Surfactant Transfer through a Liquid Membrane: Origin of Spontaneous Oscillations at the Membrane/Acceptor Phase Interface

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Instability due to surfactant redistribution in a liquid membrane system consisting of two solutions, namely source and acceptor, separated by a layer of immiscible liquid is studied theoretically and experimentally. The transfer of a surfactant from a source phase to an acceptor phase is often accompanied by spontaneous nonlinear oscillations of electrical potential and/or interfacial tension. The oscillations can be generated at each of the membrane interfaces. Here a mechanism of oscillation, which develops at the membrane/acceptor phase interface, is proposed on the basis of direct numerical simulation of the system evolution. Performed experimental studies confirm the theoretical results.

Introduction

Oscillations generated at liquid membranes are impressive examples of nonlinear phenomena originating from the surfactant transfer in systems far from equilibrium. As a rule, a liquid membrane system consists of two aqueous solutions separated by an oil solution. Aqueous phases can be situated in two arms of a U-shaped tube, and then the oil phase is poured in the base of this tube.[1–7] In another often used geometry, aqueous phases are in the inner and outer spaces of a hollow cylindrical tube inserted in a cylindrical vessel. The tube is inserted to some depth in the oil solution, poured at the bottom of the vessel (Figure 1).[8–11] Usually the source phase contains ionic surfactant (alkyltrimethylammonium halogenide,[2,4–6,10,11] sodium oleate, sodium stearate,[3] sodium dodecyl sulfate[1,7] etc.) and short chain alcohol. The organic phase contains organic acids (most frequently picric acid) as counter solute for cationic surfactants and organic bases or salts (2,2′-bipyridine, tetraethylammonium halogenides)[1,3,7] as counter solute for anionic surfactants. The acceptor phase can contain sucrose, inorganic salts, and other substances.

In such a system, the transfer of a surfactant from one aqueous solution to the other one can result in oscillations of electrical potential between the solutions and/or oscillations of interfacial tension at one of the oil/water interfaces. The oscillation begins after a certain induction period. The oscillation characteristics depend on the composition of each of the three liquid phases as well as on geometry and material of the measuring cell. It is noteworthy that, in liquid membrane systems with very similar geometries and compositions, oscillation can be generated at different interfaces.[4–6]

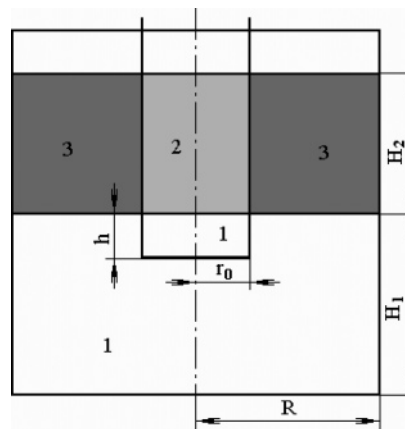Despite numerous experimental works in this field and even the attempts to employ the liquid membrane systems as taste

Figure 1. Schematic representation of the liquid membrane system: (1) liquid membrane, (2) source phase; (3) acceptor phase.

or drug sensors,[1,3,7] the oscillation mechanism has not been clear to date, as it has also not been clear at which particular interface oscillation will be generated in a certain system.[12] The chemical composition of the liquid membrane system has been usually rather complicated, different solutes have been transferred between liquid phases, chemical reactions have been possible in interfacial regions resulting in products of various surface activity, which has hampered the theoretical analysis of the problem.

Comparing the oscillations produced in liquid membrane systems at the membrane/acceptor interface and spontaneous nonlinear oscillations produced at the air/water and oil/water interfaces by surfactant transfer from the point source being in the liquid bulk,[13–18] it can be supposed that these oscillations have the same origin,[12] namely, in many cases the oscillations at membrane/acceptor interface are the result of periodically arising and fading Marangoni instability and chemical interactions are not necessary for the development of oscillations. To validate this assumption we performed a theoretical analysis of

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a simplest liquid membrane system, and it was possible to show that this system produces spontaneous nonlinear oscillations. For the theoretical analysis we used the approach successfully applied earlier for the oscillations produced by surfactant transfer from a point source.[19−22] This approach consists of a direct numerical simulation of the system behavior on the basis of the first principles. Then we studied a similar system experimentally and confirmed the theoretical conclusions. In the following, we present the results of theoretical and experimental studies and propose the mechanism governing the oscillation at the membrane/acceptor interface.

Theory

To study theoretically the real oscillation mechanism at the membrane/acceptor interface we chose a very simple liquid membrane system consisting initially of three pure liquids. The source phase, which is slightly soluble in both the membrane and acceptor phases, is considered as a surfactant for the membrane/acceptor interface. This surfactant is transferred from the source/membrane interface to the acceptor phase. The membrane and the acceptor phases are considered as immiscible. The system is composed from a hollow cylindrical tube inserted in a cylindrical vessel as shown in Figure 1.

The liquid motion in each phase is described by the set of nonlinear, non-steady-state Navier−Stokes equations and continuity equation, coupled in phases 1 and 3 with convective diffusion equations. The dependence of the solution density on the surfactant concentration is taken into account only in the buoyancy term (Boussinesq approximation). According to the system symmetry, the dependence on the angular coordinate is neglected and the equations are rewritten in terms of the stream function and vorticity in cylindrical coordinates, similar to ref 22.

In the initial state all liquid phases are supposed motionless. The surfactant concentration is equal to its solubility in the membrane phase at the membrane/source interface and is equal to zero elsewhere in the membrane and the acceptor phase. No-slip boundary conditions are used for the vessel and the tube walls. Both the membrane/source and membrane/acceptor interfaces are supposed flat and nondeformable. The intrinsic interfacial viscosity and all thermal effects are neglected. Diffusion-controlled adsorption kinetics is assumed at the membrane/acceptor interface with local equilibrium between the surface concentration and the sublayer concentration described by the Langmuir isotherm. Local equilibrium of the surfactant distribution between the membrane and acceptor phases at the interface in accordance to the partition coefficient is also supposed. The local surfactant mass balance at each point of the membrane/acceptor interface is determined by the fluxes from/to the adjacent liquid bulk phases, interfacial convection, diffusion, and contraction/expansion of the interface. In the tangential stress balance at the membrane/acceptor interface, the interfacial tension gradient was obtained by using the Szyszkowsky−Langmuir equation of state for adsorbed surfactants. The interfacial tension at the membrane/source interface was supposed to be constant, so that no motion was generated at this interface.

For the numerical simulation we performed the discretization of the governing equations with the corresponding boundary conditions by the finite difference method. The equation for the stream function was solved by the Gauss−Seidel iterative method. In the equations for the vortex and solute transfer, the two point forward difference approximation was used for the time derivatives, the three point centered differences were used

for the diffusion terms, and the modified upwind differences were used for the convective terms.[23] The simulations were performed on the regular grid 120×120 mesh points for the membrane phase and on the grids with the same resolution for the source and acceptor phases.

Experimental Section

For the experimental studies we have chosen systems corresponding to that theoretically considered; namely, we used pure alcohols (C_5-C_7) as a source phase, pure water as membrane phase, and pure alkane (dodecane) as acceptor phase. The system geometry was that as presented in Figure 1.[8−11]

Ultrapure deionized water produced by "Purelab Plus" was poured at the bottom of a glass vessel with a diameter of 40 mm to the height of $H_1 = 20$ mm (1 in Figure 1). A hollow glass tube (with diameters of 5, 8, 12, and 16 mm) was inserted into water to the desired depth h (2−6 mm). Dodecane (Aldrich, +99%, percolated twice through a column with freshly annealed Al_2O_3 powder before use) was then gently poured onto the water surface in the annular gap outside the tube (3) to the height of $H_2 \approx 15$ mm, while the respective alcohol was poured into the inner part of the tube (2) so that the dodecane/water and alcohol/water interfaces were at the same level. The alcohols pentanol (Fluka, ≥99.5%), hexanol (Fluka, ≥99.5%), and heptanol (Aldrich, 98%) were used as purchased.

Interfacial tension was measured at the dodecane/water interface using an electronic balance equipped with a platinum Wilhelmy plate. The measurement was started immediately after the formation of the liquid membrane system was completed.

Results and Discussion

We performed a series of numerical simulations of the liquid membrane system behavior varying the system geometry and the substance properties. The following values of the geometrical parameters were used in the simulations: $R = H_1 = H_2 = 20$ mm, $r_0 = 4-15$ mm, $h = 2-6$ mm. The properties of the source phase were chosen close to those of aliphatic alcohols. The properties of the membrane phase corresponded to the properties of water. The properties of the acceptor phase corresponded to those of water or dodecane. The difference in densities of the pure membrane phase and the saturated surfactant solution was varied between 0 and 4×10^{-3} g/cm^3. In most cases, the surfactant partition coefficient between the acceptor and membrane phase was taken equal to unity, but it was 0.49 for the particular pentanol/water/dodecane system and 7.3 for the particular heptanol/water/dodecane system.[24]

In all considered model systems, the numerical simulations have shown that the surfactant transfer should result in the development of spontaneous nonlinear oscillations at the membrane/acceptor interface. These oscillations are governed by the same mechanism as the oscillations produced at the liquid/liquid or air/liquid interface by surfactant transfer from a point source being in the liquid bulk phase. As this mechanism is already discussed in detail elsewhere,[18,19,22] we present here only a short description of the mechanism related to the liquid membrane system.

The essence of the hydrodynamic mechanism underlying the appearance of oscillation becomes clear from Figures 2 and 3, where the streamlines and concentration distributions are presented for the liquid membrane phase with an inserted hollow tube. Here we used the results of calculations for the tube with an outer radius of 5 mm, a thickness of the tube wall of 0.5 mm and a tube immersion depth of 3 mm.
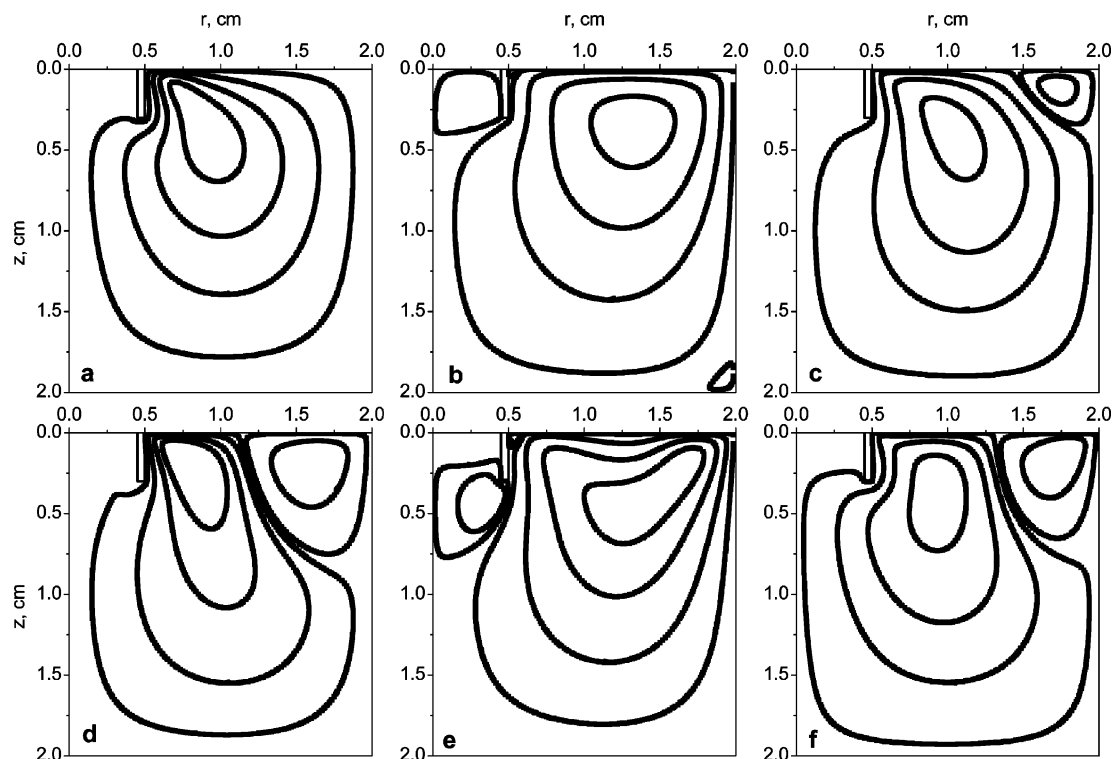
Figure 2. Streamlines distribution in the liquid membrane phase during the surfactant transfer: (a) $t = 26$ min; (b) $t = 29$ min; (c) $t = 29$ min, 45 s; (d) $t = 30$ min; (e) $t = 31$ min, 30 s; (f) $t = 34$ min (r and z are the radial and vertical coordinates, respectively).
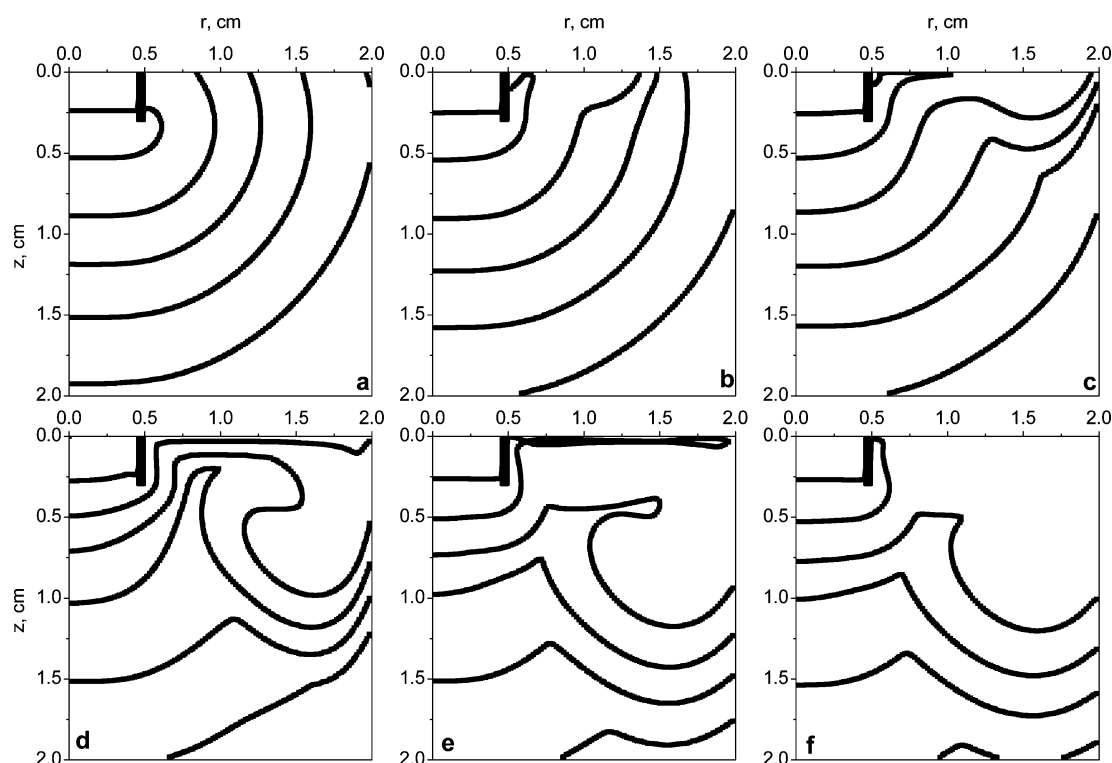

Figure 3. Distribution of the bulk concentration by the surfactant transfer through the liquid membrane: (a) $t = 26$ min; (b) $t = 28$ min, 40 s; (c) $t = 28$ min, 50 s; (d) $t = 29$ min, 13 s; (e) $t = 32$ min, 10 s; (f) $t = 34$ min (r and z are the radial and vertical coordinates, respectively).

At once after the three phases were brought into contact, the surfactant begins to dissolve in the membrane phase and to diffuse from the source/membrane interface into the membrane bulk phase inside the tube. For the case of a flat source/membrane interface assumed in the employed mathematical model, a stable stratified liquid layer inside the tube is obtained, and therefore pure diffusional mass transfer takes place here. Only when a sufficient amount of the surfactant moves out of

the tube does buoyancy-driven convection develop in the membrane phase. If the density of the surfactant solution is smaller than the density of the pure membrane phase, the direction of the convective motion corresponds to that shown in Figure 2a, and convective mass transfer reinforces the surfactant transfer to the interface. When essential amounts of the surfactant reach the membrane/acceptor interface, Marangoni convection begins in the system due to an interfacial concentra-

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tion gradient, as the surfactant concentration near the tube is much higher than near the vessel wall. The direction of this convective motion agrees with that shown in Figure 2a. It should be stressed that buoyancy as well as Marangoni convection in the considered system are initially very weak due to small concentration gradients in the bulk and at the interface, and the convective mass transfer is negligible in comparison to the diffusional mass transfer. It is seen from Figure 3a that the concentration profiles look like pure diffusional profiles during the long time after beginning the solute transfer.

There is, however, a feedback in the system which can essentially reinforce the convective mass transfer and make them predominant. As is obvious from Figure 2a, the acceleration of the convective motion causes an increase of the surfactant flux to the acceptor/membrane interface, which, in turn, leads to further acceleration of convection. The influence of this feedback on the system behavior becomes important when the transfer of the surfactant to the interface due to Marangoni convection becomes comparable with the diffusional surfactant transfer, i.e., when the concentration gradients and velocities in the system reach certain critical values. After that the convective velocity and the flux of the surfactant to the interface in the vicinity of the tube wall increases abruptly. The system passes to the fast convective stage in its evolution due to development of Marangoni instability. At this stage, as illustrated by Figure 3b–d, within some tens of seconds a large amount of surfactant is transferred to the interface and spread over it, which corresponds with an abrupt decrease of the interfacial tension at the membrane/acceptor interface.

At this time the convective pattern (Figure 2b) is almost the same as at the initial stage (Figure 2a), but the velocity of convection increases by many orders of magnitude. At the same time, the velocity at the vessel wall is equal to zero; i.e., a large velocity gradient appears near the vessel wall, causing a contraction of the interface. This, in turn, leads to the appearance of the surface concentration gradient here directed oppositely to the concentration gradient near the tube. This reverse concentration gradient retards the convective motion and even initiates a motion of the liquid in the opposite direction. The reverse convective roll extends gradually to the tube region (Figure 2c–e). It breaks up the fast convective supply of surfactant to the interface, and the system passes to the slow stage in its evolution. During this stage the convective velocity is by some orders of magnitude smaller than during the fast stage, and the diffusional mass transfer becomes important again.

It is seen from Figure 2b and 3d that, during the fast stage, the convective motion near the interface is directed along it and spreads the surfactant over the interface. However, it remains a rather dilute solution in the membrane phase under the interface. There is also a dilute solution in the acceptor phase on the other side of the interface. Thus, during the slow stage the surfactant desorbs from the interface into both the membrane and acceptor phases (Figure 3e,f) and the interfacial tension increases gradually. The diffusional fluxes from the interface to the adjacent bulk phases decrease with time due to the equilibration of concentrations. Simultaneously it remains the diffusional surfactant flux from the source/membrane interface through the tube to the membrane acceptor interface. At a certain time moment in the tube region this flux becomes larger than the flux from the interface and the direct convective roll begins to grow again. It extends, pushing the reverse roll back to the wall region (Figure 2f). When the reverse roll disappears, the Marangoni instability develops again and the system passes to the fast stage of its evolution, giving raise to the next oscillation.
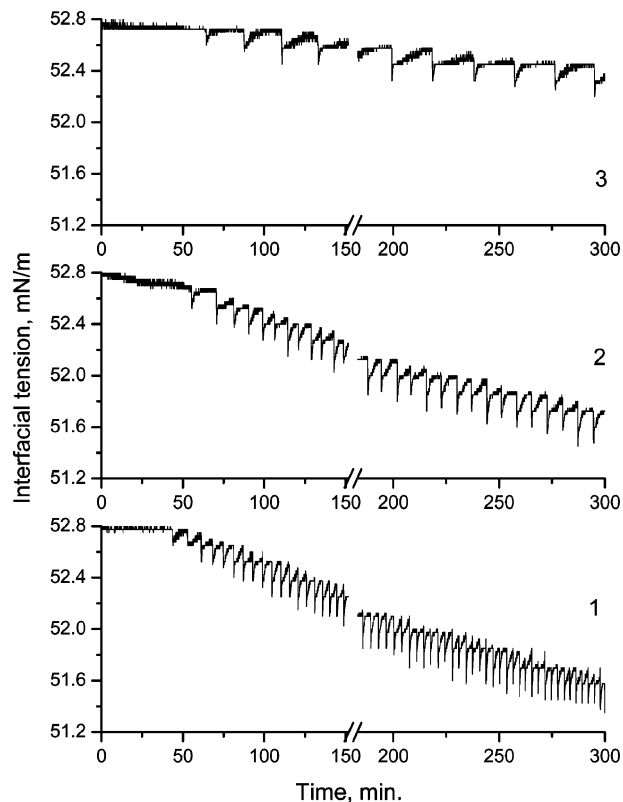

Figure 4. Oscillation generated at the dodecane/water interface by the transfer through the water membrane of (1) pentanol, (2) hexanol, (3) heptanol. Tube diameter $d = 8$ mm, tube immersion depth $h = 6$ mm (experimental results).

According to the predictions of the theoretical model considered above, we observed experimentally the oscillations of interfacial tension in the corresponding liquid membrane systems with pentanol, hexanol, and heptanol as a source phase. An example of the experimental results is presented in Figure 4. It is seen that by the same system geometry the oscillation amplitude is nearly independent of the surfactant used, whereas the oscillation period increases with the increase of the alkyl chain length of the alcohol. For liquid membrane systems the oscillation begins after a rather long induction period (40–60 min for the tube immersion depth $h = 6$ mm), confirming in this case a rather small effect of buoyancy convection in comparison to the systems with the surfactant source in the bulk.[18,22]

For more detailed comparison of the theory and experiment we performed numerical simulations for the two particular systems presented in Figure 4, namely for those with pentanol and heptanol. The results of simulations are presented in Figure 5. The calculated induction periods and oscillation periods for both substances are of the same order of magnitude as those observed in the experiments, whereas the calculated oscillation amplitude is one order of magnitude smaller than the experimental one. This difference can be related to some simplifications accepted in the mathematical model in comparison to the actual experimental system as well as to the error in the measurement of the quickly changing dynamic interfacial tension using the Wilhelmy plate. It is, however, important to note that the numerical simulations give correctly new qualitative results. According to the data in Figure 5, the oscillation amplitude is nearly independent of the alkyl chain length of the alcohol, whereas the induction period and oscillation period increase with increasing alkyl chain length. Oscillation splitting and transition
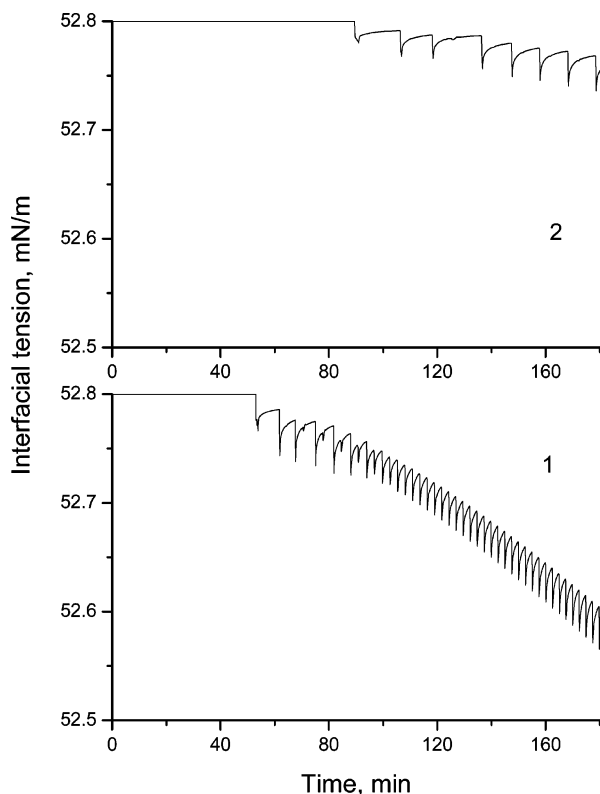
Figure 5. Oscillation generated at the dodecane/water interface by the transfer through the water membrane of (1) pentanol, (2) heptanol. Tube diameter $d = 8$ mm, tube immersion depth $h = 6$ mm (numerical results).

from oscillations with a large period to oscillation with a small period (Figure 5, curve 1) were also observed in the experiments.

Conclusions

Numerical simulations performed from the first principles (using the nonlinear, non-steady-state Navier−Stokes equations, continuity equation, and convective diffusion equation) have shown that spontaneous nonlinear oscillations produced in a liquid membrane system at the membrane/acceptor interface can be the result of Marangoni instability periodically arising and fading in the system; i.e., these oscillations are governed by the same mechanism as the oscillations produced at a liquid/liquid or air/liquid interface by surfactant transfer from the point source being in the liquid bulk phase.

Experimental studies of systems corresponding to the theoretically considered system, namely consisting of aliphatic alcohol as source phase, water as membrane phase and dodecane as acceptor phase, confirm the appearance of oscillation at the membrane/acceptor interface predicted theoretically.

The comparison of the results obtained by numerical simulations with the experimental results for two selected systems has shown that the theory to describe the oscillation mechanism is in a good qualitative agreement with the experiment. Both theory and experiment indicate that in the considered liquid membrane system the oscillation amplitude is nearly independent of the alkyl chain length of the alcohol, whereas induction period and oscillation period decrease with decreasing alkyl chain length. The obtained results should be useful for understanding the oscillation mechanism in systems more complicated from a chemical point of view.

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