CONVECTIVE STIRRING OF A STRATIFIED SURFACTANT SOLUTION BY THE OSCILLATORY SOLUTOCAPILLARY FLOW

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Abstract

The paper presents the results of experimental study of solutocapillary Marangoni convection arising in a non-uniform fluid mixture with a vertical gradient of concentration of dissolved surfactant around a stationary air bubbles immersed in the solution. The Fizeau interferometer-based technique was used for studying the convective flow structures and concentration field evolution. The tests revealed the periodic disturbances of the surfactant distribution caused by the abrupt outbursts and decays of the intensive solutocapillary flow at the bubble surface. The ground of the oscillations is conditioned by the specific competition of two different mechanisms of convective mass transfer namely the Marangoni convection which mixing up the solution and gravitational concentration motion restoring the destroyed surfactant stratification. The time dependences of the oscillations period were analyzed in relation to the average solution concentration, the surfactant concentration gradient and the Marangoni and Grashoff numbers.

Key words

Surfactant solution, concentration stratification, air bubble, interface, solutocapillary Marangoni convection, oscillations.

1 Introduction

A gas bubbles, suspended in a liquid phase, play an essential part in chemical and biochemical reactors, liquid/gas separation, material processing, crystal growth, food production, biotechnology, etc., influencing the development of hydrodynamic and mass/heat transfer processes. In a non-uniform fluid, the convective motion around the bubbles is induced by the tangential surface stress (Marangoni force), generated by the interfacial tension gradient due to heterogeneity of the temperature or composition at a fluid/gas interface. Despite an obvious similarity of the driving forces, the thermocapillary and solutocapillary Marangoni phenomena were found to be not completely analogous. The key difference is that the characteristic times of the admixture diffusion are hundred times longer than times of heat diffusion and so the values of Marangoni number, characterizing the intensity of solutocapillary convection, increase many times. This changes drastically the ratio of contributions to mass transfer made by competing gravitational and Marangoni mechanisms. The other marked distinction of the solutocapillary convection consists of surfactant adsorption which caused an increase in the local concentration of the surfactant and its redistribution over the surface, equalizing surface tension inhomogeneity. These differences give rise to new phenomena that cannot occur in thermocapillary situation.

Thus, the results of experimental observations show that if an upward-directed temperature gradient is maintained in a liquid, a thermocapillary flow forms around a bubble in the form of an axisymmetric toroidal vortex with a vertical symmetry axis. Under the action of Marangoni forces, the liquid flows along the bubble-free surface to its lower pole and slowly rises at some distance, creating a returning flow. Correspondingly, in any vertical plane drawn through a diameter, two stationary vortices that are symmetric with respect to the bubble are observed. The vertically stratified temperature distribution in the liquid also remains stationary. In contrast to thermal Marangoni convection, the described below our experiments [Birikh *et al*., 2006, 2008; Kostarev *et al*., 2004, 2006, 2007, 2008, 2009; Zuev *et al*., 2006, 2008] revealed the self-oscillatory regimes of solutal convection in an aqueous solution of surfactant with vertically stratified concentration, and the threshold character of excitation of solutocapillary flows near the free bubble surface.

2 Bubbles in a two-layer system of liquids

In the first experiment the air bubble was inserted into a two-layer system of miscible fluids, in which a thin horizontal layer (~1 mm height) of a lighter fluid overlaid a heavier one. Due to the small values of the

diffusion coefficient the liquids did not mix, only the very narrow diffusion zone between the layers was formed in the cell. The tests were performed with water and aqueous solutions of different liquid surfactants: acetic acid (concentration ranging from 0 % to 70 %) or methyl, isopropyl and ethyl alcohols with 50-100 % concentration. The acetic acid density is higher and the alcohol densities are lower than that of water. This allowed us to realize situations with a surfactant layer located above or under the water layer, or differently, with the downward or upward directed surface tension gradient.

Visualization of the distribution of the surfactant concentration in the mixture was made by means of the Fizeau interferometer. For this the experimental cuvette was an interferometric cell composed of two plane-parallel semitransparent mirror plates arranged horizontally. The observations were made from above in the reflected light. The interferometer allowed visualizing anomalies in the solution concentration as a pattern of isolines of the refraction index, which under isothermal conditions varied proportionally to the concentration. For a liquid layer 2 mm thick, the transition from one monotonous interference fringe to another corresponds to about a 0.5% variation in the alcohol concentration.

Air bubbles, injected into a two-layered liquid system by a medical syringe, took the form of a flat disk 5-15 mm in diameter, squeezed between the horizontal cell walls. Due to the vertical concentration difference the solutocapillary Marangoni flow must form tangent to free lateral bubble surface. The flow transfer the surfactant toward the lower (in experiments with alcohol) or upper (in experiments with acetic acid) poles of the bubble. The transferred lighter or denser liquid fraction has to partly dissolve in the ambient liquid and partly return (ascend or sink, respectively), creating a steady convective flow in the form of an axisymmetric vertical vortex. Instead of the thermocapillary case, this flow had a clearly expressed oscillatory character. Its development is illustrated by a series of interferograms in Fig. 1. For a time after insertion of the bubble, no flow was observed in the surrounding liquid and the concentration field around it stayed intact, as the initial horizontal concentration gradient in the liquid system was absent (Fig. 1a). However, suddenly a system of circular concentration isolines appeared (Fig. 1b). This was

the result of an abrupt injection into the surrounding solution of an excessive amount of the surfactant accumulated under the action of solutocapillary forces respectively in the lower or upper part of the surface of the bubble. Then, as the Archimedes buoyancy force restored the vertical density stratification of the solution, the disturbance of the concentration field disappeared (Fig. 1c) and the interference pattern returned to a monotonic one.

This process occurred repeatedly with a good periodicity until the liquid surrounding the bubble was uniformly mixed. The period of this oscillation (the time interval between subsequent outbreaks of strong convection) ranges from some seconds to tens of minutes and depend on time, the layer thickness, the horizontal bubble diameter, the initial concentration difference and the properties of the liquids. Fig. 2 presents the time dependence of the oscillation frequency for bubbles of various diameter D in a two-layer system consisting of a 40% solution of acetic acid and water. Apparently, as the solution is mixed and the vertical stratification is reduced, the oscillations period, initially equal to 10 sec, gradually increases and the oscillations take longer and longer and totally stop in approximately 10 min. No significant dependence of the oscillation frequency on the bubble size was observed; the frequency only slightly decreased with a reduction in the bubble size and, additionally, smaller bubbles came to rest somewhat earlier.

The oscillation frequency was actually determined by the layer thickness (i.e., the vertical bubble size) and the concentration gradient. On increasing the layer thickness or decreasing the initial difference in concentrations ΔC the oscillation period slightly increased. But the duration (the lifetime) of oscillations increased rather strongly with an increase in the initial concentration difference (Fig. 3). A characteristic feature of all observed oscillations was, however, that they all disappeared abruptly: the oscillations of the concentration field near the bubble persisted with a decreasing period over a long time interval and then died out despite some vertical concentration gradient still existing. The experimental findings indicate of the threshold character of the observed phenomenon, which is realized only at critical values of some parameters determined by both the problem geometry and the physical characteristics of liquids.

Figure 1. Interferograms of concentration field around the air bubble in horizontal layer
of stratified isopropyl alcohol solution. t: 0 (*a*), 2.0 (*b*), 10.0 (*c*) sec.
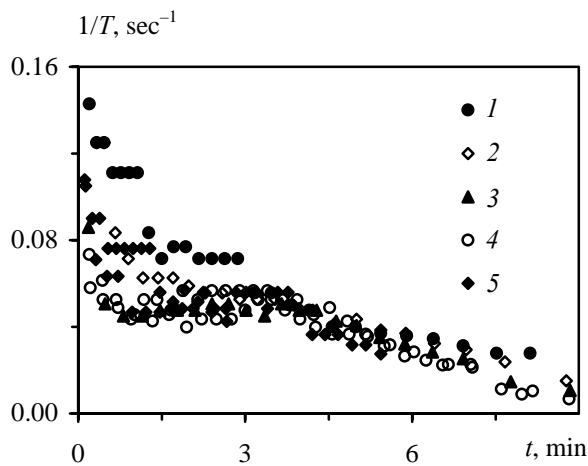
Figure 2. Variation of oscillation frequency with time. D: 15.0 (*1*), 10.7 (*2*), 7.1 (*3*), 5.1 (*4*), 2.4 (*5*) mm.
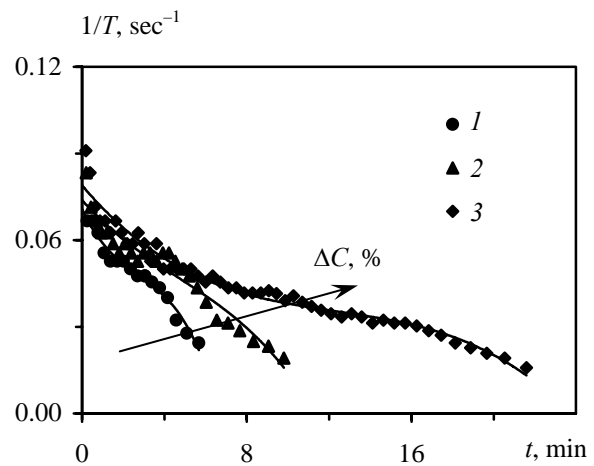

Figure 3. Variation of oscillation frequency with time. $D = 5.0$ mm. ΔC: 20 (*1*), 40 (*2*), 70 (*3*) %.

3 Bubbles in a thin vertical liquid layer

The next experiments were performed in order to visualize the vertical structure of convective flows and concentration fields. The experimental cell was set vertically on its narrow face and filled in turn half by water and half by surfactant solution. After some time the diffusion between the fluids led to the formation of an area with a stable vertical stratification of surfactant concentration. A frame in the form of a flattened thin wire ring was used to prevent the bubble from buoying up and to hold it in a fixed state in the cell center. The frame left the major part of bubble lateral surface free and did not hamper the development of the Marangoni convection. Due to the small channel thickness the arising flows and concentration distributions can be considered to be two-dimensional.

In the absence of the bubble the interference pattern of the concentration field in the stratified solution was presented by a system of horizontal lines. The injection of the bubble essentially disturbed the concentration distribution. Formation of the concentration gradient resulted in the appearance of tangential solutocapillary forces at the bubble lateral surface, which caused the development of the Marangoni convection. Fig. 4 presents the interference pattern of the concentration field around the bubble in the heterogeneous fluid mixture, formed at the top by water and at the bottom by the 70% acetic acid solution (upward surface tension gradient). The height of the bubble, which was slightly deformed by the gravitational force, was 3.8 mm, and its width – 6.0 mm. In the examined situation the capillary forces are directed to the upper pole of the bubble. Under the action of these forces the solution saturated by the surfactant moves from the lower pole region upwards forming a thin layer round the bubble (Fig. 4*a*). The formation of this layer proved to be the main characteristic feature of the solutocapillary convection which distinguished it from the thermocapillary flow. Due to long characteristic times of diffusion the excess of the surfactant transferred along the bubble surface could not fully dissolve in the surrounding fluid. As a result the solution with high surfactant concentration was accumulated near the upper pole in the form of a peculiar "cap", whereas the layer with homogeneous concentration formed around the bubble eliminated the concentration difference between the poles – the source of the Marangoni convection. As soon as the ascending solutocapillary motion along the bubble surface vanished, the dynamic equilibrium of the concentration "cap", which was heavier than the surrounding fluid, was disturbed. Under the action of the Archimedean forces the streams of the acetic acid began to move downward on the right and on the left of the bubble. This motion, in tern, was accompanied by formation of an upward-directed stream under the bubble carrying the solution with a high surfactant concentration to the bubble surface (Fig. 4*b*). The recovery of the surfactant concentration difference between the bubble poles triggered again the Marangoni forces which abruptly increased the rising flow. As a result an intensive convection motion was initiated near the lateral surface of the cylindrical bubble in the form of two symmetric vortices. During evolution these vortices captured the larger volume of the solution with high surfactant concentration. As a result the average density of the solution within the vortices increased, they shifted downwards and at a certain moment cut off the surfactant supply from the bubble lower pole (Fig. 4*c*). Once this happens, the convection ceased as fast as it had started. The whole process of evolution and decay of the intensive motion around the bubble lasted not longer than 30 seconds. Later under the action of the gravity forces the vertical concentration stratification gradually recovered approaching the initial state. Then, after a time, the whole process was repeated. The period of the observed oscillations in the system was about 1–2 min, whereas the time of these oscillations was about several hours limited by the lifetime of the gradient of the surfactant concentration in the cell.
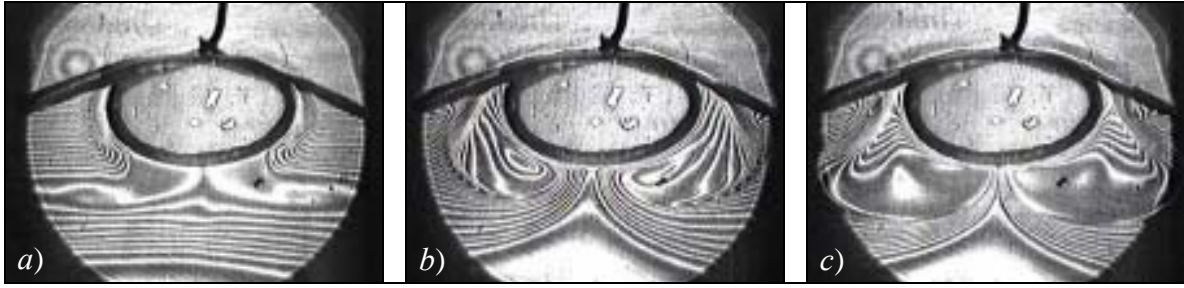
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Figure 4. Interferograms of concentration field around the air bubble in vertical layer of stratified acetic acid solution. *t*: 0 (*a*), 4.5 (*b*), 8.25 (*c*) sec.
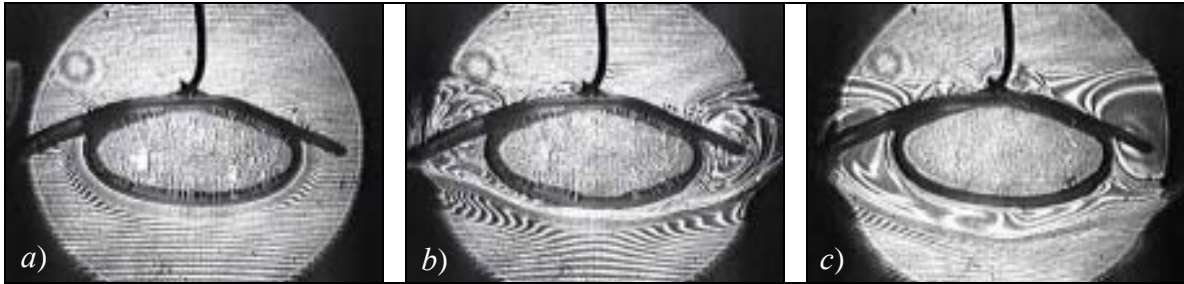

Figure 5. Interferograms of concentration field around the air bubble in vertical layer of stratified isopropyl alcohol solution. *t*: 0 (*a*), 2.0 (*b*), 10.0 (*c*) sec.

Gradually an area of the homogeneous solution formed under the bubble due to a mixing action of the vortex cells and extended in length with time. However as vertical concentration gradient near the bubble still exists, the oscillations are periodically reinitiated, though with less intensity. In experiments with 40% isopropyl alcohol solutions, in which the surface tension gradient was directed downwards (water is below), the structure of the concentration field and flows was bilateral symmetric: the surfactant on the bubble surface was carried to its lower pole and periodically initiated convective vortices rotated in opposite direction (Fig. 5).

The videotape recording of interferograms allowed us to trace the evolution of concentration field around the bubble. The measurements of the concentration distribution on the vertical coordinate were made at the time moments preceding the beginning of each cycle of oscillations when the intensity of the convective motion was minimal. In the system "water – 70% acetic acid solution" concentration decreases monotonically with liquid layer height. Then the bubble began to stir actively the surrounding fluid, reducing the concentration difference between the bubble poles and the mean concentration of the solution under the bubble. At the initial time the vertical concentration gradient ∇C was a maximum and equal to 6.5 %/mm. The corresponding values of the diffusion Marangoni *Ma* and Grasshoff *Gr* numbers were 4.1×10^6 and 1.9×10^3. Then the surfactant concentration gradient diminished rapidly with time, reaching the minimum value 4.4 %/mm ($Ma = 3.0 \times 10^6$, $Gr = 1.4 \times 10^3$) approximately 60 min after the beginning of oscillations. After this it again increased approaching some constant asymptotic value of 5.2 %/mm ($Ma = 3.1 \times 10^6$, $Gr = 2.0 \times 10^3$).

Analogous studying of the evolution of the concentration fields and the concentration gradient averaged over the bubble height was made for the "water–40% isopropyl alcohol solution" system. In this case in contrast to the solutions of acetic acid a decrease and the following increase of the concentration gradient manifest themselves to a lesser degree. Such a behavior of the gradient is evidently due to the fact that with decrease in the intensity of solutocapillary motion the recover of vertical concentration gradient near the bubble due to gravitation and diffusion occurs much slower in alcohol solutions owing to a greater viscosity and a smaller diffusion coefficient. In experiments with lesser concentrated 20% alcohol solutions such extremum is not observed any longer, and the gradient is merely decreasing in a monotonic manner from 1.0 %/mm ($Ma = 16.8 \times 10^6$, $Gr = 1.8 \times 10^3$) to 0.3 %/mm ($Ma = 3.5 \times 10^6$, $Gr = 0.4 \times 10^3$).

The period of convective oscillation changed simultaneously with a variation of the concentration gradient. In tests with 20% isopropyl alcohol solution the period increased monotonically with time and reaches the maximum within the first hour, after which it remained unchanged (curve *1* in Fig. 6). In tests with acetic acid solution the oscillation period within the first hour also increased (Fig. 6, curve *2*), but then began to decrease, which implies that the time dependence of the period in a qualitative sense was the inverse of that of the concentration gradient. Thus in both cases there existed proportionality between the frequency (inverse period) of oscillations and concentration gradient of the surrounding fluid. In Fig. 7 the dimensionless frequency, normalized to the concentration Marangoni number, is plotted on the y-coordinate and the dimensionless time is plotted on
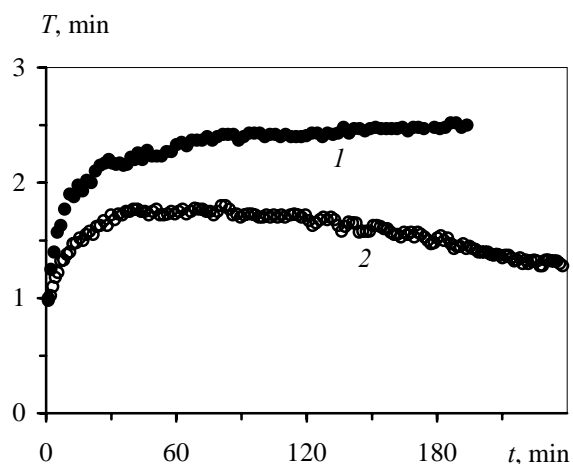
Figure 6. Time dependence of the oscillation period.
1 – isopropyl alcohol solution, *2* – acetic acid solution.

Figure 7. Dimensionless oscillation frequency.
1 – isopropyl alcohol solution, *2* – acetic acid solution.

the x-coordinate. As evident from the graph as soon as the oscillation are set up the ratio $(T/\tau)^{-1} \cdot Ma^{-1}$ turns out to be of the same value for different fluids and remains constant during the whole experiment not depending on the orientation of the concentration gradient (all experimental points for both states are well located on the straight line, which is nearly parallel to the time axis). The obtained result supports the view that just the solutocapillary Marangoni forces are the main initiator of periodical convective motion around the bubble in the heterogeneous solution of fluid surfactant.

4 Bubbles in a plane rectangular channel

In next experiments the fluid filled a thin gap between two vertically oriented glass plates. Inside the gap the fluid was bounded from above and below by solid plates, which formed a horizontal channel of height $h = 2$ mm and thickness 1.2 mm. The tests were performed for aqueous solutions of methyl, ethyl and isopropyl alcohols. The channel was initially filled with distilled water or uniform alcohol solution with weight percent concentrations ranging from 1 to 10%. An air bubble put into the channel cavity from one of its ends in such a way that it completely bridged over the channel and had one free lateral boundary. Then, from the other end, the cavity was gradually filled with a concentrated (up to 40%) alcohol solution. The fluid density difference thus produced in the channel led to the formation of a rather slow large-scale advective gravitational flow, during which a narrow "tongue" of a more concentrated surfactant solution flowed along the upper channel boundary toward the bubble surface, forming near the surface an area with upward-directed concentration gradient. The value of the concentration gradient was specified by the velocity and concentration of the inflowing surfactant flux, as well as by the initial concentration of the solution in the channel.

The interference patterns of the concentration field near the lateral boundary of the air bubble is shown in Fig. 8 and Fig. 9. In contrast to thermocapillary flow
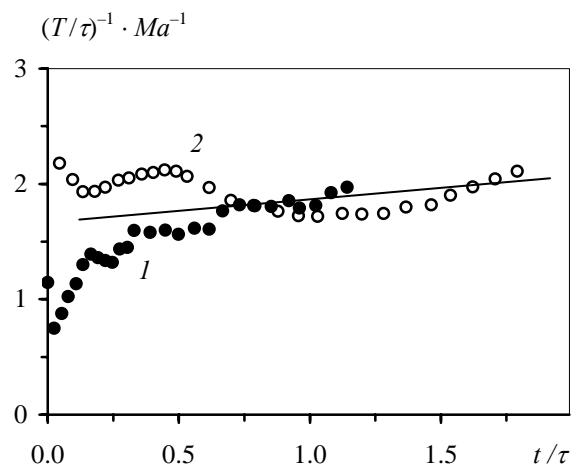
developing in a non-threshold manner at arbitrary small values of the interface temperature gradient, the solutocapillary flow was initiated not at the time when the surfactant "tongue" reached the bubble surface, but with some delay. Thus, in the experiment a time-lag Δt between the arrival of the surfactant flow at the bubble surface and the initiation of the convective vortex was as long as 28 sec. At the same time the difference of the solution concentration ΔC^* between the upper and lower bubble poles caused by a continued motion of the "tongue" reached 2.2%. Then the equilibrium was abruptly disturbed and very rapidly (during about 0.2 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 bubble surface toward the lower bubble boundary. Owing to fluid continuity, the arising flow accelerated the flux of the concentrated surfactant solution along the upper boundary of the channel towards the bubble surface, adding thereby intensity to the existing convective vortex. 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 surfactant from the top of the bubble. As a result, the vortex flow ceased abruptly and the bubble surface turned out to be surrounded by a thin layer of the surfactant solution having a uniform concentration. However, equalizing of the generated horizontal gradient of the surfactant concentration resulted in the development of a slow advective flow. This gravitational motion, by restoring the disturbed vertical stratification of the solution, again draws a concentrated surfactant solution to the upper bubble boundary. As soon as the flux of surfactant touched the bubble surface, the solutocapillary vortex recurred. The cycle repeated iteratively, with the difference that the oscillation period increased with time whereas the intensity of the vortex flow decreased due to a gradual decrease of the vertical concentration gradient. Marangoni convection ceased at the time when the concentration of the solution became almost uniform throughout the whole layer.
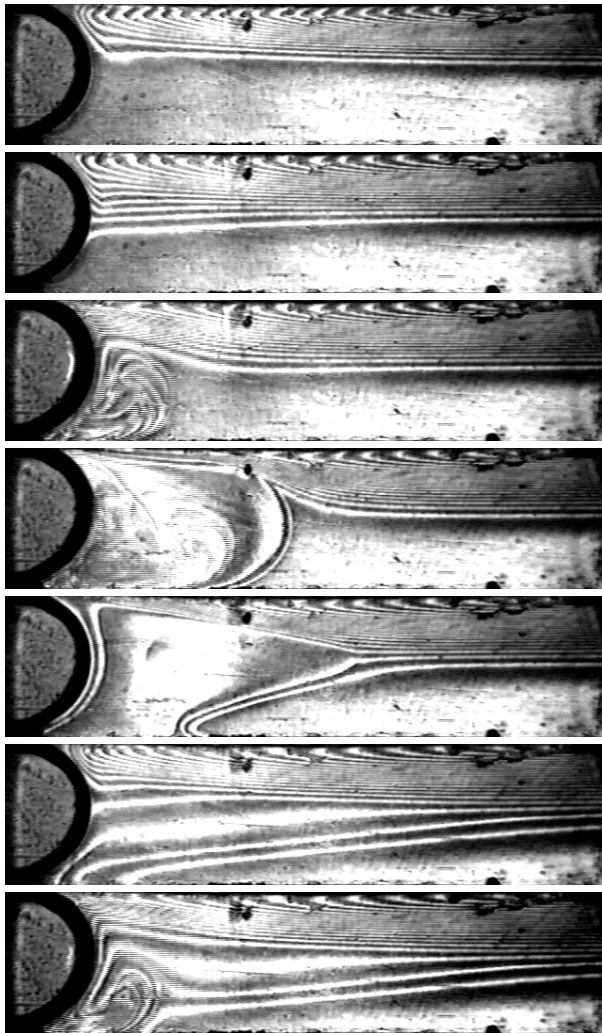
Figure 8. Interferograms of concentration field evolution around the air bubble in rectangular layer with stratified isopropyl alcohol solution.
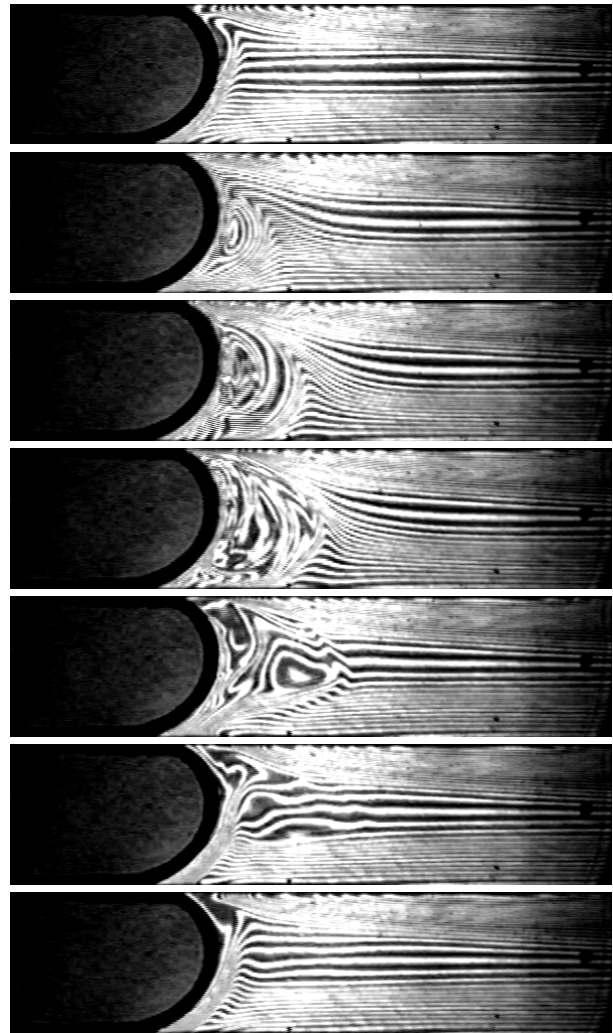*t*: 0, 28.0, 28.1, 28.2, 29.2, 34.2, 34.3 sec.

Figure 9. Interferograms of concentration field evolution around the air bubble in rectangular layer with stratified ethyl alcohol solution.
t: 0, 0.2, 0.4, 0.8, 5.0, 10.0, 20.0 sec.

A characteristic feature of this process is that during consecutive cycles the capillary flow was initiated at much less concentration differences at the bubble surface (thus, the onset of the second cycle happened at $\Delta C^* \sim 0.6\%$). At the same time, the average concentration of the surfactant at the bubble surface gradually increased, which might be one of the explanations for the essential decrease in the concentration difference at the bubble surface at the beginning of each consecutive cycle of the vortex convection motion. In order to verify this suggestion we investigated the dependence of the critical Marangoni numbers Ma^*, defined by the maximum vertical concentration difference between the bubble poles at the moment of formation of the first vortex, on the surfactant concentration in the solution surrounding the bubble. To this purpose, the channel was initially filled not with pure water but with a homogeneous aqueous solutions of alcohols with different initial concentration C_0. It was found that, as C_0 increases (and, respectively, as the surface tension at the bubble surface decreases) the values of Ma^*

decrease monotonically. Fig. 10 presents the critical Marangoni numbers at the beginning of different cycles of the vortex flow in solutions of ethanol and isopropanol (points *1* and *2*) as functions of the crispation number *Cr*, characterizing the ratio of viscous and capillary forces. The crispation numbers, in turn, were calculated using the values of the surface tension corresponding to the average surfactant concentration at the air bubble surfaces at the moments of motion intensification. The diagram also presents the results of measurements of Ma^* as a function of *Cr*, obtained from tests for solutions with different initial alcohol concentration (solid line drawn through points *3* for ethanol and *4* for isopropanol). It is seen that the values of Ma^* obtained under various conditions are rather close and all curves are qualitatively coincide.

In our experiments we also investigated the time dependence of the oscillation period of the convective flow near the bubble in solutions of ethanol, isopropanol and methanol. In all cases, the oscillation frequency of the flow near the bubble surface was first
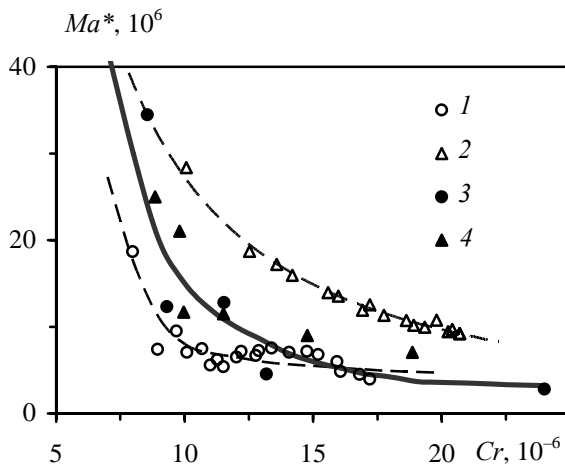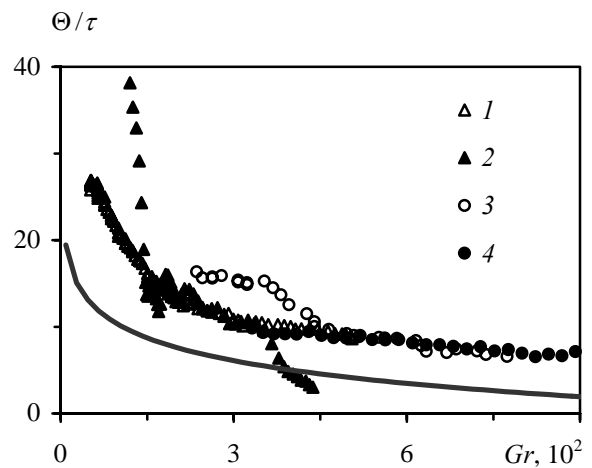
Fig. 10. Critical Marangoni numbers.

Fig. 11. Dimensionless oscillation period.

rather high (accordingly the period T was small ~5-10 sec). Then, the oscillation period increased monotonically with time, and after some time the oscillations suddenly came to an end. The experimental data obtained were compared with the results of numerical analysis [Birikh, Zuev, Kostarev and Rudakov, 2006]. The results of experiments and numerical calculations were found to be in good agreement with respect to the convective flow structure and the oscillation period. The period of the steady-state oscillations decreases with an increase of the Grasshoff number and depends weakly on the Marangoni number. This dimensionless relationship is represented in Fig. 11. The different points on the plot represent the results of experiments for various alcohol solutions (1 – ethanol at $C_0=40\%$, 2 – ethanol at $C_0=20\%$, 3 – isopropanol, 4 – methanol). The solid line corresponds to numerical calculations.

5   Conclusion

The performed experiments provide convincing evidence for the existence of intensive solutal Marangoni convection in solutions with inhomogeneous concentration of the surfactant along the free surface. The specific features of these flows are that they occur at weak diffusion and that the changes in the spatial concentration of the surfactant are mainly due to convective transfer. The arising flows in some ways are similar to thermocapillary ones and are governed by similar relationships, for example, flow intensity is proportional to the surface tension gradient. On the other hand, the solutocapillary phenomena demonstrate some specific features, which are related both to fairly large values of the Marangoni numbers and to a complicated character of formation of the surface tension gradient. The latter peculiarity is caused by slower (compared to heat transfer) diffusion of the fluid molecules with low surface tension onto the interface and adsorption of the surfactant at the inter-phase boundary. Hence, the solutocapillary convection displays well-defined

non-stationary properties. The interaction between the buoyancy and the Marangoni convective flows is responsible for the onset of auto-oscillation regime of convective motion around the gas bubbles in a vertically stratified surfactant solutions. The periodical outbursts of solutocapillary flow at the bubbles interface intensify substantially the stirring of the solution and can be used for the control of this procedure.

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