

Auto-oscillation of surface tension

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Long-time auto-oscillation of the surface tension can evolve when in an aqueous system a diethyl phthalate droplet is placed under the free water surface. The experimental conditions for development of surface tension auto-oscillations are described. Based on a theoretical analysis the mechanism of these auto-oscillations is proposed. The mechanism of the auto-oscillations results from a switching between diffusion and convection transfer of diethyl phthalate in the solution. A periodic Marangoni flow on the water surface resulting from a surface layer instability is discussed. The solubility of the amphiphile in the water and its surface activity are the main characteristics that determine the system behavior. [S1063-651X(99)09908-0]

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I. INTRODUCTION

It is well known that a free liquid surface involving heat or mass transfer represents a nonequilibrium system where instability can arise leading to the formation of dissipative structures [1]. The instability manifests itself as a convective flow induced by a surface-tension gradient. This effect known as Marangoni instability, is considered in many papers and monographs [2]. An important precondition for this effect is the existence of heat or mass transfer in the system, which results in temperature or concentration gradients in the region close to the surface. In this case, a surface-tension gradient can be produced due to its temperature and concentration dependence. The system becomes unstable due to normal flows and gradients [3,4] as well as to lateral flows and gradients [5–7].

Dissipative structures can develop due to instability only in systems which are far from equilibrium [1] above a critical heat or mass flux. This condition is expressed by dimensionless criteria. The surface-tension driven instability is characterized by the critical Marangoni number; analogously, the Bénard instability by the critical Rayleigh number [3,8,9]. They depend on the heat or mass transfer velocity in the system, on the boundary conditions and geometric characteristics of the system, and on the physicochemical properties of the substances.

Various dissipative structures are caused by Marangoni instability. The convective cells of the Bénard type are the most known example [3,8,10,11]. Sterling and Scriven [4] predicted instabilities of the oscillatory and wave type. These and other kinds of instabilities including solitary waves and surface rotation flows, were studied experimentally by Linde *et al.* (see [12] and previous works of these authors). Oscillatory instabilities and convective cells were also studied in [5,6,13,14], wave instabilities in [6,15].

In the present paper, we report first results of a type of instability, which is apparent in auto-oscillations of the surface tension. Well developed auto-oscillations of the surface

tension occur in the water-diethyl phthalate system if a captive diethyl phthalate (DEP) droplet is formed at the capillary tip immersed into the water, i.e., the droplet is under the water surface. So far, only one type of periodically exciting oscillations is known [16,17]. It occurs if a hot wire is submerged into special liquids and is placed parallel to its surface [16] or similarly, if a laser beam propagates in an absorbing liquid [17]. These oscillations were produced by temperature gradients in the liquid created by a laser beam or by a wire heated by electrical current. They are associated with propagating waves at the free surface that could be solitary waves [16] but the exact nature of these waves is still unclear. The model proposed for these oscillations [17] discounts the properties of the liquid and, therefore, cannot explain the difference in the behavior of different liquids.

The mechanism of the surface tension auto-oscillations experimentally studied in the present paper is discussed based on a theoretical analysis of the experimental results. The surface tension auto-oscillations are explained by a periodic Marangoni flow on the water surface resulting from a surface layer instability.

II. EXPERIMENT

A. Materials

DEP obtained from Fluka and Merck were used as purchased. The following features of DEP required for this work were determined. The solubility of DEP in water is 0.15 mass % (at 20 °C). The density of DEP is 1.118 kg/dm³. The equilibrium vapor pressure is small (0.05 Pa at 20 °C). The surface tension is 35.3 mN/m. The saturation of water with DEP is accompanied by adsorption of the amphiphilic DEP molecules at the phase boundary water/vapor. As a result of this adsorption process, the measured force decreases in relation to the surface concentration of DEP. The following constants of the Langmuir isotherm $\Gamma = \Gamma_m K_L C / (1 + K_L C)$ and the Henry coefficient $\alpha = \Gamma_m K_L$ for DEP were found: $\Gamma_m = 5.3 \times 10^{-6}$ mol/m², $K_L = 1.3$ m³/mol, and $\alpha = 6.9 \times 10^{-6}$ m, where Γ is the surface concentration and C is the bulk

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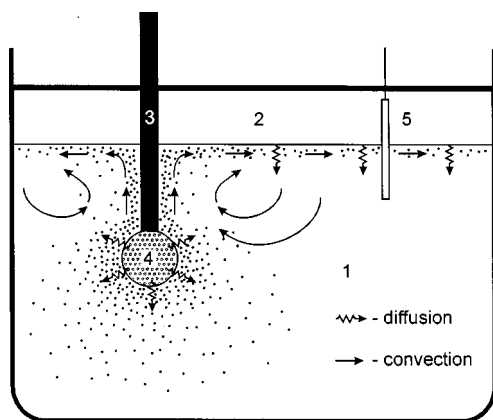


FIG. 1. Scheme of the amphiphile transfer in the measuring system. 1, solution; 2, gaseous phase; 3, capillary; 4, drop of DEP; and 5, WILHELMI plate.

concentration. The subphase was ultrapure water with a specific resistance of 18.2 M Ω /cm purified using a Millipore desktop unit.

B. Procedure

The schematic diagram of the experimental setup is presented in Fig. 1. The experiments were performed in a cylindrical glass vessel having an inner diameter of 5 cm. The vessel was filled with pure water and a glass capillary was introduced into the water on a depth of 1–3 cm. Under the water surface, a captive droplet of diethyl phthalate was formed at the capillary outlet. DEP was brought very carefully through the capillary so that the bulk water and the air/water surface initially remain clean. The drop diameter was about 3 mm. Just after that the surface-tension measurements were started. A Wilhelmy force instrument with a freshly annealed platinum plate was used for these measurements. The temperature was chosen between 20 and 30 °C and was kept constant by using a thermostat. The vessel was covered with a glass plate to avoid atmospheric convection. The distance between the covering plate and the water surface was about 1.5 cm.

The dissolution of DEP in the water starts just after the droplet formation. Nevertheless, at the beginning of the process, an appreciable change of the surface tension was not observed. This induction time, which was usually between 20 minutes and 1 hour, depends on the immersion depth of

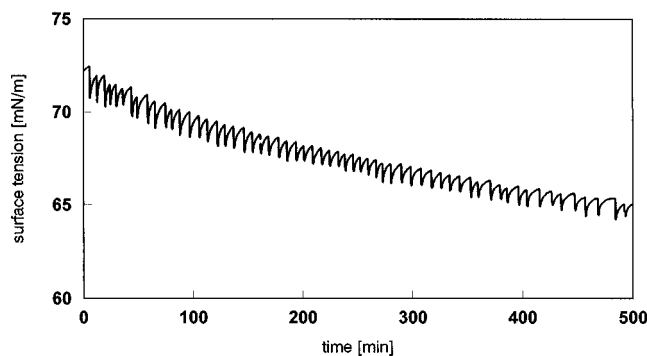


FIG. 2. Surface tension of water in the presence of diethyl phthalate vs time for the case of a glass capillary at 30 °C.

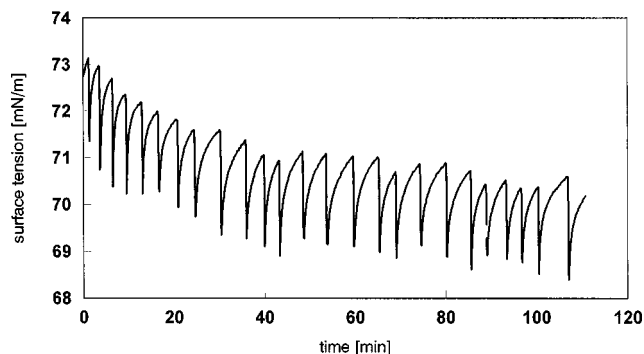


FIG. 3. Surface tension of water in the presence of diethyl phthalate vs time for the case of a Teflon tube with talcum particles on the surface at 30 °C.

the capillary outlet under the water surface. After this time interval, remarkable auto-oscillations of the measured interfacial tension were initiated. These auto-oscillations were observed over more than 8 hours. Two characteristic examples are shown in Figs. 2–4. The oscillation has an asymmetrical shape. Gradual increase of the surface tension follows after its sharp decrease. The period of the oscillation is approximately between 8 min (Fig. 2) and 4 min (Figs. 3 and 4). The differences in the periods are caused by small differences in the drop sizes and the capillary immersion depth, which were not precisely enough determined in the experiments. The amplitude of the tension oscillation varies between 1 and 2 mN/m (Fig. 4); often it is approximately 2 mN/m. The mean value of the surface tension decreases gradually with time in relation to the water saturation with DEP. The longer chain amphiphile dioctyl phthalate did not exhibit this special effect.

Additional experiments were performed to demonstrate that a periodical instability occurs at the water surface during the DEP distribution. The water surface was sprinkled with talcum. The periodical movement of the talcum particles was observed during the oscillation periods. Particularly during the sharp decrease in the surface tension intensive movements can be observed. Similar surface movement, a sharp decrease of the surface tension and its subsequent, gradual increase are observed at the deposition of very small quantities of DEP on a clean water surface. However, the auto-oscillations appear only when special prevention was made against extraneous convection in water and in gas phase.

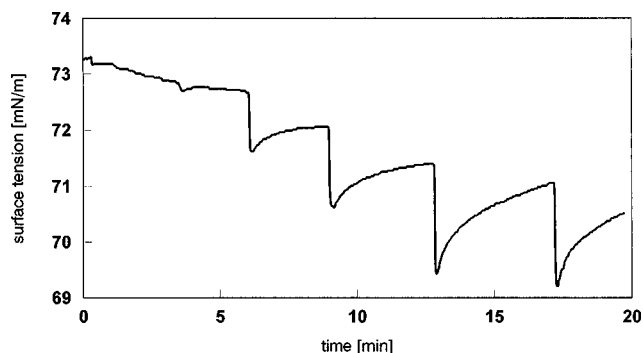


FIG. 4. Surface tension of water in the presence of diethyl phthalate vs time for the case of a Teflon tube with talcum particles on the surface at 30 °C at large time resolution.

This indicates that the instability is caused by the surface-tension gradient, which results from the nonuniform DEP distribution. It is interesting to note that the material of the capillary does not affect the auto-oscillations, as evidenced by experiments, which were performed with capillaries of hydrophobized glass or teflon.

III. THEORETICAL BACKGROUND

In the experiments, the process of the water saturation with DEP runs slowly enough because the solubility of diethyl phthalate in water is very small and thus, the diffusion fluxes cannot be large. The process of surfactant distribution in the volume is described by the convective diffusion equation

$$\frac{\partial C}{\partial t} + \mathbf{v} \cdot \nabla C = D \Delta C, \quad (1)$$

where C and D are concentration and diffusion coefficients of DEP, respectively and \mathbf{v} is the velocity field in the solution. Due to the diffusion of DEP, normal and tangential concentration gradients are gradually formed near the surface. This produces instabilities. Convective flows arising in the solution affect the diffusion process according to Eq. (1). The velocity distribution \mathbf{v} can be found from a set of Navier-Stokes equations,

$$\rho \frac{\partial \mathbf{v}}{\partial t} + \rho \mathbf{v} \cdot \nabla \mathbf{v} = -\nabla P + \mu \Delta \mathbf{v} \quad (2)$$

and the continuity equation

$$\nabla \cdot \mathbf{v} = 0, \quad (3)$$

where P is pressure and ρ and μ are the density and viscosity of water. DEP does not essentially influence density and viscosity of the solution through its small solubility. In the present system, the Rayleigh number was estimated to be three orders smaller than the Marangoni number. Therefore, the buoyancy-driven instability should not play an important role. If we neglect the gravity effect, then only one drag force remains in the system; namely, the shear stress on the surface arising due to the inhomogeneous surfactant distribution.

$$\frac{\partial v_t}{\partial z} = -\frac{1}{\mu} \nabla_s \sigma = -\frac{1}{\mu} \frac{d\sigma}{d\Gamma} \nabla_s \Gamma, \quad (4)$$

where v_t is the tangential component of velocity on the surface, z is the normal coordinate, σ is the surface tension, Γ is the Gibbs adsorption, and ∇_s is the surface gradient. Here we assume the surface tension as a definite function of the surface concentration only. The value of $d\sigma/d\Gamma$ can be found from the equation of state for the surface. The balance of surfactant on the surface is described by the equation

$$\frac{\partial \Gamma}{\partial t} + \nabla_s (\Gamma v_t - D_s \nabla_s \Gamma) + j_n = 0, \quad (5)$$

where $j_n = -D(\partial C/\partial n)_s$ is a diffusion flux of the surfactant between the surface and the water volume, $(\partial C/\partial n)_s$ is the

normal derivative of concentration on the surface, and D_s is the surface diffusivity of surfactant.

If initially the water surface is clean from surfactant and no convection flow occurs in the system then the second term in Eq. (1) and term Γv_t in Eq. (5) disappear. There is only diffusion in the system in the first stage, and the system is stable.

The instability is possible when sufficient concentration gradients accumulate in the system. Usually instability arouses above the critical Marangoni number. Marangoni flow disturbs the concentration distribution formed in the first stage owing to diffusion and leads to a more uniform concentration distribution in the system.

Usually the Marangoni instability excited by normal or by tangential gradients is separately considered. The behavior of a system, the undisturbed state of which is characterized by a uniform normal concentration gradient, depends on the Marangoni number in the form [3,10]

$$\text{Ma} = \frac{h^2}{\mu D} \left| \frac{d\sigma}{dC} \right| \frac{dC}{dz}, \quad (6)$$

where z is the normal to the surface coordinate and h is a characteristic length. The uniform concentration gradient dC/dz can be represented as $\delta C/h$, where δC is the full concentration difference in the system. Thus, the Marangoni number can be written as

$$\text{Ma} = \frac{h}{\mu D} \left| \frac{d\sigma}{dC} \right| \delta C. \quad (7)$$

Above the critical Marangoni number, the conditions for the formation of stationary convective cells are fulfilled [3].

When the system is characterized by a tangential concentration gradient its behavior depends also on the Marangoni number in the form of Eq. (6) or Eq. (7) but with a tangential gradient instead of a normal gradient [5,6].

In the case of equilibrium between the surface and neighboring solution we have

$$\nabla_s \Gamma = \frac{d\Gamma}{dC} \nabla_s C \quad (8)$$

and Eq. (4) can be brought into a dimensionless form

$$\frac{\partial \bar{v}_t}{\partial \bar{z}} = \text{Ma} \bar{\nabla}_s \bar{C}, \quad (9)$$

where the dimensionless variables $\bar{z} = z/h$, $\bar{v}_t = h v_t/D$, $\bar{C} = C/\delta C$, and Marangoni number in the form

$$\text{Ma} = \frac{h}{\mu D} \left| \frac{d\sigma}{d\Gamma} \right| \frac{d\Gamma}{dC} \delta C \quad (10)$$

are used. It is seen from Eq. (9) that the Marangoni number determines the intensity of the convective flow in the system.

For the understanding of the surface-tension auto-oscillations, both normal gradients and tangential gradients in the system must be considered. This circumstance determines the system behavior, as discussed below.

IV. ANALYSIS

A. Mechanism of the surface-tension auto-oscillations

The auto-oscillations in a water/diethyl phthalate system are explained on the basis of Marangoni instabilities arising due to an inhomogeneity in the system because concentration gradients of diethyl phthalate exist in the water volume and on its surface, which increase with time. The maximum DEP concentration exists in the bulk and surface regions near the capillary. The surface gradient of DEP causes surface movement in the direction of smaller concentration (Fig. 1). The convective flux redistributes a quantity of DEP from the bulk region adjacent to the capillary over all the surface, and the surface tension decreases fast. As the DEP concentration becomes uniform, the water movement gradually disappears. In the next stage, the surfactant partially desorbs from the surface in the regions far from the capillary (evaporation from the surface can be neglected) so that the surface tension increases. During this stage, the concentration gradients of DEP restore in the region near the capillary and the procedure repeats again.

Let us consider this mechanism in more detail. In the initial stage corresponding to the induction period, the surface is clean from the surfactant. Therefore, convection cannot be generated and convective flux of DEP is absent. Only diffusion flux of DEP takes place in the volume and an amount of surfactant accumulates slowly in the surface region near the capillary (Fig. 1). Distant parts of the surface (near the platinum plate for the surface-tension measurements) remain clean. As a result there exists a concentration gradient of DEP on the surface $\nabla_s \Gamma$ and a corresponding surface tension gradient $\nabla_s \sigma = (d\sigma/d\Gamma)\nabla_s \Gamma$, which is correlated with a shear stress along the surface (Eq. 4). Although the surface layer of water must flow owing to this shear stress, the flow velocity should be small in the first stage due to the viscous dissipation. At the beginning of the process, the diffusion flux of DEP from volume to the surface is larger than the surface flux. However, when a sufficient amount of DEP is accumulated on the surface near the capillary the surface layer of water begins to move fast in the direction of the adsorption gradient (Fig. 1).

In this second stage, the surface flux of DEP is larger than the diffusion flux from the volume and the surfactant is spread on the surface. The convection is amplified due to the fast delivery of new amounts of surfactant from the water volume on the surface and the convection flux distributes very fast the material from the capillary region completely over the surface. In agreement with the experiments, the surface tension drops sharply at this moment due to the fast developing instability.

The water surface cannot deviate considerably from the flat shape. Consequently, the water flux must be circular. This flux moves new dissolved DEP material from the volume region near the capillary to the surface and replaces it with more clean water from distant volume regions (Fig. 1). It is interesting also to notice the paper where the analogous circular convection in the liquid was produced by a vertically directed laser beam [18]. The distributions of the temperature and the velocity created by the simultaneous action of conductive and convective heat transfer are found by numerical calculations. The clean water afflux interrupts the further de-

velopment of instability. The convection creates the temporary equilibrium in the system and disappears. The system returns to stable conditions.

In absence of the surface flux, the surfactant becomes partially dissolved in the water volume (Fig. 1). A gradual increase in the surface tension is observed in this time interval. Simultaneously a new amount of surfactant accumulates slowly in the surface region near the capillary owing to the diffusion from the capillary tip. As a result the concentration gradient of DEP on the surface is restored in this time interval and then the process repeats again. Based on this mechanism the observed auto-oscillations of the interfacial tension can be understood.

The main feature of this mechanism is a competition between diffusion and convection transfer of the amphiphile in the system. In the first stage, diffusion is dominating and creates the DEP concentration field in the water volume and on the surface. In the next stage, convection becomes dominating and destroys the concentration field. The convection develops fast, so that the convective stage is short whereas the diffusion stage is large.

It is clear also that convection takes place in the diffusion stage due to the tangential concentration gradient. The flow velocity is, however, small as long as the concentration gradient is not large enough. Initially the concentration gradient near the surface is zero and it increases slowly due to diffusion. As the flow velocity is determined by the concentration gradient the convection term in Eq. (1) increases as the second degree of this gradient and is negligible in comparison to the linear terms. Correspondingly inertial terms in the Eq. (2) are small at small flow velocity in comparison to the viscose term. The work of the surface force is mainly spent by viscose dissipation.

B. Concentration gradients in the system

The convective term in Eq. (1) is negligible in the first stable stage. Then the nonstationary concentration distribution in the volume around the DEP drop can be evaluated taking into account only diffusion transfer. Assuming the DEP concentration on the water/DEP boundary is constant and is equivalent to the DEP solubility in water we can write in the spherical coordinate system with the center in the center of the drop

$$C(t, r) = C_0 \frac{r_0}{r} \left[1 - \operatorname{erf} \left(\frac{r - r_0}{2\sqrt{Dt}} \right) \right], \quad (11)$$

where r is a radial coordinate, r_0 is the radius of the drop, C_0 is the DEP solubility, and $\operatorname{erf}(x) = (2/\sqrt{\pi}) \int_0^x e^{-\eta^2} d\eta$ is the error function. The diffusion flux in the distance r from the center is

$$j(t, r) = -D \frac{\partial C}{\partial r} = DC_0 \frac{r_0}{r^2} \left[1 + \frac{r}{\sqrt{\pi Dt}} e^{-(r-r_0)^2/4Dt} - \operatorname{erf} \left(\frac{r - r_0}{2\sqrt{Dt}} \right) \right]. \quad (12)$$

The dependence of this flux on time is shown in Fig. 5 for three different distances r . It can be seen that the diffusion

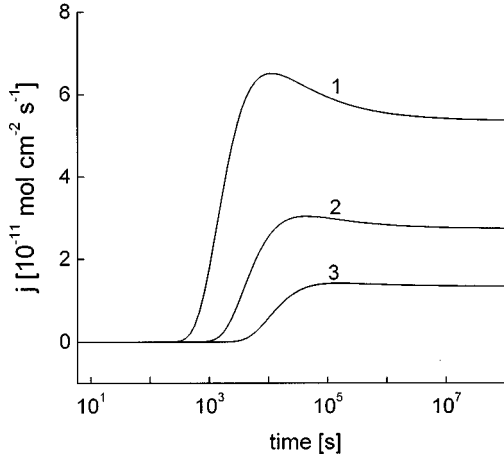


FIG. 5. The dependencies of the diffusion flux vs time on different distances from the center of drop: 1–5 mm, 2–7 mm, and 3–10 mm at $r_0=2$ mm.

flux becomes appreciable after a certain delay depending on the distance from the drop. This delay agrees with the induction time found in the experiments. All amphiphilic molecules, which reach the surface, should be adsorbed by it. As in the initial stage the concentration at high distances from the drop are small, the deviation from the spherically symmetrical concentration distribution caused by the surface should be small. For approximate estimations, a spherical distribution can be assumed. This approximation gives us some underestimated value of diffusion flux to the surface. Neglecting the surface flux divergence in Eq. (5) we obtain for the amount of the amphiphile on the surface

$$\frac{\partial \Gamma}{\partial t} \approx -j_n = D \left. \frac{\partial C}{\partial z} \right|_{z=0} = -D \left. \frac{\partial C}{\partial r} \frac{h}{r} \right|_{r=\sqrt{h^2+\bar{r}^2}}, \quad (13)$$

where z and \bar{r} are the cylindrical coordinates (z axis directed along the capillary: $z=0$ corresponds to the surface) and h is the submersion depth of the capillary.

For typical values of h and D ($h \sim 2$ cm, $D \sim 10^{-5}$ cm²/s), the value of the expression $(r^2 - r_0^2)/4Dt$ is large in comparison to the unity during the initial time interval large enough (until t is small as compared to 10^5 s). As the induction time found in the experiment satisfies this condition we can use the approximation $\text{erf}(x) \approx 1 - (e^{-x^2}/x\sqrt{\pi})$ (at $x \gg 1$). At this condition we can integrate Eq. (13) with Eq. (12) and obtain an approximate expression for the adsorption change with time,

$$\Gamma(t) \approx \frac{4\tilde{N}_0 r_0 h}{r^2(r-r_0)^2} \frac{(Dt)^{3/2}}{\pi^{1/2}} e^{-(r-r_0)^2/4Dt}, \quad (14)$$

where $r = \sqrt{h^2 + \bar{r}^2}$. The time dependence of $\Gamma(t)$ is shown in Fig. 6. Note $\Gamma(t)$ is obtained with the assumption that the adsorption kinetics is limited by diffusion transfer and the surface concentration Γ is far from saturation that corresponds to the initial stage.

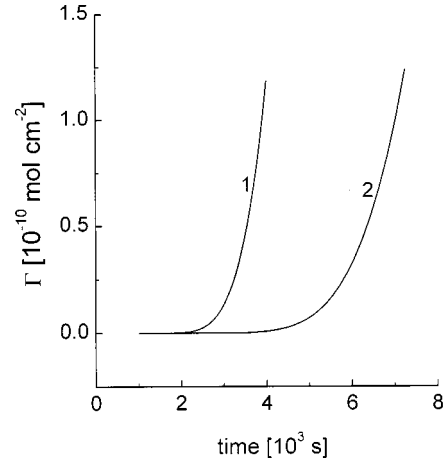


FIG. 6. The dependencies of the surface concentration vs time on different distances from the capillary: 1–5 mm and 2–10 mm at $r_0=2$ mm and $h=10$ mm.

C. System characterization

It is important for the stability analysis that the system considered here is characterized by the nonsteady diffusion flux. The surface concentration gradient $\partial \Gamma / \partial \bar{r}$ and the normal concentration gradient near the surface $\partial C / \partial z$ are changed with time within wide limits and dependent strongly on the coordinates. The Marangoni number discussed above characterizes the system as a whole but it does not reflect the local conditions for a given point in a certain time moment. However, it is clear that in such a system, where concentration gradients are time and radial dependent, the appropriate critical conditions for instability should arise only in a definite part of the system and in a definite time moment but not in the whole system simultaneously. The ‘‘global’’ Marangoni number discussed does not reflect the possibility of instability in our system.

The two dimensionless values,

$$M_1 = \frac{h^2}{\mu D} \frac{d\sigma}{d\Gamma} \frac{d\Gamma}{d\bar{r}} \quad (15)$$

and

$$M_2 = \frac{h^2}{\mu D} \left| \frac{d\sigma}{dC} \right| \frac{dC}{dz} \quad (16)$$

can be considered as dimensionless surface concentration gradients and bulk normal concentration gradients, respectively, or as ‘‘local’’ Marangoni numbers for a nonsteady system. In a very small region near the surface during a very small time interval the concentration gradients are approximately constant and M_1 and M_2 characterize the state of this region in this time interval.

If the value of M_2 is very small the normal concentration gradient can be neglected and the system discussed here is similar to systems with a tangential gradient considered in the literature [5–7]. The tangential gradient produces the convective flow, which attempts to distribute the amphiphile over the surface. The intensity of this convective flow is characterized by the value M_1 .

If the value of M_1 is very small we have a system with normal gradient only. As known, the convection in this system is only possible when the Marangony number M_2 is larger than its critical value [3,10]. The normal concentration gradient is maximal in the region near the capillary. When it increases up to the critical value this region becomes unstable. The convection begins here and spreads rapidly over all the surface. Thus the tangential gradient and the normal gradient play a different role in the system studied. The normal concentration gradient is a source of instability in the system provided it is larger than the critical concentration gradient. If M_2 reaches the critical value, the convection develops rapidly. The normal gradient forms due to diffusion, but this is only possible if the convection caused by the tangential gradient is small enough. Contrary to the normal gradient, the tangential gradient produces convection without a threshold. This convection prevents the formation of a sufficiently large normal concentration gradient if the M_1 value is large. Consequently, in this case, instability cannot occur. If, however, the M_1 value is small, the convective flow caused by the tangential gradient is not intensive and cannot prevent the formation of a normal concentration gradient. Under these conditions, instability is possible. For a quantitative analysis, we need to know the numerical value of the critical M_2 number. The critical values are usually strongly dependent on the boundary conditions. In the present case, the boundary conditions should reflect the adsorption of DEP molecules onto the surface. The critical Marangoni numbers available in the literature [3,10] cannot be used for the analysis of the present system due to the very different boundary conditions. To obtain the value of the critical number M_2 for our system, we need to perform the stability analysis with boundary conditions, which takes into account the amphiphile adsorption onto the surface.

Using the concentration distributions of Eqs. (11) and (14) one obtains

$$M_1 \approx \frac{C_0 r_0 h}{\mu D} \left| \frac{d\sigma}{d\Gamma} \right| \frac{h^3 \bar{r}}{\sqrt{\pi}(h^2 + \bar{r}^2)^2} e^{-(\sqrt{h^2 + \bar{r}^2} - r_0)^2 / 4Dt} \left(\frac{4Dt}{h^2} \right)^{1/2}, \quad (17)$$

$$M_2 \approx \frac{2C_0 r_0}{\mu D} \left| \frac{d\sigma}{d\Gamma} \right| \frac{d\Gamma}{dC} \frac{h^2}{\sqrt{\pi}(h^2 + \bar{r}^2)} \times e^{-(\sqrt{h^2 + \bar{r}^2} - r_0)^2 / 4Dt} \left(\frac{h^2}{4Dt} \right)^{1/2}. \quad (18)$$

It can be seen that the values of both M_1 and M_2 increase with time in the initial stage. However, their time dependencies are different: M_1 , initially smaller than M_2 , increases quicker than M_2 .

The M_2 value contains the parameter $d\Gamma/dC$, which is absent in M_1 . The existence of this free parameter is obviously the main reason that the development of auto-oscillations is limited on amphiphiles such as diethyl phthalate with very special properties. Two different types of system behavior can be expected depending on the values of the solubility C_0 and the surface activity coefficient $\alpha \approx d\Gamma/dC$. If the solubility of the amphiphile is large the M_1 value increases fast. As the intensity of the convection is

characterized by M_1 , the convective flow should also increase fast and consequently, the initial stage is reduced. The convective flux reaches fast the order of the diffusional flux and thus, the accumulation of the amphiphile near the capillary is prevented. The material is distributed over the whole system. During this short time, the M_2 value cannot increase up to the critical value so that the criteria of instability are not fulfilled.

In the opposite case of a small solubility of the amphiphile, the M_1 value increases slowly. The initial stage is long. A sufficient amount of surfactant can accumulate by diffusion near the capillary. In this time, the M_2 value can increase up to its critical value so that instability can occur in the system. In spite of the small C_0 , the M_2 value can be large because of a large $d\Gamma/dC$.

This qualitative presentation of the mechanism suggests that optimal conditions for auto-oscillations exist when the amphiphile has a small solubility and a large enough surface activity. Diethyl phthalate corresponds to these conditions, whereas the most traditional surfactants are too soluble in water in spite of their high surface activity.

Note that the solubility of the surfactant should not be extremely small. It follows from Eq. (18) that the M_2 dependence on time has a maximum and in the case of extremely small solubility M_2 can never reach the critical value, even at an infinitely large initial stage. This is the case for dioctyl phthalate, the solubility of which in water is much smaller than that of diethyl phthalate.

It is seen in Eqs. (17) and (18) that the M_1 and M_2 values depend on the dimensionless parameters S_1 and S_2 , respectively,

$$S_1 = \frac{C_0 r_0 h}{\mu D} \left| \frac{d\sigma}{d\Gamma} \right|, \quad (19)$$

$$S_2 = \frac{C_0 r_0}{\mu D} \left| \frac{d\sigma}{d\Gamma} \right| \frac{d\Gamma}{dC}. \quad (20)$$

Parameter S_1 characterizes a contribution of the convection to the surfactant distribution at the surface. The larger S_1 is, the quicker the convection commences to develop. At small S_1 , the convection will be negligible over a long time. When the surface concentration Γ is far from saturation we have $|d\sigma/d\Gamma| \approx RT$. The main characteristic of the amphiphile, which affects the parameter S_1 , is its solubility in water. For DEP ($C_0 = 0.15$ mass %) at $r_0 = 2$ mm and $h = 1$ cm we obtain $S_1 = 3.3 \times 10^{11}$. The S_1 value can be modified within narrow limits by the choice of the droplet radius. The parameter S_2 for the same conditions is found as $S_2 = 2.3 \times 10^8$.

Comparison of Eqs. (15) and (19) shows that a value $C_0 r_0 / h$ can be considered as an effective adsorption gradient $d\Gamma/dr$ in our system. Analogously, it follows from Eqs. (16) and (20) that a value $C_0 r_0 / h^2$ can be considered as an effective concentration gradient dC/dz in the system. Further experiments will be of interest, which are performed with amphiphiles having different parameters S_1 and S_2 . The parameter S_1 should be comparatively small whereas the parameter S_2 should be comparatively large to initiate auto-oscillations in the system.

An important circumstance should be carefully analyzed. It follows from Eqs. (8) and (15) that in the general case, the M_1 value should also depend on $d\Gamma/dC$. This contradiction

is explained by the fact that in the initial stage of the process of water saturation with surfactant the bulk concentration near the air/water interface is very small and practically does not affect the diffusion flux of a surfactant to the surface. The surface concentration is determined as an integral from this flux on time and, therefore, it also does not depend on $d\Gamma/dC$. In the Appendix an approximate solution for $\Gamma(t)$ is obtained, which takes into account the influence of the surface on the diffusion flux

$$\Gamma(t) \approx \frac{8C_0 r_0 (Dt)^{3/2}}{\sqrt{\pi R(R-r_0)^2}} e^{-(R-r_0)^2/4Dt} \left(1 - \frac{2Dt}{\alpha(R-r_0)} - \frac{6Dt}{(R-r_0)^2} \right), \quad (21)$$

where $\alpha \approx d\Gamma/dC$ is the Henry constant and R is the radius of a sphere, which conventionally represents the air/water interface. Equation (21) is obtained for the spherically symmetrical case and should be considered as a rough approximation of the dependence of Γ on α . If the radius R is much larger than the drop radius r_0 , the part of the spherical surface close to the vertical symmetry axes can be approximately considered as a flat surface. It follows from Eq. (21) that the dependence on $d\Gamma/dC$ can be ignored for times much smaller than a characteristic time $t_c = \alpha(R-r_0)/D$. For $\alpha \sim 3 \times 10^{-3}$ cm, $D \sim 5 \times 10^{-6}$ cm²/s, $r_0 = 0.2$ cm, and $R \sim 1$ cm, a characteristic time in the order of ten minutes is obtained. Note that for a one-dimensional system this characteristic time should be α^2/D . The analysis performed above is only correct for times smaller than the characteristic time $t_c = \alpha(R-r_0)/D$. For amphiphiles with a small surface activity this time is rather small and auto-oscillations cannot be expected, whereas for substances with large surface activity auto-oscillations are possible.

The comparison of Eqs. (14) and (21) shows that for small times and $R \approx r \approx h$ these dependencies $\Gamma(t)$ coincide with the exception of the numerical coefficient, which is two times smaller in the case of Eq. (14). As already discussed, Eqs. (13) and (14) indicate some underestimated values of the diffusion flux to the surface and the surface concentration.

V. CONCLUSIONS

Experimental evidence has been provided that long-time auto-oscillations of the surface tension can evolve. So far, such surface tension auto-oscillations have been studied only in a special system water/diethyl phthalate. Series of experiments have shown that long-time auto-oscillations of the surface tension can be measured when a droplet of the amphiphile diethyl phthalate at a capillary tip is immersed into water. The oscillations are mainly affected by the specific properties of the amphiphile, but also by the immersion depth of the capillary. The mechanism of these auto-oscillations is based on a competition between the diffusion and convection transfer of the amphiphilic material in the system. In the first slow stage, diffusion is dominating and creates a concentration field of the amphiphile in the water volume and at the surface. In the next fast stage, convection becomes dominating and destroys the concentration field.

Theoretical analysis of the experimental results is based

on considerations of the concentration gradients in the system and the characterization of the system parameters. These auto-oscillations are caused by a periodic Marangoni flow on the water surface owing to a surface layer instability. The existence of such periodic Marangoni flow can be experimentally shown. This flow can create the observed surface-tension auto-oscillations. The system behavior depends mainly on two dimensionless parameters S_1 and S_2 , which correlate specifically to the tangential and normal Marangoni number, respectively. The main surfactant characteristics affecting the system behavior are its solubility in water and its surface activity. It can be concluded from the qualitative analysis that a small solubility and rather high surface activity of the amphiphile are significant preconditions for the development of surface-tension auto-oscillations.

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APPENDIX

Consider a spherical amphiphile droplet with the radius r_0 in the center of a water drop with the radius R ($R \gg r_0$). The outside water surface is assumed to be in contact with air. Such a model allows the approximate estimation of the effect of the air/water interface, where adsorption takes place on the diffusion flux of the amphiphile to this surface.

Applying the Laplace transformation the nonstationary diffusion equation, Eq. (1), (without convective term) can be brought for zero initial conditions into the form

$$\frac{d^2 C(s,r)}{dr^2} + \frac{2}{r} \frac{dC(s,r)}{dr} - \frac{s}{D} C(s,r) = 0, \quad (A1)$$

where s is a Laplace variable. Equation (A1) has a solution

$$C(s,r) = \frac{A}{\sqrt{r}} I_{1/2}(r\sqrt{s/D}) + \frac{B}{\sqrt{r}} K_{1/2}(r\sqrt{s/D}), \quad (A2)$$

where $I_{1/2}(x)$ and $K_{1/2}(x)$ are modified Bessel's functions of first and second kind and A and B are constants, which should be found from the boundary conditions. At the water/amphiphile boundary (at $r=r_0$) the concentration is constant,

$$C(r_0) = C_0. \quad (A3)$$

At the air/water boundary (at $r=R$) the following conditions hold:

$$\frac{\partial \Gamma}{\partial t} = -D \left. \frac{\partial C}{\partial r} \right|_{r=R} \quad (A4)$$

and

$$\Gamma(t) = \alpha C(t,R), \quad (A5)$$

where $\alpha = d\Gamma/dC$. The solution corresponding to these boundary conditions is

$$C(s,r) = \frac{C_0 r_0}{sr} \frac{\frac{1}{\alpha} \sqrt{(D/s)} \operatorname{ch}[(r-R)\sqrt{s/D}] + \left(\frac{1}{\alpha R} \frac{D}{s} - 1\right) \operatorname{sh}[(r-R)\sqrt{s/D}]}{\frac{1}{\alpha} \sqrt{(D/s)} \operatorname{ch}[(r_0-R)\sqrt{s/D}] + \left(\frac{1}{\alpha R} \frac{D}{s} - 1\right) \operatorname{sh}[(r_0-R)\sqrt{s/D}]} \quad (\text{A6})$$

and

$$\Gamma(s) = \frac{C_0 r_0}{sr} \frac{\sqrt{D/s}}{\frac{1}{\alpha} \sqrt{(D/s)} \operatorname{ch}[(r_0-R)\sqrt{s/D}] + \left(\frac{1}{\alpha R} \frac{D}{s} - 1\right) \operatorname{sh}[(r_0-R)\sqrt{s/D}]} \quad (\text{A7})$$

This is a kind of transition process for a step-type perturbation. For this process, asymptotic behavior of the $\Gamma(t)$ corresponds to large values of variable s ($s \rightarrow \infty$) at small times

$$\Gamma(s) \cong \frac{2C_0 r_0 \sqrt{D}}{Rs(\sqrt{s} + \sqrt{D/\alpha})} e^{-(R-r_0)\sqrt{s/D}} \quad (\text{A8})$$

The inverse Laplace transformation gives

$$\Gamma(t) \cong \frac{2C_0 r_0 \alpha}{R} \left[\operatorname{erfc} \frac{R-r_0}{2\sqrt{Dt}} - \exp\left(\frac{R-r_0}{\alpha} + \frac{\sqrt{Dt}}{\alpha^2}\right) \operatorname{erfc}\left(\frac{R-r_0}{2\sqrt{Dt}} + \frac{\sqrt{Dt}}{\alpha}\right) \right] \quad (\text{A9})$$

where $\operatorname{erfc}(x) = 1 - \operatorname{erf}(x)$ is the complementary error function. In the initial stage when the following conditions are fulfilled,

$$\frac{Dt}{(R-r_0)} \ll 1 \quad \text{and} \quad \frac{Dt}{\alpha(R-r_0)} \ll 1, \quad (\text{A10})$$

an approximate expression for $\Gamma(t)$ is obtained,

$$\Gamma(t) \approx \frac{8C_0 r_0 (Dt)^{3/2}}{\sqrt{\pi R} (R-r_0)^2} e^{-(R-r_0)^2/4Dt} \left(1 - \frac{2Dt}{\alpha(R-r_0)} - \frac{6Dt}{(R-r_0)^2} \right) \quad (\text{A11})$$

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