

Development of Concentration-Capillary Convection on an Interfacial Surface

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Abstract—The onset of Marangoni convection initiated by introducing a surfactant solution drop onto a horizontal liquid interface is studied experimentally and theoretically. It is revealed that the film of admixtures adsorbed by this surface from the bulk of the contacting liquids begins to move only as a certain shear stress is reached, that is, the capillary flow development is of threshold nature. If compared with Marangoni convection development on the free liquid surface, the threshold shear stress may turn out to be either lower or higher, depending on the surfactant admixture concentration in both liquids and the pattern of changes in the surface tension with approaching the interfacial surface. In order to describe the threshold development of concentration convection, a nonlinear dependence of the shear stress at the liquid surface on the liquid velocity is proposed. In a numerical experiment, the convective flow pattern on the interface is determined and the time dependence of the flow intensity is obtained.

Keywords: Newtonian liquids, surfactants, adsorbed film, Marangoni convection.

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Recent investigations have obviously shown that the pattern and intensity of capillary motion depend on both the spatial distribution and value of the surface tension drop created and the properties of the liquid surface [1–3]. In their turn, the properties of the surface are determined not by the liquid nature alone but also by the composition and concentration of the admixtures adsorbed by the surface from the liquid bulk and the contacting medium. For example, alkanes and phthalates present in the water bulk in concentrations of the order of several micrograms per liter impart to the liquid surface the properties typical of a viscoplastic liquid [4]. Note that the possibility for the water surface to acquire non-Newtonian properties as a result of adsorption of admixtures was first mentioned by V.G. Levich and A.N. Frumkin when interpreting the dependence of the velocity of the rising bubble on its size [5]. Subsequently, this hypothesis was confirmed by the experiments of A.V. Gorodetskaya on rising air bubbles in water of different purification efficiencies [6].

The character of the effect of adsorbed mixtures on capillary flow can in many respects be anticipated basing on experiments with surfactant solutions. In particular, the presence of surfactants in the liquid may lead to phenomena similar to the absence of thermocapillary drift in surfactant solutions on the basis of organic liquids [7], the rapid cessation of thermocapillary drift in aqueous alcohol solutions [8], a decrease in intensity and even suppression of thermal Marangoni convection from local heat sources [9, 10], and the threshold onset of capillary motion as a surfactant diffuses across the interfacial surface [11, 12].

In contrast to the surfactants purposefully used in experiments, the composition and concentration of admixtures in the liquid usually remain unknown, being only indirectly determined by the systems of industrial and laboratory purification. It is these uncontrolled admixtures that form the main source of low repeatedness of the results in most of experiments on studying Marangoni convection.

The traditional method to reduce the admixture effect is to take the liquid with maximum purification and minimum surface tension σ (the lower σ , the smaller amount of admixtures displays surfactant properties with respect to the liquid taken).

If it is necessary to use a liquid with high surface tension, it may be promising to use an interfacial surface. As a rule, it is possible to find for the liquid with high σ such a contacting liquid that the interfacial tension is lower than the individual tension. Moreover, in the absence of equilibrium admixture distribution in the liquid system the admixture adsorption is accompanied by diffusion transfer across the interface. If the admixture adsorption rate is lower for one liquid (donor) than the desorption rate for the other (recipient), we can anticipate a substantial decrease in the surface admixture concentration at the interface as compared with the case of equilibrium admixture distribution observed at the free surface. We can use this fact for, for example, decrease in the surface tension threshold drop necessary for Marangoni convection onset [3]. It is the checking of this hypothesis that has become the main problem for the experimental part of the present study. Moreover, the experimental results enabled us to verify the theoretical model of Marangoni concentration convection in the system of liquids with the interfacial boundary that displays non-Newtonian properties.

1. EXPERIMENTAL TECHNIQUES

The experimental cuvette had the shape of a vertical rectangular cell of plane-parallel glass with an inner cavity measuring $9.0 \times 5.0 \times 0.4 \text{ cm}^3$ (Fig. 1). The concentration fields and flow patterns were visualized using a Fizeau interferometer [13] with the video recording of the signal. The observation was performed from the side of wide cell facets.

In the isothermal case, the interferometer visualized the concentration inhomogeneities within the solution in the form of a system of isolines that represented bands of equal optical length. Since the liquids used had small diffusion coefficients (the corresponding Schmidt numbers $Sc \geq 10^3$) the concentration field can be assumed to be “frozen” in the moving liquid bulk, which enabled us to determine from the interferograms the flow pattern and to follow its evolution.

The interferograms were recorded using a digital Basler 402 K video-recorder. It gave the image of the central part of the cuvette with a frequency of 24 fr/s and maximum resolution of 2300×1700 , which allowed us to use fairly concentrated surfactant solutions.

We experimentally investigated the process of capillary motion onset in response to the introduction of a microdrop ($V = 5 \mu\text{l}$) of controlled surfactant solution with mass concentration C onto the horizontal interfacial surface between water and an organic liquid immiscible with it (chlorobenzene or cyclohexane). The drop was created using a pipette with a dispensing accuracy of $0.1 \mu\text{l}$.

As the surfactant we took isopropyl alcohol and acetic acid, whose physicochemical characteristics are presented in the table [14, 15]. Depending on its density, the surfactant was solved in one of the contacting liquids, so that the surfactant solution drop introduced from the side of this liquid moved toward the interface under the action of the Archimedean force.

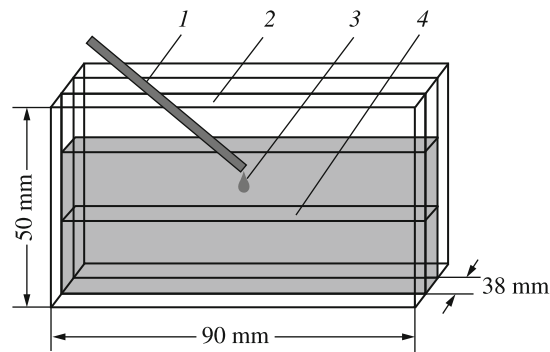


Fig. 1. Diagram of the experimental cuvette: hollow needle (1); semi-transparent mirrors (2); surfactant solution drop (3); interfacial boundary of two liquids (4).

Table

Liquid, purification efficiency	Chemical formula	ρ , g/cm ³ $T = 20^\circ\text{C}$	σ , dyn/cm	D , 10 ⁻⁵ cm ² /s
Water deionized	H ₂ O	1.00	72.8	1.00
Isopropyl alcohol (chemical purity)	C ₃ H ₇ OH	0.78	21.2	1.20
Acetic acid (chemical purity)	CH ₃ COOH	1.05	27.2	1.29
Chlorbenzene (chemical purity)	C ₆ H ₅ Cl	1.11	33.2	1.02
Cyclohexane "For chromatography"	C ₆ H ₁₂	0.78	25.3	0.84

As shown in [3, 6], the concentration of uncontrolled surfactant admixtures is predetermined by their purification efficiency and the quality of preparation of the cuvette whose walls may be covered by the film of poorly soluble substances. In view of this, after each set of experiments the cuvette was (a) mechanically cleaned several times using a "Fairy" detergent; (b) placed under running water for an hour; and (c) washed by a liter of distilled water.

In order to make purification better, distilled water was filtered several times through a "Vodoley" deionizer (production association "Khimelectronica", Moscow) until its electrical conductivity was lowered by an order (from 2.4 to 0.15 $\mu\text{S}/\text{cm}$). Deionized water was used for the final washing of the cuvette.

All experiments were performed in the isothermal regime at the temperature of the environment and operating liquids equal to $(23 \pm 1)^\circ\text{C}$.

2. RESULTS OF THE EXPERIMENT

We managed to confirm the assumption made of the possibility to lower the threshold in the concentration of the surfactant introduced and, correspondingly, in the created shear stress necessary for the onset of capillary convection on the interfacial surface in the experiment on the two-layer system "deionized water – chlorbenzene" (interfacial tension $\Delta\sigma = 38.1$ dyn/cm [14]). A drop of isopropyl alcohol solution in chlorbenzene was introduced onto the interfacial surface from the side of chlorbenzene, the heavier liquid in the system.

In Fig. 2, two series of interferograms are presented. The first series (left column) demonstrates how the surfactant drop reaches in the form of a jet with $C_d = 2\%$ the liquid interface (Fig. 2a) and then spreads gravitationally without development of capillary motion (Fig. 2b–2d). Increase in the surfactant concentration in the drop up to $C_d = 3\%$ produces a "flash" of Marangoni convection (Fig. 2f–2g). The capillary motion is characterized by a fair symmetry about the interface and low penetration into both the water and chlorbenzene bulks. In both liquids the flow symmetry is most pronounced in the final stage of the Marangoni convection "flash" when a return surface motion begins (Fig. 2h). This motion appears owing to the finite size of the interfacial surface: the film of admixtures, which was first pushed by the capillary motion to the cavity boundaries, returns to the initial position with the solution (desorption) of the introduced surfactant within the bulk of the contacting liquids. The collision of the liquid flows produced by the return motion of the interface generates characteristic surfactant jets that "spurt" deep from the interfacial surface. There is shown the moment when, owing to the inertia of the main bulks of the contacting liquids, the jet transforms into symmetric vortices.

From analysis of the interferograms it follows that the development of Marangoni convection on the interfacial boundary is of pronounced threshold nature and the motion starts at a concentration half as small as in the case of introduction of isopropyl alcohol onto the free surface of deionized water from the liquid phase side [4]. The capillary motion arises with a discernable delay ($\Delta t \sim 0.6$ s) as compared with the moment at which the jet visually touches the interfacial boundary [3]. In this time the surfactant not only reaches the interface but even in part diffuses across it. In principle, it is the presence of the surfactant which

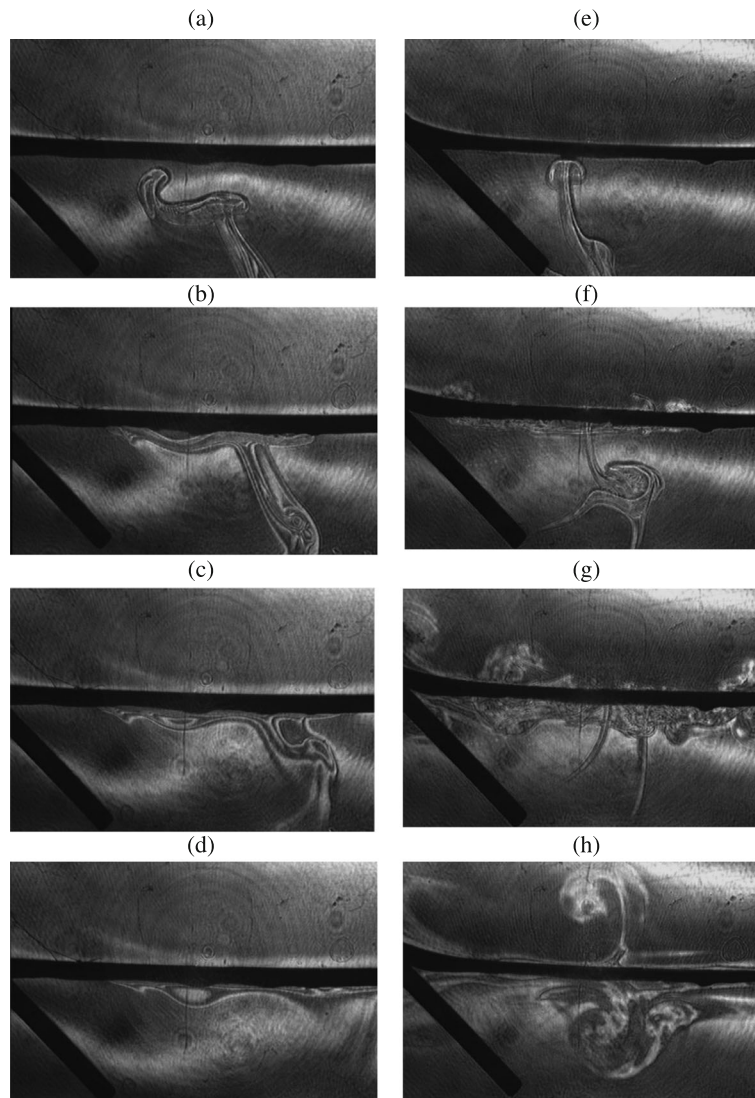


Fig. 2. Evolution of the concentration field after an isopropyl alcohol solution drop is introduced onto the water–chlorobenzene interface from the side of chlorobenzene at $C_d = 2\%$ (time from the touching moment: (a–d) 1.64; 2.64; 3.56; 5.00 s) and at $C_d = 3\%$ ((e–h) 1.12; 1.72, 2.08, 3.00 s), $b = 0.38$ cm.

penetrated into water before the capillary motion started that enables us to visualize the flow pattern during the “flash” of Marangoni convection.

Note that water turned out to be a good solvent for part of uncontrolled surface-active admixtures of chlorobenzene. We were led to this conclusion by the results of the experiment on introducing an isopropyl alcohol solution drop onto the free surface of chlorobenzene. The threshold surfactant concentration difference is equal to 6%, that is, twice as high as for the chlorobenzene–water interface.

In the problem with an interfacial surface a certain doubt in the reliability of the results can arise owing to surfactant introduction from the side of chlorobenzene, not water, as in the experiment compared. In order to remove this inconsistency, we can take as a surfactant acetic acid whose density is greater than that of water. Figure 3 shows two series of interferograms of the concentration field evolution in the distilled water–chlorobenzene system in response to the introduction of a drop of aqueous solution of acetic acid onto the interfacial surface from the side of water.

The “flash” of capillary convection occurs practically in 0.3 s after the drop touched the interface at a concentration $C_d \sim 2\%$. For comparison, note that if an acetic acid solution drop is introduced onto

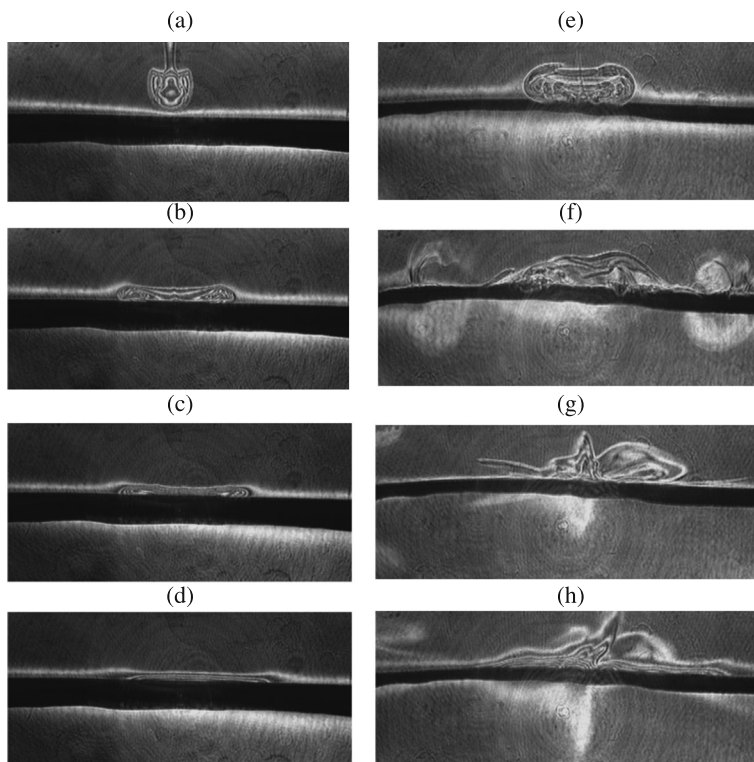


Fig. 3. Evolution of the concentration field after an aqueous acetic acid solution drop is introduced onto the water–chlorobenzene interface from the side of water at $C_d = 1\%$ (time from the touching moment: (a–d) 0.84; 2; 5; 15 s) and at $C_d = 2\%$ ((e–h) 1.2; 1.56, 2.52, 5 s), $b = 0.38$ cm.

the free surface of water from the side of the liquid phase, the threshold concentration is of the order of 10%. Moreover, if the acid solution drop is introduced onto the free surface of chlorobenzene, the threshold concentration is greater than 25%. The difference so strong in threshold values between isopropyl alcohol and acetic acid can be attributable to the high solvability of the latter in chlorobenzene, which reduces the surface acid activity with respect to it.

In spite of the happy confirmation of the hypothesis of possibility to reduce the limiting shear stress, experiments with other liquid pairs demonstrate the inverse effect. For example, in the deionized water–cyclohexane system the threshold concentration of isopropyl alcohol turned out twice as great as in the case of alcohol drop introduction onto the free surface of water from the side of the liquid phase. As the performed chromatographic analysis of admixtures showed, this unexpected result was caused by a fairly high content of alkanes and other non-polar organic compounds in cyclohexane (in practice, the efficiency of purification of a substance “For chromatography” only implies the absence of a certain number of admixtures). Part of the admixtures detected in cyclohexane is surface-active for its free surface (for example, *n*-hexane, $\sigma = 18.4$ dyn/cm) and the others (with $\sigma > 25.3$ dyn/cm) are located in the liquid bulk.

As cyclohexane contacts water, the surface tension of its boundary increases sharply (up to $\Delta\sigma \sim 50.6$ dyn/cm) owing to which a substantial part of earlier neutral admixtures becomes surface-active, enriching the content and increasing the concentration of uncontrolled surfactant admixtures of deionized water, mainly alkanes and phthalates [4]. As a result, for creating the shear stress necessary for the development of capillary motion, the threshold concentration of the introduced surfactant should be increased substantially. Thus, for varying the threshold shear stress value, it turns out that of importance is not the solvability alone of the admixtures in the contacting liquids but also the change in surface tension with transition to the interfacial surface.

3. MATHEMATICAL MODEL

Consider in the two-dimensional formulation the problem of the concentration convection in the system of two horizontal layers with the undeformable interface. Beneath it, at a certain depth, there is a “cloudlet” of solvable surfactant, lighter than the surrounding liquid. Being a light admixture, the surfactant decreases the liquid density: $\rho = \rho_0(1 - \beta C)$, where C is the surfactant concentration. At the initial moment the “cloudlet” begins to rise leading to gravity convection and surfactant transfer toward the interface. Since the surface tension of the liquid interface σ depends on the surface surfactant concentration Γ by the law $\sigma = \sigma_0 - \sigma_1\Gamma$, the inhomogeneous surfactant distribution may produce Marangoni convection. For the upper layer formed by a passive gas which does not affect the motion in the lower layer, the development of the gravity and Marangoni convection in such a system was considered earlier in [3].

In the present study we investigate the case when a strong action of the contacting medium can be anticipated: in both layers the kinetic characteristics of the liquids are close. As a limiting case, we will consider liquids identical in all characteristics but such that their interface displays a surface tension. In this model the number of parameters strongly decreases and the effect of the interface properties on the convective flow pattern can easily be studied.

We will start the mathematical formulation of the problem of the concentration convection in the two-layer system from discussing the boundary conditions at the interface determined by the coordinate $z = h$ (the coordinate origin lies at the lower rigid plane). It is assumed that the transition of surfactant molecules from the bulk phases onto the interfacial surface is realized by the adsorption/desorption processes and the interface is treated as a separate phase with a surface concentration Γ . At the interface between the boundary and bulk phases the substance conservation law can be written down in the form

$$-D\frac{\partial C_1}{\partial z} = k_1 C_1 - k_{-1}\Gamma, \quad D\frac{\partial C_2}{\partial z} = k_1 C_2 - k_{-1}\Gamma. \quad (3.1)$$

Here and in what follows, the subscript “1” relates to the lower layer and “2” to the upper one. On the left sides of the equations, the surfactant diffusion flux from the bulk phases to the surface is written. On the right sides of the equations, the first term describes the substance amount that enters the surface phase by adsorption per unit time (k_1 is the adsorption coefficient same for the lower and upper liquids) and the second describes the inverse process (k_{-1} is the desorption coefficient).

For the surface phase, we write down the substance conservation law with account for a possible convective substance transfer along it (along the x axis), surface diffusion, and the exchange with the bulk phases:

$$\frac{\partial \Gamma}{\partial t} + \frac{\partial}{\partial x}(v_x \Gamma) = D_s \frac{\partial^2 \Gamma}{\partial x^2} + k_1 C_1 + k_2 C_2 - (k_{-1} + k_{-2})\Gamma, \quad (3.2)$$

where D_s is the surface diffusion coefficient.

The interfacial surface is assumed to be flat: $v_z = 0$. The equation for the shear stress can be written with account for the finiteness of the surface phase mass and surface momentum diffusion in the form

$$\Gamma \left(\frac{\partial v_x}{\partial t} + v_x \frac{\partial v_x}{\partial x} \right) = \eta_s \frac{\partial^2 v_x}{\partial x^2} - \eta \left(\frac{\partial v_{1x}}{\partial z} - \frac{\partial v_{2x}}{\partial z} \right) + \frac{\partial \sigma}{\partial x}. \quad (3.3)$$

Here, η is the volume dynamic viscosity of the liquids and η_s the surface phase viscosity whose value depends on the shear stress at the surface $z = h$. In order to simplify the numerical model, when calculating the surface divergence of the surface tensor of viscous stresses, we will neglect the dilatational surface viscosity and the derivative of the surface viscosity with respect to the longitudinal coordinate.

We will describe the rheological properties of the surface phase by specifying η_s as a function of the tangential stress at the interfacial surface. The experiments described in Sect. 2 testify that at small tangential stresses (small surfactant concentration gradients and slow motions in the bulk phases) the surface remains

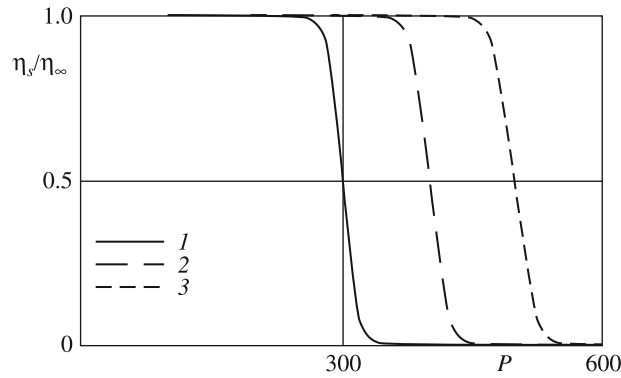


Fig. 4. Form of the function η_s for $a = 5$, $\eta_0 = 0$, and several values of $P_0 = 300$ (1); 400 (2); 500 (3).

at rest, that is, behaves as a rigid surface. As the tangential stresses reach a certain threshold P_0 , the quasi-rigid surface breaks down, the surface viscosity sharply decreases, and the surface phase begins to move. Such properties of the surface viscosity can be described, for example, by the function

$$\eta_s = \eta_\infty \{ \exp[(P - P_0)a^{-1}] + 1 \}^{-1} + \eta_0. \tag{3.4}$$

Here, $P = | -\eta(\partial v_{1x}/\partial z - \partial v_{2x}/\partial z) + \partial \sigma/\partial x |$ is the actual value of the tangential stress and a is the width of the region transient in stresses from the extremely high value of the surface viscosity η_∞ to its minimum value η_0 . The form of the function η_s is shown in Fig. 4.

The transition between the limiting viscosity values will be rapid if a is small as compared with P_0 . The rheological equation (3.4) describes the particular case of a rigid surface as $P_0 \rightarrow \infty$ and $\eta_\infty \rightarrow \infty$ and the case of a “Newtonian” surface as $\eta_\infty \rightarrow 0$.

All boundaries of the cavity are assumed to be impermeable to the surfactant. At the rigid (lower $z = 0$, upper $z = h_2$, and lateral) boundaries the no-slip conditions are assigned. If we take for variables the stream function ψ , the vortex ϕ , and the surfactant concentration C , these conditions take the form

$$\begin{aligned} z = 0 : \quad & \psi_1 = 0, \quad \frac{\partial \psi_1}{\partial z} = 0, \quad \frac{\partial C_1}{\partial z} = 0, \\ z = h_2 : \quad & \psi_2 = 0, \quad \frac{\partial \psi_2}{\partial z} = 0, \quad \frac{\partial C_2}{\partial z} = 0, \\ x = \pm L : \quad & \psi = 0, \quad \frac{\partial \psi}{\partial x} = 0, \quad \frac{\partial C}{\partial x} = 0. \end{aligned} \tag{3.5}$$

We will describe the liquid motion in the Boussinesq approximation. As units for distance, time, stream function, and the volume and surface surfactant concentrations we will take, respectively, h , h^2/ν , ν , C_0 , and $C_0 h$, where h is the thickness of the lower layer, ν the kinematic viscosity of the liquids, and C_0 the initial surfactant concentration in the cloudlet. We will use the same notation for the dimensional and dimensionless quantities since from the text and the form of the equations it is always clear of which quantities do we speak. In the adopted variables the dimensionless convection equations can be written down as follows:

$$\begin{aligned} \frac{\partial \phi_i}{\partial t} + \frac{\partial \psi_i}{\partial z} \frac{\partial \phi_i}{\partial x} - \frac{\partial \psi_i}{\partial x} \frac{\partial \phi_i}{\partial z} &= \Delta \phi_i - \text{Gr} \frac{\partial C_i}{\partial x}, \quad \Delta \psi_i = -\phi_i, \\ \frac{\partial C_i}{\partial t} + \frac{\partial \psi_i}{\partial z} \frac{\partial C_i}{\partial x} - \frac{\partial \psi_i}{\partial x} \frac{\partial C_i}{\partial z} &= \text{Sc}^{-1} \Delta C_i, \quad i = 1, 2, \\ \text{Gr} = \frac{g\beta C_0 h^3}{\nu^2}, \quad \text{Sc} = \frac{\nu}{D}. \end{aligned} \tag{3.6}$$

In the dimensionless variables boundary conditions (3.5) remain unchangeable, whereas conditions (3.1)–(3.3) take the following form:

$$\begin{aligned}
 -\frac{\partial C_1}{\partial z} &= K_a C_1 - K_d \Gamma, & \frac{\partial C_2}{\partial z} &= K_a C_2 - K_d \Gamma, & (3.7) \\
 \frac{\partial \Gamma}{\partial t} + \frac{\partial}{\partial x} \left(\frac{\partial \psi_1}{\partial z} \Gamma \right) &= \text{Sc}^{-1} \left(D_s \frac{\partial^2 \Gamma}{\partial x^2} + K_a C_1 - K_d \Gamma \right), \\
 B \Gamma \left(\frac{\partial^2 \psi_1}{\partial t \partial z} + \frac{\partial \psi_1}{\partial z} \frac{\partial^2 \psi_1}{\partial x \partial z} \right) &= \eta_s \frac{\partial^3 \psi_1}{\partial x^2 \partial z} - \left(\frac{\partial^2 \psi_1}{\partial z^2} - \frac{\partial^2 \psi_2}{\partial z^2} \right) - \text{Sc}^{-1} \text{Ma}_s \frac{\partial \Gamma}{\partial x}, \\
 K_a &= \frac{k_1 h}{D}, & K_d &= \frac{k_{-1} h^2}{D}, & B &= \frac{C_0}{\rho}, & \text{Ma}_s &= \frac{\sigma_1 C_0 h^2}{\eta D},
 \end{aligned}$$

Here, η_s is the dimensionless surface viscosity measured in the ηh units. As previously, its value is determined by (3.4) where the parameters η_∞ and η_0 should be taken in the ηh units. The parameter B characterizes the inertia properties of the surface. In the calculations presented in what follows $B = 0.1$ and Ma_s is the ‘‘surface’’ Marangoni number defined in terms of $\sigma_1 = -\partial\sigma/\partial\Gamma$. Note that the number Ma is usually defined in terms of the derivative $\partial\sigma/\partial C$. If we take into account that in equilibrium between the surface and bulk phases $\Gamma = \delta C$, where δ is the Gibbs length, then between the mentioned Marangoni numbers the following simple relationship can be established:

$$\text{Ma}_s = -\frac{\partial\sigma}{\partial\Gamma} \frac{C_0 h^2}{\eta D} = -\frac{\partial\sigma}{\partial c} \frac{\partial c}{\partial\Gamma} \frac{C_0 h^2}{\eta D} = \text{Ma} \frac{h}{\delta} = \text{Ma} \frac{K_d}{K_a}.$$

Let the liquid be initially at rest ($\psi = 0$ and $\phi = 0$) and contain no surfactant ($C = 0$), except for a circle of radius r_0 with coordinates of the center $(0, 0.5)$, within which the surfactant is distributed uniformly. Under the action of the Archimedean force this surfactant cloudlet will rise to the interface and spread over it. When in the surface phase a gradient of the surfactant concentration arises, Marangoni convection may start. Then, in a numerical experiment, we investigate the effect of the interface properties on the Marangoni convection onset moment.

The surfactant solutions used in the experiment have a small diffusion coefficient. The concentration turns out to be practically frozen in the streamlines but the surfactant transport onto the interfacial surface is, nevertheless, provided by the diffusion process. Owing to slow diffusion, the dimensionless adsorption and desorption coefficients K_a and K_d are large: $K_a, K_d \sim 10^4$. Equations (3.7) are boundary conditions for the diffusion equations (3.6). In this form it is difficult to use these equations in the finite-difference form. Taking into account that diffusion is weak, the adsorption and desorption processes have enough time to be compensated, and the surfactant is transferred by convective flow, boundary conditions (3.7) can be written down in the form convenient for numerical realization

$$z = 1 : \quad \frac{\partial C_1}{\partial z} = 0, \quad C_2 = \frac{K_d}{K_a} \Gamma.$$

The nonstationary boundary-value problem formulated was solved by the finite-difference method on square grids measuring from 80×80 to 160×160 using the Crank–Nicolson’s implicit scheme in the half-domain with conditions of symmetry about the line $x = 0$. The Poisson equation for the stream function was solved by the method of successive over-relaxation. The surfactant was introduced onto the interface from the side of the lower layer in the shape of a rising drop whose diameter was equal to 0.1 of the layer thickness. The computation domain consisted of three regions (two liquids and the surface phase between them) the solutions in which were stitched together with account for the physical boundary conditions.

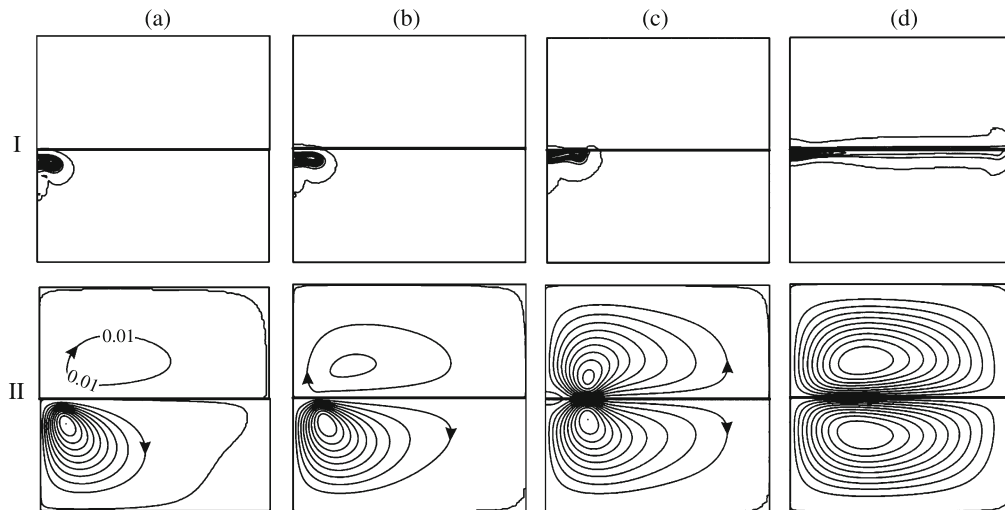


Fig. 5. Isolines of surfactant concentration (I) and stream function (II): limiting shear stress at the interface for $P_0 = 30$; $Gr = 500$; $Ma = 10^8$; $a = 5$; $\eta_\infty = 100$; $Sc = 1500$; $K_a = 10^3$; $K_d = 10^4$; $t = 0.5$ (a); 0.75 (b); 1.0 (c); 2.0 (d).

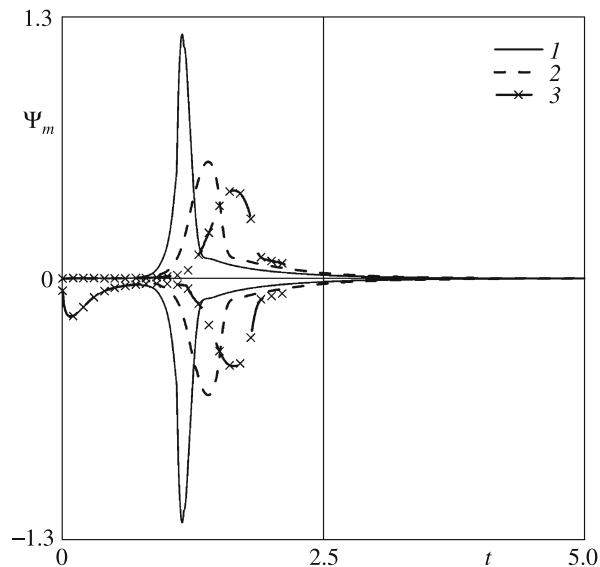


Fig. 6. Dependence on t of the maximum stream function value in the layers: the lower curves describe the development of motion in the lower layer and the upper curves in the upper layer at $Gr = 500$; $Ma = 10^8$; $a = 5$; $\eta_\infty = 100$; $Sc = 1500$; $K_a = 10^3$; $K_d = 10^4$; $P_0 = 30$ (1); 300 (2); 1000 (3).

In Fig. 5 the evolution of the surfactant concentration and stream function distributions is shown for different times.

First, after the surfactant drop is created, gravity convection ensues in the lower liquid layer (Fig. 5a). Then, after the surfactant penetrated across the interface, gravity motion develops in the upper layer, its intensity being two orders lower than in the lower layer (Fig. 5b). The “flash” of Marangoni convection only occurs after a certain amount of surfactant, which provides the limiting shear stress, is transported onto the interface (Fig. 5c). As in the physical experiment, capillary motion “flares” in both layers simultaneously. Since the layers have the same thickness, the flow intensity is approximately same. Note that with replacement of the gravity mechanism of motion by the capillary one, in the upper layer the convective vortex changes rotation direction. After Marangoni convection developed, the surfactant concentration rapidly equalizes along the interface in both layers (Fig. 5d) and the convective motion is damped.

Varying the level of the non-Newtonian interface properties, we showed that with increase in the limiting shear stress, capillary convection ensues later but its pattern is same as at small P_0 . In Fig. 6, the time dependence of the maximum stream function in the layers is presented for various limiting shear stresses at the interfacial surface. It can well be seen that the Marangoni convection intensity falls with increase in the limiting shear stress.

Summary. Comparison between the data of the physical and numerical experiments shows that the threshold Marangoni convection development can be represented as a consequence of the manifestation of non-Newtonian surface properties which are a result of the presence of the film of adsorbed admixtures. The qualitative coincidence of the surfactant concentration field patterns visualized in experiments and obtained using numerical simulation confirms the proposed interpretation of the experimental results. In their turn, certain other coincidences (the surfactant penetration into the contacting liquid bulk before the capillary motion ensues and the simultaneous and fairly symmetric development of this motion in both liquids) confirms that the theoretical model was taken correctly, which substantially widens the opportunities of application of the experimental data obtained.

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