution presented in Fig. 10a to that in Fig. 10b is possible only at a high enough surface velocity when the convective transfer over the surface is faster than the surfactant supply to the interface. During the following slow stage, the diffusion fluxes to the interface from the donor phase are smaller than those from the interface to the acceptor phase, and the interfacial concentration gradually decreases (interfacial tension increases) until essential normal concentration gradients build up again giving rise to the next instability run, i.e., to the next oscillation.

Thus, as it has been shown in [52,53], the hydrodynamic mechanism discussed in sections 2 and 3, related to the periodical development of Marangoni instability and its termination due to non-linear effects caused by local contraction and expansion of the interface and visco-elastic properties of the adsorbed surfactant layer, can be responsible for the non-linear oscillations in biphasic system and for the oscillations at the donor/membrane interface in a liquid membrane system. Analysis of the results of numerical simulations has shown [53] that the oscillations should be observed in a certain concentration range, depending on CMC value of the surfactant, its surface activity and partition coefficient. Transition from non-oscillatory behavior to oscillations and back to non-oscillatory behavior with the increase of surfactant concentration was observed experimentally [53] for both $C_8\text{EO}_4$ and $C_8\text{EO}_5$.

The increase of the number of solutes and chemical reactions involved complicates the system behavior considerably. In particular, local changes in interfacial concentrations of solutes can change the direction of reactions and in this way can affect the instability development [54] and even establish additional feedback mechanisms [55]. One of the most interesting
results concerning the effect of chemical reactions on the development of Marangoni instability was already mentioned in the previous section [47].

The system studied in [47] was composed of aqueous solution of KOH overlaid by solution of miristoi chloride or miristic acid in hexane. Similar to octanoic acid studied in [55], the rate of dissociation of mirisic acid after its transfer to the aqueous phase depends on pH. At high pH, it is completely dissociated, whereas at low pH it is in a protonated state. At intermediate pH, dimers composed of dissociated and protonated acid (acid-soap complexes) can be formed having a very high surface activity: the surface tension of the solution containing dimers can be lowered to 20 mN m⁻¹ [56] which is much lower than the minimum surface tension attainable with common surfactants including dissociated miristic acid [47]. It is noteworthy that dissociated acid forms micelles, whereas acid-soap complexes form vesicles, promoting enhanced solubilization of surfactant. Such complicated chemistry results in a drastic (two orders of magnitude) increase in the transfer rate of surfactant after CMC is reached in the aqueous phase, and, in terms of convective pattern formation, a transition from stationary convective cells to oscillating tongues is observed [47].

Another example of considerable effects of chemical reactions on instability development in biphasic system is given in [57, 58], where oscillatory instability has been observed at the oil/water interface during extraction of metal cations from aqueous solution using bis(2ethylhexyl) phosphate (DEHP) dissolved initially in the oil phase (heptane or nitrobenzene). Instability was observed only for Ca²⁺ and Fe³⁺ cations, whereas oscillations did not appear in the presence of Mg²⁺, Sr²⁺, Ba²⁺, Cu²⁺ or Co²⁺. Importance of system chemistry is evident in this case because Ca²⁺ and Fe³⁺ are the only two cations in this series forming oil-soluble complexes with DEHP. It is also noteworthy, that for the systems with Ca²⁺ and Fe³⁺, formation of surface aggregates was observed in [57,58] using Brewster Angle Microscopy. Formation of aggregates at the interface was also observed in the biphasic system containing FeCl₃ or ZnCl₂ in aqueous phase and stearyltrimethylammonium chloride in nitrobenzene [59]. The role of surface aggregates in the instability development is still unclear, therefore further study of these interesting and practically important systems is desirable.

Thus, despite the evidences that oscillations in biphasic systems or at the donor/membrane interface in liquid membrane systems in many cases can be explained by pure hydrodynamic mechanism without any chemical reactions [40-53], the chemical reactions included can drastically affect the instability development and the dynamic system behavior. Therefore, further comprehensive study on interactions between chemical and hydrodynamic processes is necessary to understand the detailed mechanism of oscillations in considered systems and the methods of their control.

It is noteworthy that intensive convection in the membrane phase related to the instability development at the donor/membrane interface, mixes the solution and prevents formation of concentration gradients in the membrane phase near the membrane/acceptor interface, and therefore, prevents the development of instability at this interface. That is why in most cases, instability is observed either at donor/membrane or membrane/acceptor interface, but very rarely on both interfaces simultaneously [41].

5 Conclusions

Transfer of a surfactant through oil/water interface often results in the development of Marangoni instability. In some systems, the instability develops an oscillatory regime, though the linear stability analysis predicts stationary convection. The oscillation characteristics depend on the properties of the surfactant, including the partition coefficient, on other solutes present in the liquid phases, and often also on the system geometry. Three different systems demonstrating such oscillatory behavior are considered here, and it is shown that oscillations in these systems can be explained in the framework of the same mechanism, namely, the mechanism of periodically arising and terminating Marangoni instability. Termination of Marangoni instability is related to visco-elastic properties of the adsorbed surfactant layer: at high surface velocities, local expansions and contractions of the surface result in appearance of surfactant concentration and interfacial tension gradients retarding Marangoni-convection.

The role of chemical reactions in the considered systems is not completely understood, yet. Obviously, the presence of additional solutes and chemical reactions are crucial for hydrodynamics under consideration, and the interactions between chemical and hydrodynamic processes should be the subject of further comprehensive study. However, the question about a pure thermodynamic mechanism of oscillations of surface tension and electrical potential is still open. To solve this problem, further studies on the possibility of autocatalytic adsorption in the systems demonstrating oscillations and determination of the values of the kinetic coefficients are necessary.
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