

OSCILLATORY MODES OF SOLUTOCAPILLARY MARANGONI CONVECTION AT A DROP-LIQUID INTERFACE

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Abstract

The concentration convection in an isothermal liquid with a surfactant concentration gradient, arising near a fluid drop clamped between the vertical walls of a horizontal channel is studied numerically within the framework of simple mathematical model with the surface phase at the drop-liquid interface formed by adsorption/desorption process. The interaction between the buoyancy and the Marangoni convective flows is responsible for the onset of auto-oscillation regime. In numeric experiments, more than 20 outbursts of the Marangoni convection were observed. Such oscillations have been experimentally investigated with the help of interferometric technique. The surfactant distributions obtained numerically at different oscillation phases agree well the experimental data.

Key words

Surfactant solution, insoluble drop, interface, solutocapillary Marangoni convection, oscillations.

1 Introduction

In recent years, convective flows at the interface formed by gas bubbles and immiscible liquid drops in the heterogeneous solutions of surface-tension active substances (surfactants) have been the focus of close attention of many researchers. The specific feature of these flows is that they occur at weak diffusion (the values of the Schmidt numbers are about 10^3) and changes in the spatial concentration of the surfactant are mainly due to convective transfer. A series of experimental studies [Kostarev *et al.*, 2004; 2005; 2006; 2007] using interferometric technique has revealed an interesting phenomenon – the onset of self-oscillatory regimes of the convection motion near the bubble and drop surfaces in an aqueous solution with vertical surfactant

concentration gradient. The flow oscillations were caused by specific competition of two solutal (capillary and gravitational) convective mechanisms of mass transfer having different characteristic times. Initially, a fluid flow arises as an outbreak of the solutocapillary Marangoni convection in the vicinity of the interface and then over an appreciable period of time it develops as a buoyancy-driven motion. This oscillations can be observed during a tens of minutes and after a lapse of time abruptly ceased. The period and duration of the oscillations depended on initial concentration gradient, solution average concentration and physico-chemical parameters, geometry of the liquid bulk, bubbles/drops dimensions.

In [Birikh *et al.*, 2006] such self-oscillations were described in the framework of the mathematical model with diffusion transfer of the surfactant to the air bubble surface (without formation of the surface phase). In this paper, we simulate the solutal Marangoni convection near the interface of the liquid drop entrapped between the walls of a plane lengthy channel of rectangular cross-section, filled with a stratified surfactant solution. We consider the boundary conditions version at the fluid-fluid interface in which a surfactant, soluble in both fluids, passes the phase boundary due to adsorption/desorption processes and forms a surface phase.

2 Experimental observation

Investigations were made with the help of the experimental setup represented schematically in Fig. 1. The working fluid (aqueous solutions of isopropyl alcohol) filled the cavity in the form of extended horizontal channel of rectangular cross-section of height $h = 2$ mm and thickness 1.2 mm, which was confined between two vertical interference glass walls coated with reflecting semi-transparent material (see Fig. 1a) purposely for making observations. Due to a small thickness of the

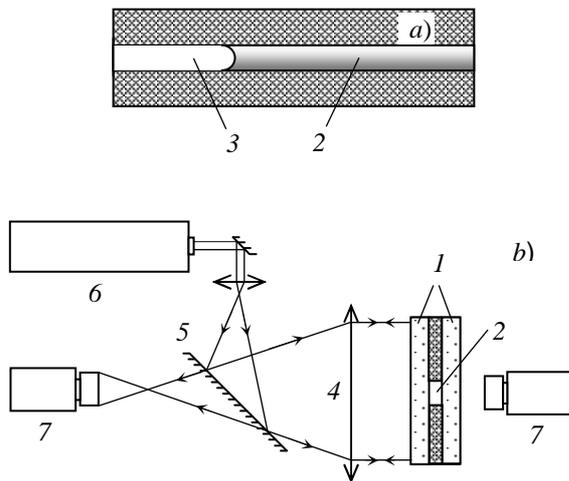


Figure 1: Schematics of experimental setup:
 1 — interferometric semi-transparent glasses;
 2 — channel with fluid; 3 — air bubble;
 4 — objective lens; 5 — semi-transparent mirror;
 6 — laser; 7 — video camera.

layer the arising flows and the distribution of concentration (averaged across the layer) turned out to be two-dimensional. Such configuration of the experimental cuvette opens up the possibility of comparison the results of experiments with the results of numerical simulation. The content distribution in the fluid mixture was visualized with the aid of the Fizeau interferometer (Fig. 1b) as a pattern of isolines of the refraction index, which under isothermal conditions depends on the alcohol concentration. The difference in the values of the refraction index between two adjacent monochromatic interference bands calculated for this particular channel thickness amount to 0.27×10^{-3} . In view of non-linear character of concentration dependence of the refraction index this corresponded to variation of the isopropyl alcohol concentration 0.33–0.35%. The interference patterns were recorded in transmitted and reflected light by video camera (25 sec^{-1} , resolution of 640×480). The maximum error of the concentration measurements did not exceed 0.1%. All measurement were carried out at constant ambient temperature $20 \pm 1^\circ \text{C}$.

Initially the cavity was filled by the pure water. A drop of chlorobenzene, which is immiscible in the water, was injected by means of a syringe into a channel cavity from one of its ends in such a way that completely bridged over the channel and had free lateral surface. Then, from the other end, the cavity was gradually filled with concentrated solutions of isopropyl alcohol (with weight percent concentration ranging from 10 to 40%), while excess of water was pumped out. Since alcohol is lighter than water, this led to formation of a rather slow large-scale advective gravitational flow in the channel, during which a narrow "tongue" of a more

concentrated surfactant solution flowed along the upper channel boundary toward the drop forming near the interface a region with upward-directed concentration gradient.

Fig. 2 show the serial interference patterns of the concentration field near the lateral boundary of the chlorobenzene drop in the alcohol solution. In distinction from thermocapillary flow known to develop in a non-threshold manner at arbitrary small values of the interface temperature gradient, the solutocapillary flow was found to initiate not at the time when the surfactant "tongue" reached the drop surface, but with some delay (Figs. 2a-2c). It can be seen from interferograms that the isopropanol reaches the surface of the drop and even diffuses through it generating in chlorobenzene a gradient of surfactant concentration as well before the origin of Marangoni convection at the interface. Then the equilibrium was abruptly disturbed (at $\Delta t \sim 1 \text{ min}$ after the "tongue" of the surfactant has touched the drop surface and at the difference of the solution concentration ΔC^* between the upper and lower drop ends equalized to 2.2%). Then very quickly (during $\sim 1 \text{ sec}$) a rather intensive Marangoni flow was initiated in the form of a vortex cell, in which the surfactant under the action of solutocapillary forces was carried along the interface toward the lower drop margin (Fig. 2d). Owing to fluid continuity the arising flow accelerated the flux of the concentrated surfactant solution along the upper boundary of the channel towards the drop surface, adding thereby intensity to the existing convective vortex (Fig. 2e). However, the originated vortex cell, entrapping more and more portions of highly concentrated surfactant solution, became increasingly light. Rising up it eventually cut off the arriving jet of the alcohol from the top of the drop. As a result, the vortex flow ceased abruptly and the drop interface turned out to be surrounded by a thin layer of the surfactant solution having the uniform concentration (Fig. 2f). After that the vertical stratification of the solution began to slowly restore under the action of buoyancy force.

However, decay of the capillary flows did not imply cessation of the fluid motion in the channel because equalizing of the generated horizontal gradient of the surfactant concentration made the advective flow draw again a concentrated surfactant solution to the upper pole of the drop (Fig. 2g). After the flux of the surfactant touched the drop surface, the solutocapillary vortex recurred (Fig. 2h). The cycle repeated iteratively, with the difference that the oscillation period increased with time whereas intensity of the vortex flow decreased due to a gradual decrease of the vertical concentration gradient as a result of convective stirring of the fluid. The Marangoni convection entirely ceased at the time when concentration of the solution was equalized throughout the whole length of the channel.

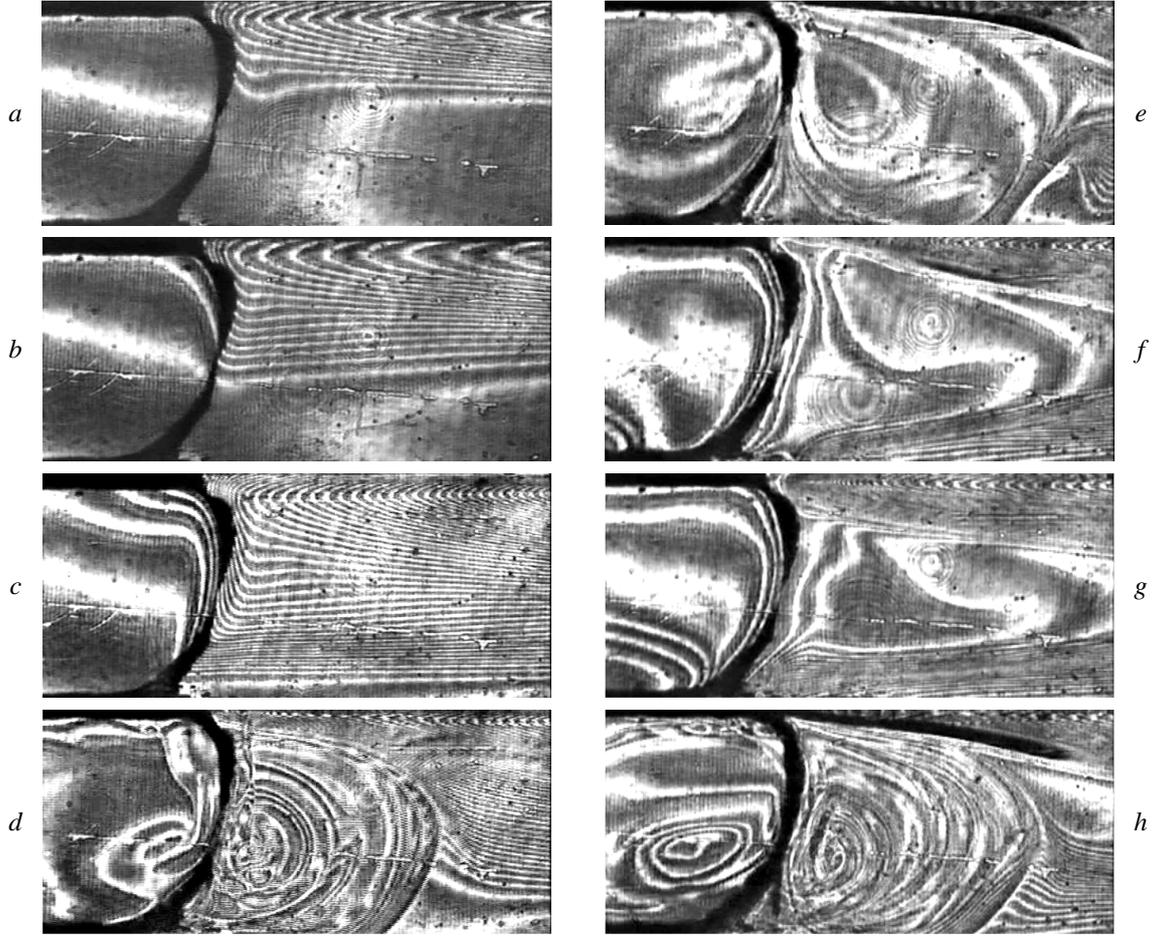


Figure 2: Interferograms of concentration fields for a chlorobenzene drop in isopropyl alcohol solution at $t = 0$ (a), 30 (b), 60 (c), 61 (d), 66 (e), 70 (f), 76 (g), 77 (h) sec.

3 Mathematical model

Let us consider a two-dimensional problem of solutal convection in a plane horizontal channel filled with a fluid, which has horizontally non-uniform distribution of a surfactant with its maximum concentration at one of the channel ends. At the other end of the channel, where surfactant concentration is zero, we place a drop of dissimilar fluid insoluble in the base fluid. The drop is taken to be large enough to block off the gap in the channel. To simplify a numerical model we assume that the boundary between the fluid in the channel (phase 1) and the drop (phase 2) is vertical.

The region geometry is shown in Fig. 3. The drop width, d , is equal to channel height, h , and channel length, L , is equal to $5h$.

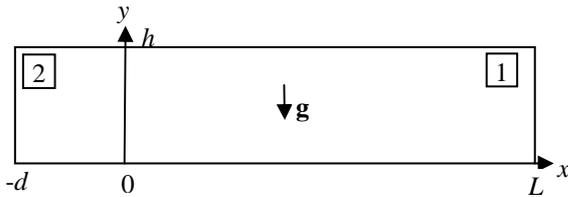


Figure 3: Geometry of the calculating region.

The surfactant is soluble in both fluids and diminishes their density proportionally to the volumetric concentration c : $\rho_i = \rho_{i0}(1 - \beta_i c)$.

A transition of the substance from one region to another is realized through the surface phase due to the adsorption process (transfer of the surfactant molecules from the volume phase onto the phase boundary) and the inverse process of desorption. The quantity of the surfactant at the interface (in the surface phase) is characterized by surface concentration Γ . Its variation in time at each point of the interface is described by the transfer equation

$$\frac{\partial \Gamma}{\partial t} + \frac{\partial}{\partial y}(v_y \Gamma) = D_s \frac{\partial^2 \Gamma}{\partial y^2} + k_a^{(1)} c^{(1)} + k_a^{(2)} c^{(2)} - (k_d^{(1)} + k_d^{(2)}) \Gamma. \quad (1)$$

Here the second term in the left-hand side of the equation describes a convective transfer of the surfactant along the surface and the first term in the right-hand side describes the surface diffusion of the surfactant. The next two terms define the adsorption flux of the substance from the volume phase to the surface phase and the last term specifies the inverse desorption flux. All coefficients in equation (1) are

assumed to be constant. The surface tension at the interface σ depends on the concentration of the surfactant retained at the interface Γ : $\sigma = \sigma_0 - \sigma_1 \Gamma$.

The interfacial forces cause the motion of the surface phase, which is described by equation

$$\Gamma \frac{\partial v_y}{\partial t} + \Gamma v_y \frac{\partial v_y}{\partial y} = \eta^{(1)} \frac{\partial v_y^{(1)}}{\partial x} - \eta^{(2)} \frac{\partial v_y^{(2)}}{\partial x} - \sigma_1 \frac{\partial \Gamma}{\partial y}, \quad (2)$$

where $\eta^{(i)}$ is the dynamic viscosity of the i -th phase, σ_1 is the solutal coefficient of the surface tension. When writing this expression, we include in the right-hand part only forces that are responsible for the surface motion taking no account of the surface friction.

The volumetric inhomogeneity of surfactant concentration in the channel causes gravitational convection. Viscous stresses at the interface set in motion the surface phase, which, in turn transmits motion to the other volume phase. At the same time, the gravitational convection generates at the interface a surface tension gradient, which gives rise to an intensive motion of the phase boundary. The viscous stresses at the interface change the motion patterns in the volume phases. This results in the onset of the Marangoni convection, which develops on the background of the gravitational convection. The competition between these two modes of the convective motion is subject to a careful analysis.

A full system of equations for free convection written in terms of dimensionless stream function ψ , vortex φ and concentration c has the following form:

$$\frac{\partial \varphi}{\partial t} + \frac{\partial \psi}{\partial y} \frac{\partial \varphi}{\partial x} - \frac{\partial \psi}{\partial x} \frac{\partial \varphi}{\partial y} = v_i \Delta \varphi - \beta_i Gr \frac{\partial c}{\partial x},$$

$$\Delta \psi = -\varphi,$$

$$\frac{\partial c}{\partial t} + \frac{\partial \psi}{\partial y} \frac{\partial c}{\partial x} - \frac{\partial \psi}{\partial x} \frac{\partial c}{\partial y} = D_i Sc^{-1} \Delta c, \quad i = 1, 2. \quad (3)$$

$$Gr = g \beta^{(1)} C_0 h^3 / (v^{(1)})^2, \quad Sc = v^{(1)} / D^{(1)},$$

$$v_1 = 1, v_2 = v^{(2)} / v^{(1)}, \quad \beta_1 = 1, \quad \beta_2 = \beta^{(2)} / \beta^{(1)},$$

$$D_1 = 1, \quad D_2 = D^{(2)} / D^{(1)}.$$

Here Gr and Sc are the Grashoff and Schmidt numbers, determined from the parameters of the fluid in the channel, h is the height of the channel, C_0 is the maximal value of the surfactant concentration in the initial state, g is gravitational acceleration, $\beta^{(i)}$, $v^{(i)}$ and $D^{(i)}$ are the coefficients of volumetric expansion, kinematic viscosity and diffusion of fluids. For units of measurements we take distance h , time $h^2 / v^{(1)}$, stream function $v^{(1)}$, concentration C_0 , and surface concentration $C_0 h$.

We assume that the external boundaries of the channel and the drop are solid and impermeable to the surfactant and meet the following boundary conditions:

$$\begin{aligned} x = -d, L: \quad \psi = 0, \quad \frac{\partial \psi}{\partial x} = 0, \quad \frac{\partial c}{\partial x} = 0; \\ y = 0, 1: \quad \psi = 0, \quad \frac{\partial \psi}{\partial y} = 0, \quad \frac{\partial c}{\partial y} = 0. \end{aligned} \quad (4)$$

The conditions at the interface $x = 0$ expressed in terms of the stream function and vortex are written in dimensionless form as

$$\psi^{(1)} = \psi^{(2)} = 0, \quad \frac{\partial \psi^{(1)}}{\partial x} = \frac{\partial \psi^{(2)}}{\partial x}, \quad (5)$$

$$\begin{aligned} -B\Gamma \frac{\partial^2 \psi}{\partial t \partial x} + B\Gamma \frac{\partial \psi}{\partial x} \frac{\partial^2 \psi}{\partial y \partial x} = \varphi^{(1)} - \eta_2 \varphi^{(2)} - \\ -Ma Sc^{-1} \frac{\partial \Gamma}{\partial y}, \end{aligned} \quad (6)$$

$$\begin{aligned} \frac{\partial \Gamma}{\partial t} + \frac{\partial}{\partial y} (v_y \Gamma) = Sc_s^{-1} \frac{\partial^2 \Gamma}{\partial y^2} + Sc^{-1} [Ka_1 c^{(1)} + \\ + D_2 Ka_2 c^{(2)} - (Kd_1 + D_2 Kd_2) \Gamma], \end{aligned} \quad (7)$$

$$\frac{\partial c^{(1)}}{\partial x} = Ka_1 c^{(1)} - Kd_1 \Gamma, \quad (8)$$

$$-\frac{\partial c^{(2)}}{\partial x} = Ka_2 c^{(2)} - Kd_2 \Gamma, \quad (9)$$

$$Ma = \sigma_1 C_0 h^2 / \eta^{(1)} D^{(1)},$$

$$Ka_i = k_a^{(i)} h / D^{(i)}, \quad Kd_i = k_d^{(i)} h^2 / D^{(i)}.$$

Here Ma is the Marangoni number, Ka_i and Kd_i are non-dimensional coefficients of adsorption and desorption, $\eta_2 = \eta^{(2)} / \eta^{(1)}$ is the relative dynamic viscosity of the drop. The condition for a vortex at the drop surface is derived from the tangential stress balance condition.

Initially, the fluid is assumed to be in a quiescent state ($\psi = 0$, $\varphi = 0$), and distribution of the surfactant in the channel is specified by a horizontal concentration gradient as follows:

$$\begin{aligned} -d \leq x \leq 0: \quad c(x, y, 0) = 0, \\ 0 < x \leq L: \\ c(x, y, 0) = 0.5 \cdot [1 + \text{th}(2(2x - L)) / \text{th}(2L)]. \end{aligned} \quad (10)$$

Such distribution suggests that at the initial moment of time the surfactant in the drop and at the drop surface is lacking. The gravitational convection developed with time in the channel carries the surfactant onto the drop boundary. Accumulation of the surfactant at the drop surface leads to generation of the surface tension gradient initiating the Marangoni convection.

The non-stationary boundary value problem (3)-(10) was solved for two regions by the finite difference method on the 40×40 and 200×40 square meshes using the implicit Crank-Nicolson scheme. The solution to the Poisson equation was found by the subsequent upper relaxation method.

4 Results of numerical simulation

Of considerable practical interest are the systems, in which the Schmidt number has a high value ($Sc \sim 10^3$). In this case, transport of the surfactant through the fluid is realized by convective motion. Surfactant transfer between the liquid drop and the surrounding fluid occurs through the surface phase and is controlled by adsorption-desorption mechanism. Since the characteristic times of adsorption and desorption are much shorter than the diffusion time, the dimensionless coefficients Ka_i and Kd_i are also large ($\sim 10^5 - 10^6$). Because of this, numerical realization of conditions (8)-(9) poses certain difficulties, which can be overcome by making use of an ultra-fine grid along the horizontal coordinate. In view of the fact that equilibrium between the surface phase and the adjacent regions of the volumetric phases is established rapidly compared to the diffusion time, the right-hand sides of equations (8)-(9) are assumed to be equal to zero. Then, the condition in the channel is written as

$$\partial c^{(1)} / \partial x = 0, \quad (11)$$

which means that absorption of the surfactant by the surface practically does not affect the diffusion transfer of the surfactant in the channel. For the drop, we cannot express condition (9) in the form of (11), which inhibits the access of the surfactant to the drop. Therefore condition (9) is written as

$$c^{(2)} = Kd_2 \Gamma / Ka_2. \quad (12)$$

Intensity of the fluid motion in the channel and in the drop is defined by the values of the Grashoff and Marangoni numbers; a necessary condition for the onset of the oscillatory mode of solutal convection is $Ma \gg Gr$.

The structure of the convective motion has been investigated for two liquids – water-benzene with ethanol (surfactant) initially placed in the water

phase. The parameters of this system have the following values: $\eta_2 = 0.3$, $\nu_2 = 0.2$, $\beta_2 = 1.1$ and $D_2 = 1.4$. Fig. 4 shows the dependence of the flow intensity in the channel on time for the following values of parameters: $Gr = 400$, $Ma = 10^8$, $B = 0.1$, $Sc = Sc_s = 10^3$, $Ka_1 = 10^5$, $Kd_1 = 2 \cdot 10^6$, $Ka_2 = 3 \cdot 10^5$ and $Kd_2 = 10^6$.

Periodicity of the outbursts of the Marangoni convection is practically independent of the drop properties, but their duration differs markedly. Intensity of motion in the drop is by an order of magnitude smaller than intensity of the channel motion.

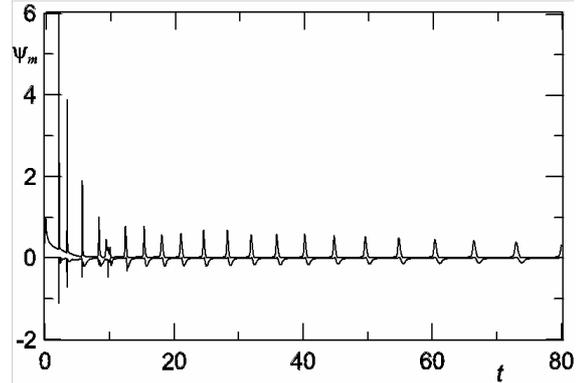


Figure 4. Time dependence of maximal and minimal values of stream function in the channel for $\eta_2 = 0.3$.

The flow structures and surfactant distributions before the first outburst of the Marangoni convection ($t = 2.0$), at the time of the first and most intensive outburst of the Marangoni convection ($t = 2.18$), at the time of the buoyancy convection ($t = 3.0$) and at time $t = 15.7$, corresponding to the decay of the next convection outburst and formation of the intensive secondary vortex are shown in Fig. 5.

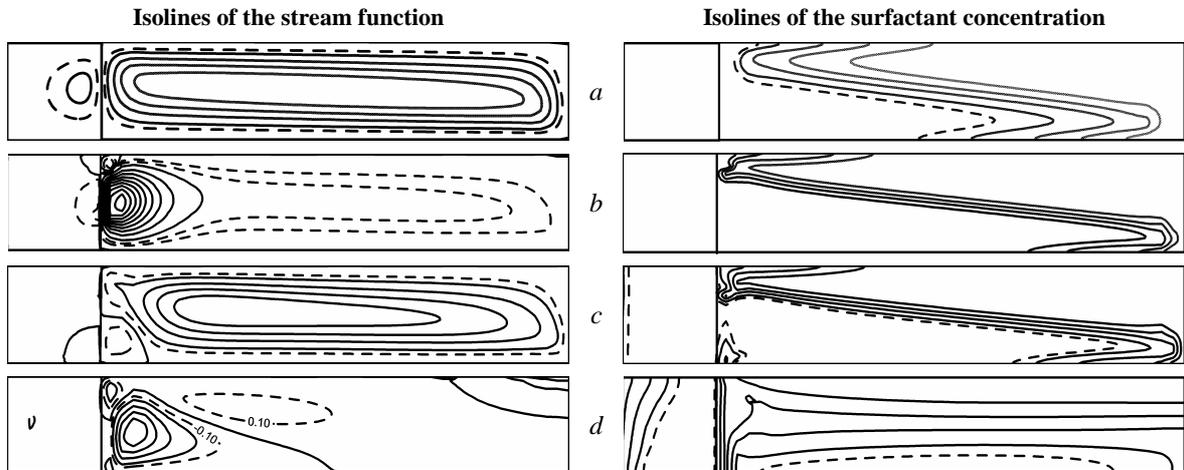


Figure 5. Isolines of the stream function and surfactant concentration at $t = 2.00$ (a), 2.18 (b), 3.00 (c) and 15.7 (d).

An intensive channel Marangoni-driven motion is observed in the vicinity of the drop boundary at a distance of order of channel height from the drop surface. The flow in the drop is rather weak because of small dynamic viscosity ($\eta_2 = \eta^{(2)} / \eta^{(1)} = 0.3$). Full time of the first outburst of the Marangoni convection is approximately equal to one unit of dimensionless time.

The next outbursts of the Marangoni convection have smaller amplitudes but longer duration. The Marangoni convection generates a rather intensive vortex with the opposite sign. At large times a vertical gradient of surfactant concentration is generated in the channel, and the global advective flow ceases. It is succeeded by the gravitational convection at the drop surface, which tends to restore a stable stratification of the surfactant. With the appearance of the concentration gradient at the drop surface the Marangoni convection once again stirs the fluid. Convective oscillations will continue until the fluid in the channel is completely stirred.

The period of the established outbursts of the Marangoni convection closely depended on the Grasshoff number as far as just the gravitational convection carried surfactant to the drop interface. This relationship is represented in Fig. 6, where the Grasshoff number is defined by the initial surfactant concentration gradient.

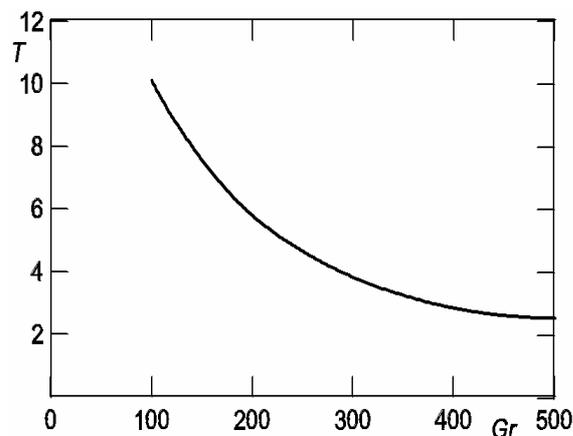


Figure 6: Variation of the dimensionless auto-oscillations period with the Grasshoff number.

5 Conclusion

Concentration convective motion in a rectangular horizontal channel, containing a drop of insoluble liquid was numerically simulated. The model of adsorption-desorption surfactant transfer through the interface with formation of surface phase were elaborated. It was found that for large Schmidt numbers ($\sim 10^3$) in the cavity with non-homogeneous surfactant distribution, convective auto-oscillations, caused by the interaction of bouncy-driven convection and Marangoni-driven convection, might appear in this model. Volumetric distribution of the surfactant concentration at different oscillation time points qualitatively coincide with the experimental results.

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