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Research article

Excitation of relaxation oscillations at a curved interface under the conditions of an internal problem

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The oscillatory mode of solutal Marangoni convection during the absorption of a surfactant from a homogeneous external solution into a water droplet is studied numerically. This is caused by the effect of gravity, which promotes the sedimentation of surfactant molecules in an aqueous medium. This version of oscillatory convection arising under the conditions of an internal problem was recently discovered experimentally. In the present paper, we consider the case of a chemically inert system, in which there are no reactions. The effects of interfacial deformation are assumed to be insignificant and thus they are neglected. The mathematical model includes the Navier-Stokes equations written in the Hele-Shaw and Boussinesq approximations, and the equations of surfactant transport in the system. We assume that the characteristic time of surfactant adsorption is shorter than the time of its diffusion in both solutions, which makes it possible to ignore the formation of a surface phase. The boundary value problem includes the equilibrium condition of the system, which takes into account different values of the chemical potential in the phases. It is shown that a water droplet accumulates the surfactant molecules that diffuse from the organic phase. The problem is solved in dimensional form using the COMSOL Multiphysics package and based on a set of physical constants for acetic acid which, like many other members of the carboxylic acid family, has the properties of surfactant in water. It was found that direct numerical simulation of the system is able to reproduce the relaxation oscillations observed in the experiment only under the additional phenomenological assumption of non-Newtonian rheology of the interface, which was previously proposed for the external problem. The physical mechanism which may be responsible for the delayed onset of Marangoni instability is discussed. We demonstrate that periodic oscillations are generated inside the drop due to the competition between the Marangoni effect and the gravity-dependent convective instability of the solution. Using direct numerical simulation, we identified the structures of convective motion at the interface and in its neighborhood, determined the flow intensity as a function of time, and obtained the range of change in the oscillation period.

Keywords: computational experiment, surfactant, Marangoni convection, interphase boundary, relaxation oscillations

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1. Introduction

The study of mass transfer processes at the boundary of two immiscible liquid multicomponent solutions — is an urgent and complex problem. It involves a number of physical phenomena, including: adsorption/desorption processes of surface-active substances (surfactants); all sorts of phase transitions both at the interphase boundary (monolayer formation [1]) and near it (e.g., spontaneous association of surfactant molecules in solution — micelle formation [2]); diffusion processes of components, which may depend both on the concentration of the component in question (concentration-dependent diffusion [3]) and also take into account the influence of other components (cross-diffusion [4]); mass transfer due to solutal Marangoni convection [5] arising from the inhomogeneity of surfactant distribution at the boundary of liquids; Rayleigh-Benard concentration convection in the volume of liquids if there is a gravity field or other inertial field. In the case of nonisothermal conditions, the above may be supplemented by Marangoni thermocapillary instability aggravated by the effects of thermoconcentration convection [6]. The combination or competition of these mechanisms leads to the development of oscillatory convective modes. A considerable number of works of mainly experimental character have been devoted to their study (see a recent review on this subject [5]).

Analysis of publications shows that oscillatory currents near stationary bubbles and droplets in stratified surfactant solutions have been well studied [6–10]. Relaxation oscillations were probably first observed near the surface of a horizontal air bubble surrounded by an aqueous solution of one of surfactants (acetic acid and a set of alcohols were used) [7]. Later the effect was reproduced by the same authors near the liquid-liquid surface, but also in conditions of the external problem the behavior of a drop of chlorobenzene surrounded by an aqueous solution of isopropanol was studied [8]. A discussion of the first works on this subject is given in the review [9]. In the work of other authors, the effect is independently "rediscovered" in [10], where the behavior of paraffin oil droplets in environmental aqueous solution of 2-propanol was studied. The application of relaxation oscillations around a bubble or droplet to mixing of ingredients in a flow-type microfluidic reactor is reviewed in [11]. In all the work cited above, stratification of dissolved surfactant was created around the inclusion, which stimulated the onset of concentration-driven Marangoni convection. A short burst of intense mass transfer near the surface led to local disappearance of the surfactant gradient and cessation of convection. It is shown that a return mechanism is required for the origin of periodic oscillations, which can serve, for example, as a gravity field. Some time after convection attenuation, the surfactant solution was stratified again, and the system returned to the initial state. In addition, studies have shown that to observe oscillations, a surfactant whose molecules obey diffusion kinetics is required. In this case, the characteristic diffusion time of the surfactant is much longer than its adsorption time. Molecules with a long hydrophobic part, which obey barrier kinetics, are absorbed by the interfacial surface and form a monolayer that prevents the development of Marangoni convection.

Mathematical models of relaxation oscillations in conditions of the external problem are presented in [12–14]. In all cases, implicitly or explicitly, the effect of delay in the operation of Marangoni convection was assumed. For example, in work [13, 14], the authors introduced into the model a phenomenological assumption about special rheological properties of the interfacial surface, which required a certain threshold of force on the boundary to be reached to begin its motion. This requirement is absent in [12]; however, the problem formulation still implicitly had a lag condition: the surfactant source was located at some depth from the surface, which led to a delay in the release of surfactant molecules onto the surface. It should be noted that the interfacial boundary in [12–14] was assumed to be flat.

Recently, a new variant of the oscillatory mode of solutal Marangoni convection, which is excited under the conditions of the internal problem [15], i.e., inside a drop sandwiched between wide plates and having the shape of a flattened cylinder, has been experimentally discovered. This mode is associated with absorption of surfactant from a homogeneous external solution into the drop and the subsequent formation of a stable vertical stratification of the medium in density and, accordingly, the appearance of a concentration difference along the lateral surface of the drop. In the experiment, a drop of distilled water was placed in an organic solution based on chlorobenzene, benzene, and acetic acid. The initial concentration of acid in the triple mixture varied from 0.25 to 2.0 mol/L. In the course of the experiments, the concentration of acid in a drop of water varied from 0 to 8 mol/L, that is, it accumulated there at a higher concentration than in the initial solution. Relaxation oscillations in this case were generated primarily inside the drop.

The present work has several objectives:

– applies the mathematical model proposed in [13, 14], but in application to the internal problem;

– mass transfer processes are considered both inside and around the droplet, hence the interfacial boundary is curved, which has a significant effect, as shown in [10], on the kind of relaxation oscillations;

– research is conducted in the mode of computer simulation, which is approximated to experimental conditions, which implies the use of equations in dimensional form and the setting of maximally realistic values of physical quantities.

The modeling was performed with the COMSOL Multiphysics package. The numerical results are compared with experimental data [15].

2. Problem Statement

2.1. Mathematical model

In the experiment [15], a rectangular cuvette with surfactant solution had dimensions of 90×25×1.2 mm, which means a strong compression in one of the horizontal directions. The water drop sandwiched between the wide vertical plates of the cuvette took the form of a flattened cylinder whose radius was more than an order of magnitude larger than the narrow gap in the cuvette. The position of the drop was stabilized using the "hydroweighting" technique [14–16], according to which a vertical density gradient is created in the surfactant, and the droplet itself finds a position of equal density. The density field of the external medium in relation to the drop was selected by mixing different amounts of benzene and chlorobenzene. Additional stabilization of the drop was provided by capillary effects near the interfacial surface stretched between the wide plates of the cell.

In full-scale tests, noticeable deformations of the droplet surface are not observed at any stages of mass transfer development in the system. In addition, a priori estimates show that the characteristic size of convective vortices also significantly exceeds the gap between the drop and the cuvette wall; this allows us to use the Hele-Shaw approximation with a transition to a two-dimensional formulation of the problem.

Thus, we will consider a rectangular region of dimensions 90×40 mm, which is filled with an organic mixture of benzene and chlorobenzene with acetic acid dissolved in it. The concentration of the surfactant solution does not exceed 2 mol/L. At the center of the region is a stationary drop 6 mm in diameter, which at the initial instant of time consists of pure water. It is assumed that the shape of the drop is fixed and the drop is stationary. The drop and its surrounding region are considered as two fixed domains, in each of which we will set the equations of convection and diffusion of solutions, and at the boundary of the domains (on the interfacial surface) we will take into account the appropriate boundary conditions. Physical processes in the given problem assume adsorption of acetic acid by the drop surface and subsequent desorption of acid molecules on both sides of the interfacial surface. The latter leads to penetration of the acid into the drop and the formation of an aqueous acid solution. The physical properties of the liquids filling the domains are presented in the table. Information on properties of acetic acid solutions in water and benzene is taken from sources indicated. Here mf_1 — mass fraction of acetic acid in aqueous solution. Some characteristics of solutions depend on concentration. Thus, the dependence of the density of the solution on concentration becomes the cause of different buoyancy of the elements of the system. This can cause the development of convection in liquids near the surface of the drop, on which the mass-exchange diffusion process occurs. The dependence of the surface tension coefficient on concentration stimulates the nucleation of concentration-capillary Marangoni convection on the surface of the droplet. The relationship between viscosity and concentration is also considered. Since weak solutions of acetic acid are considered in the problem, all characteristics of the solutions depend on their concentration in a linear fashion.

Table. Properties of the water/organic mixture system (50% benzene and 50% chlorobenzene) with interfacial mass transfer of acetic acid; index 1 corresponds to the aqueous phase, index 2 to the organic phase

Physical quantity	Designation	Dimension	Value	Source
Molar mass of water	μ_1	g/mol	18	[17]
Molar mass of organic mixture	μ_2	g/mol	95	[17]
Density of water	ρ_{01}	kg/m^3	998	[15]
Density of an aqueous acid solution	ρ_1	kg/m^3	$\rho_{01}+0.00834$[kg/mol]$\cdot c_1$	[18]
Density of organic mixture	ρ_{02}	kg/m^3	1048	[15]
Density of organic acid solution	ρ_2	kg/m^3	$\rho_{02}-0.00197$[kg/mol]$\cdot c_2$	[18]
Dynamic viscosity of an aqueous acid solution	η_1	Pa·s	$(1.0+2.1\cdot mf_1)\cdot 10^{-3}$	[18]
Dynamic viscosity of an organic acid solution	η_{21}	Pa·s	$0.74\cdot 10^{-3}$	[17]
Acid diffusion coefficient in water	D_1	m^2/s	10^{-9}	[17]
Acid diffusion coefficient in organic solution	D_2	m^2/s	10^{-9}	[17]
Surface tension at the water/benzene interface	σ_0	N/m	0.035	[18]
Surface tension at the water/benzene/acid interface	σ	N/m	$0.0343+0.174mf_1$	[18]
Acid separation coefficient at the water/mixture interface	k_μ	b/r	7	[19]
Acid mass transfer coefficient at the water/mixture interface	k_c	m/s	$10^{-6}\div 10^{-5}$	[15]
Initial acid concentration in an organic mixture	c_0	mol/l	$0.5\div 2$	[15]
Hele-Shaw cell thickness	d	mm	1.2	[15]

Let us formulate the mathematical model. We assume that the flow in the volume of the drop and in the region is laminar and is described, respectively, by the Navier-Stokes equations in the Boussinesq [20] and Hele-Shaw [21] approximations and by the continuity equation:

$$\rho_{0i}\left(\frac{\partial \mathbf{u}_i}{\partial t}+\frac{6}{5}(\mathbf{u}_i\cdot\nabla)\mathbf{u}_i\right)=-\nabla p_i+\eta_i\nabla^2\mathbf{u}_i-\frac{3\eta_i}{d^2}\mathbf{u}_i+\rho_i\mathbf{g}, \tag{1}$$

$$\nabla\cdot\mathbf{u}_i=0, \tag{2}$$

where the index i takes the values 1 (for an aqueous droplet) and 2 (for an external environment — organic solution), t — time, ρ_{0i} — density of the solvent, $\mathbf{g}$ — the free-fall acceleration vector, $\mathbf{u}_i$, p_i — the velocity and pressure of the fluid, ∇ — the Nabla operator, $\jmath_i$, æ$_i$ — the dynamic viscosity coefficient and the density of the solute.

The equations of acetic acid transfer in phases are as follows:

$$\frac{\partial c_i}{\partial t}+(\mathbf{u}_i\cdot\nabla)c_i=D_i\nabla^2 c_i, \tag{3}$$

where c_i — concentration and D_i — diffusion coefficient of the acid in the corresponding phase.

The experimental data [15] show that the acid is absorbed by a drop of water from the surrounding solution. At the same time, due to the effect of contraction (reduction of the initial volume due to compression), acetic acid molecules show different behavior in the aqueous and organic phases. In relationship to the mixture of benzene and chlorobenzene, the acid acts as a light impurity (negative contraction). Dissolution of acetic acid in water is accompanied by positive contraction, and it follows that the acid should be regarded here as a heavy impurity. Under the action of gravity, the aqueous solution of acid begins to stratify in the drop: at the bottom of the drop it has a high concentration. Outside the drop, the solution stratifies much more weakly due to smoothing by diffusion and small volume convection. Thus, in the part of the droplet adjacent to the interphase boundary, the conditions for the occurrence of Marangoni convection add up. Therefore, the surface tension coefficient is calculated from the volume concentration of aqueous acetic acid solution near the inner lateral surface of the drop according to the formula [18]:

$$\sigma = 0.0343 - 0.174 mf_1 \text{ N/m}, \tag{4}$$

The COMSOL Multiphysics package offers an appropriate model for simulating solutal Marangoni convection, which occurs when the surface tension at the boundary of liquids depends on the concentration of solutes or the temperature distribution. Its contribution to the movement of the fluid is realized through a dynamic condition for the balance of stresses arising at the interfacial surface [22]:

$$\left[-p\mathbf{I} + \eta\left(\nabla\mathbf{u} + \nabla_\tau \cdot \mathbf{n}(\nabla\mathbf{u})^{\mathrm{T}} - \frac{2}{3}(\nabla\cdot\mathbf{u})\mathbf{I}\right)\right]\mathbf{n} = \sigma(\nabla_\tau\cdot\mathbf{n})\mathbf{n} - \nabla_\tau\sigma, \tag{5}$$

where the index τ denotes the direction tangential to the boundary, and the brackets[...] contain the difference of values at the rupture. In equation (5), the left-hand side contains the difference of the viscous stress tensors given in media 1 and 2, while the right-hand side contains the terms related to surface tension; the first term includes the mean curvature of the surface, while the second term can be regarded as the Marangoni stress arising from variations in the surface tension coefficient along the surface of the droplet.

When setting the boundary conditions for concentrations of acetic acid solutions in the vicinity of the drop and in the drop, the difference of the corresponding chemical potentials in benzene–chlorobenzene and water should be taken into account. It is known that at the boundary of two liquids the flux of particles of matter **J** is proportional to the concentration and the gradient of the chemical potential μ:

$$\mathbf{J} \sim -c(\nabla_n\mu)_{p,T}, \quad \mu \equiv \left(\frac{\partial G}{\partial N}\right)_{p,T}, \tag{6}$$

where G — the Gibbs energy, N — the number of particles in the system. It should be noted that the chemical potential of a solution depends on its concentration:

$$\mu_i = \mu_{i0}(T) + RT\ln\left(\frac{c_i}{c_{i0}}\right), \tag{7}$$

where μ_{i0} — standard chemical potential at a dissolved concentration of $c_{i0} = 1$mol/L. It depends on the dissolved substance and the solvent. The standard chemical potentials of acetic acid in water and in benzene differ markedly. The equilibrium condition at which the mass transfer of the droplet with the environment ceases can be obtained from (6) and (7) as follows:

$$c_1 = k_\mu c_2, \quad k_\mu = \frac{\tilde{\mu}_{20}}{\tilde{\mu}_{10}}, \quad \tilde{\mu}_{i0} \equiv \exp\left(\frac{\mu_{i0}}{RT}\right). \tag{8}$$

After the system reaches equilibrium, the concentration of acid in the drop will be higher by a factor of k_μ, i.e., the water drop in this problem acts as an acid accumulator. This multiplier is called the partition coefficient (see Table).

In the mathematical model, the key assumption is the hypothesis of special rheological properties of the interfacial boundary. In work [13, 14], this surface was assumed to have non-Newtonian behavior. This means that it comes to move only after the external force applied to it exceeds some value. Following this, we assume that there is a surfactant rheology on the surface of the drop such that the stress f_M due to the Marangoni concentration effect is calculated by the formula:

$$f_M = -H(|\nabla_\tau\sigma| - f_0)\nabla_\tau\sigma, \tag{9}$$

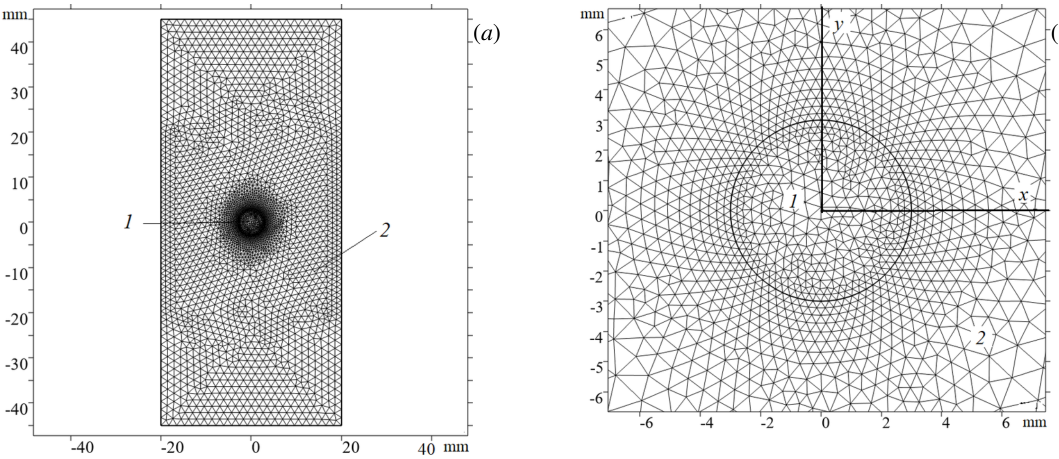

Fig. 1. The computational grid for the entire computational domain (*a*) and in increased size near the drop (*b*); numerals *1* and *2* denote the computational subareas of the drop and the external environment

where $H(x)$ — Haviside function, f_0 — threshold for the occurrence of concentration-capillary convection. Thus, viscous stresses on the surface of the droplet that appear due to the Marangoni effect are accounted for only at those moments in time and on that portion of the surface where they exceed a threshold value. If the stress (9) has not reached the threshold value, the surface remains stationary.

Let us formulate the boundary conditions of the problem as follows:

$$\mathit{\Lambda}: \quad \mathbf{u}_i = 0, \quad -\mathbf{n}\cdot\mathbf{J} = 0, \tag{10}$$

$$\mathit{\Gamma}: \quad u_{in} = 0, \quad u_{1\tau} = u_{2\tau}, \quad \mathbf{n}\cdot\mathbf{J}_1 = -\mathbf{n}\cdot\mathbf{J}_2 = k_c(c_2 - k_\mu c_1), \tag{11}$$

where $\mathit{\Lambda}$ and $\mathit{\Gamma}$ denote, respectively, the outer boundary of the Hele-Shaw cell and the interfacial boundary. As can be seen from (10), at the walls of the region the liquid velocity is zero and there is no flow of acetic acid through the solid walls. On the surface of the drop (11), the normal component of the velocity is zero and the tangential component is continuous. The boundary conditions for acid transport (diffusion) across the drop surface are represented by the flux equality and phase equilibrium condition, where k_c — the acid mass transfer coefficient at the water/organic mixture boundary.

The initial conditions of the problem are of the form:

$$t = 0: \quad \mathbf{u}_1 = 0, \quad \mathbf{u}_2 = 0, \quad c_1 = 0, \quad c_2 = c_0, \tag{12}$$

where c_0 — the initial concentration of acetic acid in the organic phase.

2.2. Numerical implementation of the model

The COMSOL Multiphysics package was used to solve the boundary value problem (1)–(12). The computational domain was partitioned into elements using a triangular mesh with densification near the drop surface (Fig. 1). A Cartesian coordinate system was used in the computational model, with the origin at the center of the drop (Fig. 1*b*), and as an auxiliary — polar coordinate system whose radius and polar angle were defined as $r^2 = x^2 + y^2$, $x = r\cos(\varphi - 90°)$, $y = r\sin(\varphi - 90°)$.

Preliminary calculations have shown that smoothing is critical in calculating the surface tension coefficient on curved surfaces. The drawing 2*a* shows the acetic acid concentration field calculated without considering the Marangoni tension at time $t = 100$ s. The drawing 2*b*, *c* on the surface of the drop shows the dependence on polar angle φ of the surface tension coefficient calculated in accordance with expression (4) and the shear stress calculated by formula (9). The results are presented both before and after the smoothing procedure. It can be seen from the figures that even small deviations from the smooth behavior of the surface tension function cause a sharp spike in the shear stress on the surface. And such a pattern is observed even after a rather long time from the moment when the large concentration gradients associated with the initial transient stage of evolution have already been smoothed out. Consideration of the dynamics at small times only exacerbates the discontinuous nature of the data. To solve this problem, the surface tension coefficient was

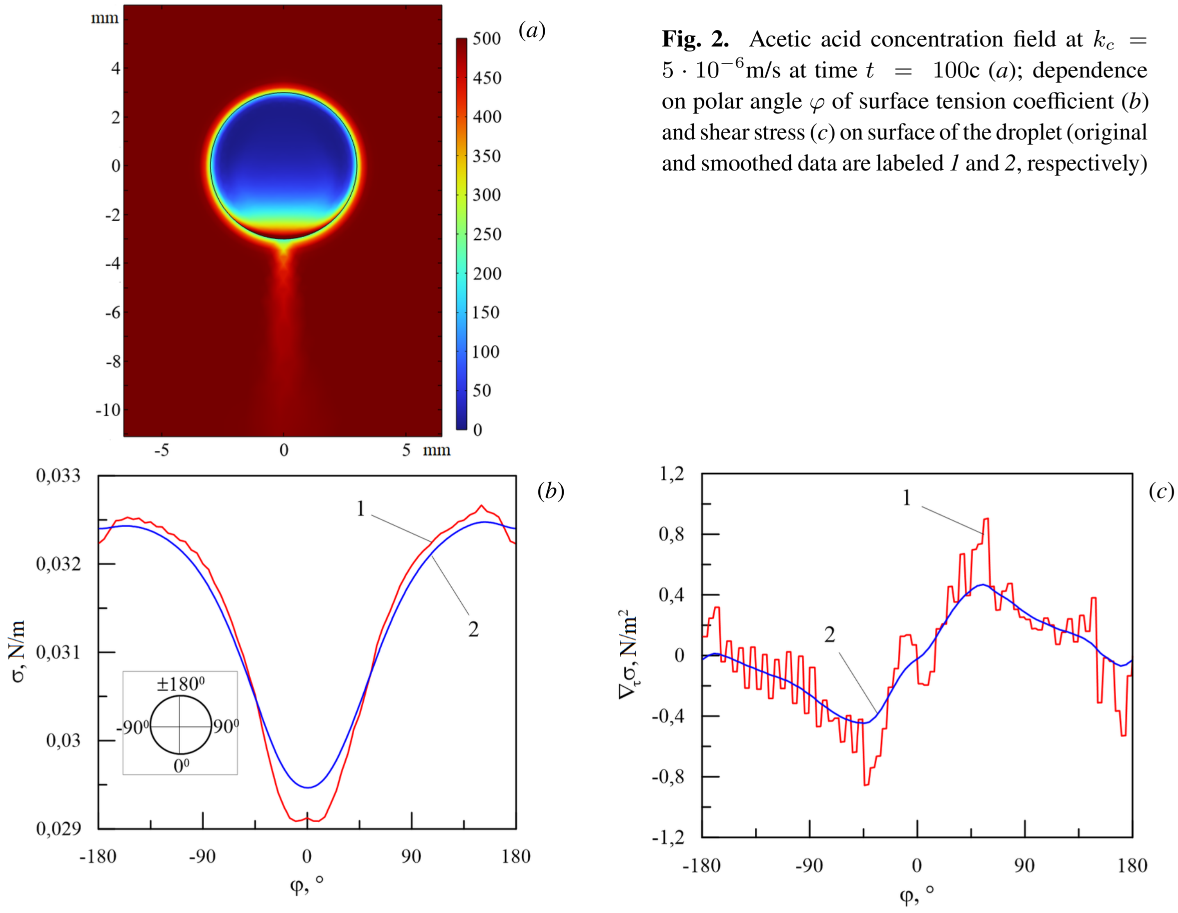

Fig. 2. Acetic acid concentration field at $k_c = 5 \cdot 10^{-6}$m/s at time $t = 100$c (a); dependence on polar angle φ of surface tension coefficient (b) and shear stress (c) on surface of the droplet (original and smoothed data are labeled *1* and *2*, respectively)

smoothed using a Helmholtz filter:

$$\nabla \cdot \left(-R^2 \nabla U\right) + U = D, \tag{13}$$

where D — input data, U — filtered data, R — filter radius (adjustment parameter). In calculations, $R = 10^{-3}$ was assumed. The curves *2* in Figures 2*b*, *c* correspond to the data smoothed with the Helmholtz filter (13).

3. Numerical Results

Numerical simulations show that the mathematical model described above adequately depicts the oscillatory mode of acetic acid absorption by a water droplet under conditions of the internal problem. We present the results of the sumulations for a drop with a diameter of 6 mm and a threshold constant for the occurrence of concentration-capillary convection $f_0 = 0.4$ N/m^2. Figure 3 shows the time dependences of the tangential stress f_M measured at two points with values of angle $\varphi - 45^\circ$ and 45°, corresponding to the right and left parts of the droplet surface. It can be seen that relaxation oscillations do not instantly occur, but after some time, during which the Marangoni shear stress reaches a critical value f_0. For the parameters assumed in the calculation, this time is about 45 s.

Each oscillation period consists of two phases that run with substantially different characteristic times. This leads to a law of oscillation that is very different from harmonic oscillation. The slow process (relaxation) is represented by the diffusion of acetic acid in aqueous solution under the influence of gravity. The fast process is due to the Marangoni flash convection, which does the work of moving the surfactant molecules in the field of gravity to the initial state with a higher value of potential energy. Under these conditions, the oscillation period (on the order of 5 s, see Figure 3) is actually determined by the characteristic diffusion time required to move the surfactant molecules to the lower part of the droplet surface and create there the required concentration gradient on the curved interfacial surface. Figure 4*a* shows the instantaneous velocity fields that occur during the slow (relaxation) phase, and Figure 4*b* — at the outbreak of Marangoni convection. In force of the continuity of tangential stresses at the interphase boundary, convective vortices are formed

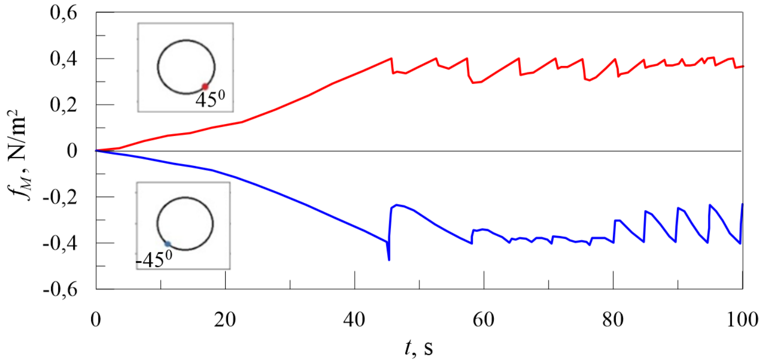

Fig. 3. Variations of tangential stresses on the interfacial surface as a function of time for the case $f_0 = 0.4$ N/m^2; data are obtained for points on the surface of the drop with values of polar angle $-45°$ and $45°$

both inside and outside the droplet. From the figure, it generally appears that the main events occur at the bottom of the droplet, where surfactant molecules accumulate. Acetic acid in aqueous solutions is a heavy impurity, so in the field of gravity the molecules settle out. For surfactants that behave as a light component in water (e.g., alcohols), the effect may be reversed, and oscillations will be generated in the upper part of the droplet. The velocity is maximized at points that are at approximately an angle of –45° to the vertical (Fig. 4*b*). We found that the liquid jet along the surface generated by the Marangoni instability does not rise above $\varphi = 90°$ as the magnitude of the tangential stress falls below a threshold value.

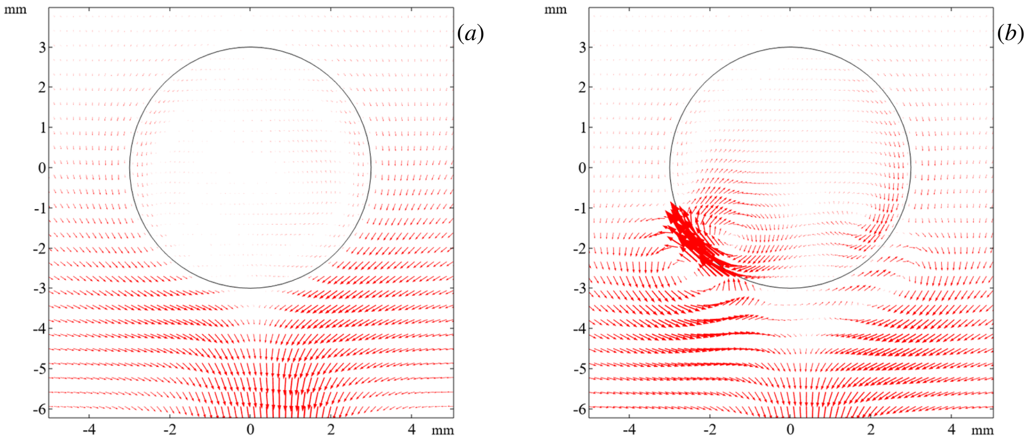

Fig. 4. Velocity field at moment of relaxation (*a*) and immediately after a burst of concentration-capillary convection (*b*); droplet diameter 6 mm, threshold value of tangential stress $f_0 = 0.4$N/m^2

It is worth paying attention to that there are two competing oscillators in the system, since the conditions for the Marangoni convection outbreak are independently formed in the left and right parts of the drop. In this case, synchronization of oscillations is not observed as a rule. For example, Figure 4*b* shows how concentration-capillary flow is excited in the left side of the droplet, while the right half remains, in together, stationary at this time. The time sweeps presented in drawing 3 illustrate this conclusion. Nevertheless, nonlinear oscillator interaction is present. In drawing 3, it is noticeable that time windows of increased activity of one oscillator are accompanied by suppression of a competitor. For example, between the times 55 and 80 s, the right-hand side of the droplet is most pronounced, and after 80 s the oscillators switch roles. The nonlinearity of the interaction is due to counter effects. On the one hand, the convective vortex throws surfactant molecules upward along the surface, but due to the force of the closed flow, it pulls other molecules to the surface from the central part of the drop (see Fig. 4*b*). The latter helps the competitive oscillator to form the desired surfactant concentration gradient along the surface more quickly. However, the sign of the tangential stresses of the oscillators are different (Fig. 3), which leads to suppression of one of the oscillators when convection flashes at the competitor.

Also in the figure 4 one can see weak gravitational convection, which is detected both at the relaxation moment and at the outbreak of Marangoni convection. This effect is well observed in the right side of the droplet, with fluid motion directed downward both inside the droplet and from outside the interfacial surface side. This convection is a consequence of contraction. In the external solution, which is initially homogeneous, acetic acid acts as a light impurity. Therefore, as the surfactant diffuses into the interior of the droplet (because of the difference in chemical potentials between the water and the organic mixture, the droplet serves as a surfactant concentrator), the light component is lost and the buoyancy of the mixture is reduced. A downward movement of the solution begins, which looks like a long jet under the drop. A similar phenomenon is also observed in physical experiments [5].

The pictures of successive changes in the surfactant concentration field during the oscillation are shown in Figure 5. The phases of relaxation (Fig. 5*a*), maximum development of Marangoni convection, which at this time was excited almost symmetrically on both sides of the drop (Fig. 5*b*), and attenuation of concentration-capillary convection (Fig. 5*c*) are presented. The formation of a jet of organic solvent depleted of acetic acid molecules is clearly visible in the drawing. The recoil from the attenuating Marangoni vortex on the outside of the interfacial boundary also contributes to the jet (Fig. 5*c*, vortex on the left). In general, it can be concluded that only the lower part of the droplet is involved in the mass transfer process.

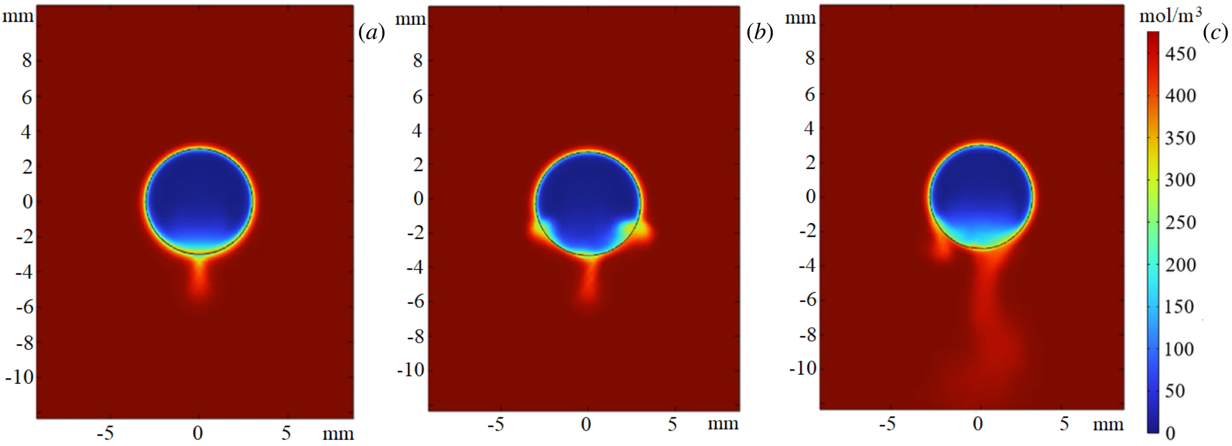

Fig. 5. Surfactant concentration fields at consecutive time points t, p: 40 (*a*), 45 (*b*), 50 (*c*), for $f_0 = 0.4$ N/m^2

The parameter f_0 is found to be bifurcational. Figure 6 shows the bifurcation diagram of the period-averaged amplitude of relaxation oscillations depending on the threshold value f_0. The amplitude curve has a typical form for the Andronov-Hopf bifurcation. Strong fluctuations are observed near the threshold. The perturbations lead to sporadic bursts of weak oscillations that decay after a few periods. Determination of the amplitude of the oscillations is accompanied here by an error greater in comparison with the parameter range in which the oscillations have a pronounced stable character. The bifurcation point ${f_0}^*$ is in the interval from 0.15 to 0.2 N/m^2. In the case where the (9) hypothesis is not applied at the interphase boundary, i.e., $f_0 = 0$, relaxation oscillations were not observed in numerical experiments.

Figure 6 illustrates how the value of parameter f_0 was chosen. As can be seen, the condition $f_0 > {f_0}^*$ is required to excite oscillations, which ensures that a process above the bifurcation point is considered. Further, the value of f_0 is chosen so that the amplitude and period of the oscillations are closest to experimentally observed values. The parameter f_0 determines the force that generates the instantaneous finite impulse imparted to the interfacial surface. The magnitude of this momentum determines how far by inertia the surface will move and, hence, how long it will then take to return to the initial state. When f_0 is varied, the amplitude and period of the oscillations vary within sufficiently wide limits. For example, if the value of f_0 is made too large, the interfacial surface will shift by inertia all the way to the upper part of the droplet. At the same time, experimental data indicate (see [15]) that the surface never rises above the horizontal symmetry line of the droplet. The value of f_0 was chosen such that in numerous experiments these requirements were fulfilled (see Phys. 5*b*).

4. Discussion and Conclusion

According to the classical understanding of the solutal Marangoni effect, the concentration-capillary convection begins at any, however small, value of the surfactant concentration gradient applied to the interface. The formula (9) implies that the gradient must first reach a certain critical value, after which convection is excited. In the problem discussed in this paper, it turns out that the hypothesis (9) is the key to describing relaxation oscillations. This conclusion can be reformulated in a

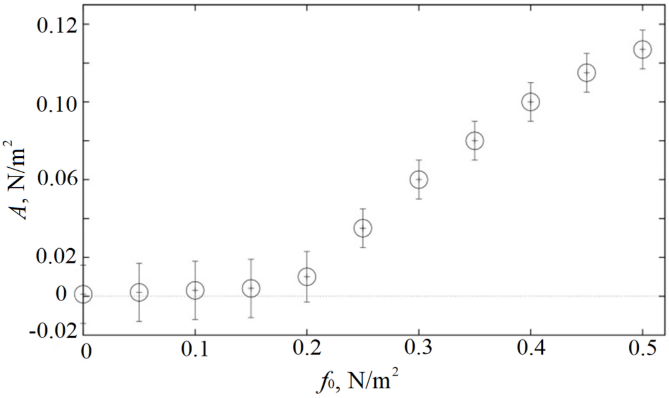

Fig. 6. Average amplitude of tangential stress fluctuations as a function of the parameter f_0 that sets the threshold for the onset of Marangoni convection (simulations performed for a droplet with a diameter of 6 mm)

different way. It can be postulated that some time must elapse between the formation of a surfactant concentration gradient along a surface and the onset of motion of that surface. An alternative to the formula of (9) would be an inverse relationship between the magnitude of the surface tension and the velocity of fluid motion on the surface, triggered with some characteristic lag time. Such a hypothesis also leads to excitation of relaxation oscillations in the mathematical model.

The problem with the formula (9) and any similar hypotheses is that they are phenomenological in nature. In fact, the lack of experimentally confirmed information about the specific physical mechanism that underlies the phenomenon is compensated for by a well-known mathematical technique that is guaranteed to excite oscillations in numerical simulations. As is well known, time delay is a typical cause of oscillation excitation in dynamic systems [23]. The lack of information is partly due to the difficulty of conducting experimental studies of concentration fields, for which there is a small selection of possibilities for visualizing them and obtaining quantitative data [9]. In some papers (see, e.g., [14]), a hypothetical explanation is given as to why such a non-classical manifestation of the Marangoni effect occurs. As a rule, water contains uncontrolled surfactant impurities (most often of organic origin) that are hard to purify, and most experimenters ignore this procedure. If an impurity is introduced into a biphasic system in which one of the phases is water, it is rapidly adsorbed by the interfacial surface with the formation of a surface phase. When the molecules of the controlled surfactant approach the surface, it takes time for them to squeeze the parasitic impurity out of the surface (which they usually do not manage to do until the end). This explanation seems logical, but it is not sufficient. First, the very declaration that something "uncontrollable" is present in the experiment already radically changes the results of the physical experiment and, from the point of view of the methodology of science, looks vulnerable. It seems to the authors of the paper that it is necessary to make efforts to design an experiment without such — "uncontrolled" — interference. Unfortunately, this is not easy to realize, since the Phyzo-interferometry method, the main method for measuring concentration fields, works well only for double solutions, and two surfactants competing in solvent already constitute a triple solution. Second, the situation requires theorists to create a mathematical model that does not have phenomenological assumptions of one kind or another in their formulation. In conclusion, we note that in this paper we numerically investigated the problem of inducing relaxation oscillations inside a quasi-dimensional water drop having a circular shape and surrounded by a homogeneous organic surfactant solution. It is shown that the oscillations can be described only under an additional assumption about the threshold character of the solutal Marangoni effect. It is shown that the parameter setting the threshold value is the control parameter of the Andronov–Hopf bifurcation. The bifurcation point above which oscillations are excited in the system is determined.

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