Instability of solutocapillary flow in the presence of insoluble surfactant

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Abstract

The stability of the solutocapillary Marangoni flow initiated by a localized concentration source in the presence of an adsorbed layer of insoluble surfactant is investigated experimentally. It has been established that the main axisymmetric flow becomes unstable with respect to azimuthally periodic disturbances, which leads to the appearance of the surface flow with a multi-vortex structure. The structure of the secondary flow is investigated depending on the intensity of the main flow and the surface density of the surfactant. It has been shown that the azimuthal wave number increases with the growth of the Marangoni number and decreases with the growth of the surface density of the surfactant. A threshold value of the surface density of the surfactant, at which the Marangoni flow does not occur, has been defined.

Introduction

The presence of the surface tension gradient induced by heterogeneities in temperature, chemical composition or electric potential along the surface of the fluid gives rise to a surface (or capillary) flow. The resulting surface motion is called, respectively, thermal, solutal or electrocapillary Marangoni flow. Interest in this subject is related, first of all to a wide class of both fundamental and applied problems, in which this class of flows has been intensively studied during last few decades.

The structure of surface flows reflects the configuration of heterogeneity distribution at the interface that provokes the appearance of surface tension gradient. As a rule, the structure of such flows is easy to predict, and it can be modelled relatively well based on theoretical and numerical studies. However, there are a number of experimental works, in which the structure of the observed surface flows differs significantly from that predicted theoretically and stemming from the problem symmetry. For example, experimental investigation of the thermal and solutocapillary convection from a concentrated source made in [1 - 3] revealed the occurrence of a multivortex flow on the surface, whereas the numerous experimental and theoretical studies showed the formation of a steady-state axisymmetric radial flow in this situation.

In our opinion, these discrepancies are most likely caused by surfactants (frequently uncontrolled in experiments), which generate an adsorption layer at the interface. For example, it was shown in [4] that the use of anti-wetting covering in the problems of the liquid bridge leads to its partial dissolution in the working fluid and, consequently, to the appearance of the adsorbed film, which changes dramatically the results of the experiments. The results gained by a series of qualitative experiments [5 - 6] have shown that thorough cleaning of the water/air interface lead to the formation of flow structures predicted by theoretical models and consistent with the symmetry of the problem. The content of even small amounts of surface-active impurities at the interface, specifically deposited on the surface [5] or associated with inadequate fluid purification [6], leads to instability of the initial surface flow and the formation of more complex secondary structures at the interface. A more detailed experimental investigation and theoretical description of this phenomenon has not yet been done.

The idea of the influence of adsorbed layers of surfactants a well-studied on the problem of rising bubbles in the solution of surfactants. The explanation was first given by Frumkin and Levich [7]. To date, their hypothesis has been successfully verified in several experimental studies conducted with highly purified water and aqueous solutions of surfactants [8 - 11]. However, no direct experimental observation of the distribution of concentration and velocity on the bubble surface has been performed due to the small (a fraction of a millimeter) size of the region under study. Numerical simulation that has been carried out to take into account the adsorption-desorption process of surfactant molecules on the surface of the bubble shows qualitatively good agreement with the available experimental results [12 - 13]. Quantitative comparison of the results is a rather complicated procedure because much effort is required to measure accurately such parameters of adsorbed films as the rate of adsorption/desorption, characteristic relaxation time of the layer, etc.

In some studies the problem of the interaction of surfactant films with convective flows on the surface [14 - 16] it was found that surfactants exert a destabilizing effect at the early stage of thermocapillary convection, whereas in the other papers the presence of a surfactant has a stabilizing effect at the beginning of convection, leading to an increase in the threshold of the Marangoni number [17 - 19]. No attempts have been made to carry out experimental studies of the layer stability in the context of the Pearson problem.

It is seen that the proposed situation, in which the development of the surface flow is complicated by the presence of the adsorbed layer of surface-active impurities is widely met in practice, but is still poorly explored. The existence of the adsorbed film of surface-active impurities leads to a change in the boundary conditions (surface tension, surface rheology). The redistribution of the surfactant molecules by a convective flow can lead to inhomogeneous boundary conditions and, consequently, to loss of symmetry of the main flow. From this point of view there is a need of making a more comprehensive study of the evolution and stability of the surface flows in the presence of adsorbed surfactant films, which will allow us to formulate the boundary conditions suitable for such problems. The main purpose of the study is the investigation of the interaction in the context of a simple model situation: the stability of an axially symmetric solute-capillary flow induced by a concentrated source located at the surface. The paper presents the results of experimental study into the structure and evolution of solutocapillary flow on the surface of the liquid, depending on the intensity of convective motion (the solutal Marangoni number-la) and the surface concentration of surface-active impurities.

Experimental setup and methods.

The main difficulty in the experimental investigation of this class of problems is the establishment of the "zero" surface, i. e., the surface, which is initially free of molecules of other substances, which can be used to generate the required surface flow and eliminate the influence of complicating factors. The existence of initially pure "zero" surface is also a prerequisite for the creation of the surface layer with controlled properties and concentration. There are two ways of creating such conditions. The first is to select a sample liquid. To extend the scope of research we used water as a base fluid. Out of commonly used fluids (except molten metals and salts) water possesses the largest surface tension, which makes the choice of surfactant practically unlimited. However, preparation of a "zero" surface for water is quite a challenge. To solve this problem, we applied the second method, which includes thorough cleaning of the liquid and experimental setup and constant observation of the state of the interface.

A high level of water purification was achieved by applying successively the processes of Bi distillation and deionization, which enable us to remove practically all impurities. For the removal of impurities was accomplished by employing a Langmuir - Blodgett barrier system and aspirator. The degree of contamination of the surface is controlled by Wilhelmy balance. After completing the procedures of surface cleaning, par of water was pumped out. The water - air interface dropped to about the middle height of the cuvette, where the cuvette walls were transparent, which allowed us to apply the optical methods of structure visualization. The solutocapillary Marangoni flow was created in the following way. On the free surface of a horizontal layer of water (1, Fig.1) we placed a thin slice (0.9 mm outer diameter) of a stainless steel tube 2, through which a weakly concentrated aqueous solution of ethyl alcohol is feed by pump 3. Even small concentrations of the ethyl alcohol solution substantially lowers the surface tension, which leads to the appearance of convective flow at the interface, directed oppositely to a concentration gradient, i.e., from the center to the periphery of the cuvette. Ethyl alcohol is also a surfactant, but in weakly concentrated solutions it does not form stable adsorbed films capable of affecting the stability of solutocapillary flow.

Experiments have shown that the convective flow created at the surface in such a way remains stable, i.e., preserves the axial symmetry throughout the experiment. Changing concentration of the solution of ethyl alcohol and flow rate we can change the intensity of convective flow. For flow visualization we used the standard knife- edge technique in combination with light-scattering particles suspended in solution - glass, hollow spherical particles of neutral buoyancy. The particles undergo pre-treatment to remove contaminants from their surface. Knife-edge, created by laser 4 (wavelength 532 nm, power 200 mW) and lens system 5 moved along the surface of the liquid. The flow patterns were recorded by camera 6.

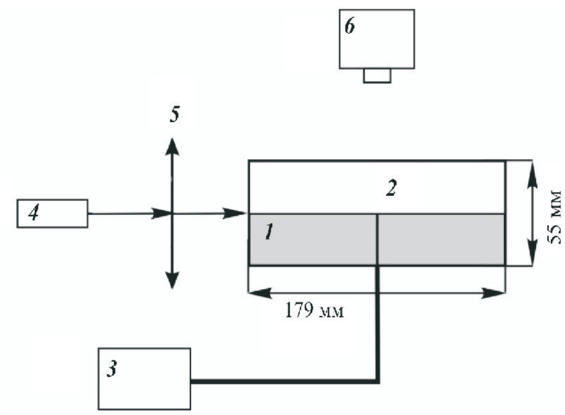

Fig.1 Scematics of experimental setup: 1 - water layer, 2 - a tube for feeding aqueous solution of ethyl alcohol, 3 - feeding pump, 4 - laser, 5 - lens system, 6 - photo camera

To create a film of surfactant on the surface of water we used insoluble surfactant (oleic acid). In this case, the molecules of surface-active impurities are located on the surface and do not penetrating into the liquid, which makes it possible to create a constant and controllable surface concentration. The fluid motion at the interface can only lead to a redistribution of the molecules within the surface phase, which may change the local, but not the total concentration of molecules on the surface. To create a film on the surface of water we dissolved the surfactant in highly volatile and water - insoluble organic solvent - hexane. With the help of a microsyringe the solution was injected onto the surface of water. It rapidly spread over the surface covering all available area. As the solvent evaporates, a homogeneous surface layer is formed. At the beginning of each experiment, we specified the feed rate of the solution, its concentration and the surface density of the surfactant molecules. These quantities were used to form two dimensionless governing parameters of the problem: the degree of saturation of the layer by the molecules of surface-active impurities.

$$\frac{\Gamma}{\Gamma_e}$$

where Γ - surface concentration of impurities, Γ_e - surface concentration of the saturated mono-layer of a surfactant. The effective Marangoni number is.

$$Ma = \frac{q}{D\eta^2} \cdot \frac{d\sigma}{dC} \cdot C$$

where q - dimensional mass flux of the surfactant solution, η - dynamic viscosity, D - diffusion coefficient, σ - surface tension, C - volume concentration. During experiment we investigated the structure of arising flow as a function of these dimensionless parameters.

The results of experiments and discussion

The structure of the concentration-capillary motion on the surface essentially depends on the intensity of the Marangoni flow and the surface density of the surfactant. In the absence of the surfactant an axially symmetric flow (radial flow) stable over the entire range of the Marangoni numbers used in experiments is formed at the interface. Such a structure of the flow formed in the absence of the surfactant served as additional criterion of the water surface purity at the beginning of each experiment. The deviation of the flow structure from the axial symmetry was the reason for of interrupting the test and repeating the procedure of water purification and setup cleaning. The presence of a surfactant of any surface density leads to instability of the main flow and the formation of secondary structures in the form of a multivortex flow, periodic in the azimuthal direction.

The characteristic structures obtained experimentally for a fixed of Γ/Γ_e=0.35 and different values of the Marangoni number Ma are given in (Fig.2). It is seen that at small value of the Marangoni number the developed flow has a two-vortex structure (a). With an increase in the flow velocity the structure loses stability at some value of Ma, giving way to a four-vortex structure (b). A further increase of the mass flux leads to the appearance of a more complicated structure with a greater number of vortices (6 and 8 vortices in Fig.2 (c) and (d), respectively). The value of the interval, in which there exists a stationary two-vortex flow decreases with increasing wave number. Moreover, with increasing intensity of the convective motion and at a constant surfactant content, in the vicinity of the source one can observe the formation of the zone of axially symmetric flow, which increases with the growth of Marangoni number. Similar evolution of the surface flow is observed at a fixed value of the Marangoni number and variable value of Γ/Γ_e (Fig.3).

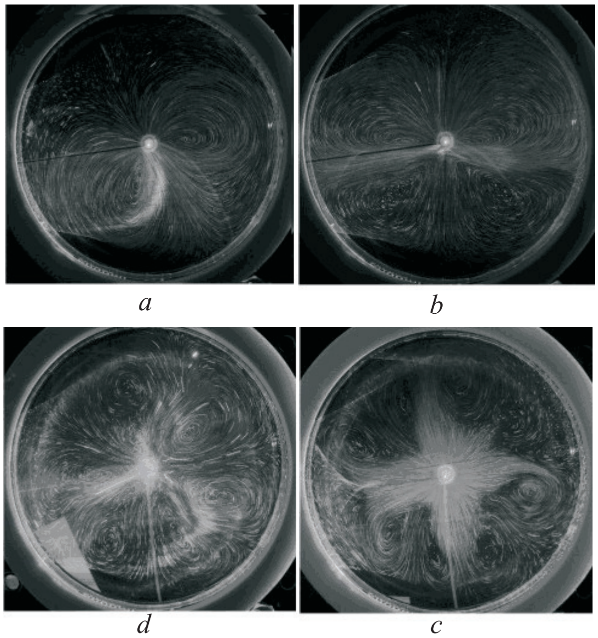

Fig.2 Characteristic flow patterns 1 at Γ/Γ_e=0.35 and $Ma \cdot 10^7$: 0.5 (a), 1.0 (b), 2.5 (c), 4.0 (d)

In this case, the number of vortices decreases with the growth of the surfactant content at the surface.

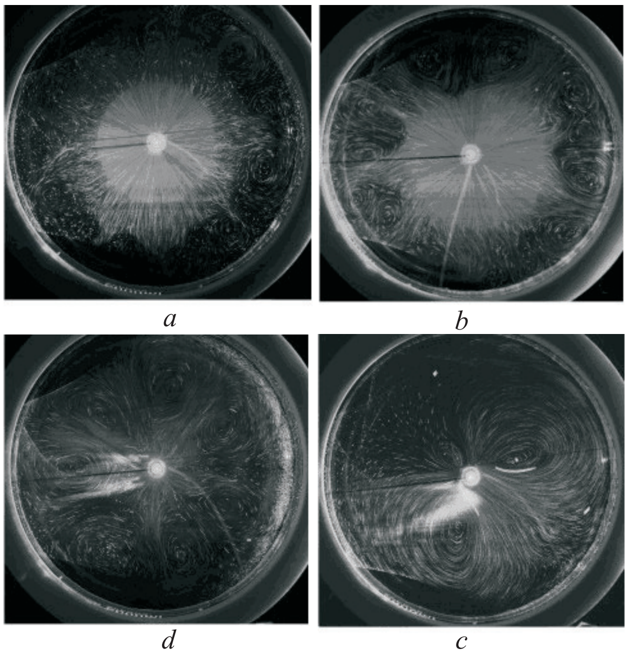

Fig.3 Characteristic flow patterns 2 at $Ma = 0.5 \cdot 10^7$ and Γ/Γ_e: 0.2 (a), 0.25 (b), 0.3 (c), 0.35 (d)

When Γ/Γ_e approaches a certain threshold value depending on the Marangoni number, no surface flow is formed at the surface. It is also seen that the size of the region of the axially symmetric flow in the central part of the cuvette reduces with an increase in the quantity of the surfactant at the interface. On the basis of the character of the multi-vortex flow described above, its symmetry and structure of the initiated flow we can derive a wave number, which is defined as $k_\varphi = 2\pi/\varphi$, (where φ is the angular dimension of the structure). It essentially depends on the Marangoni number and surface density of the surfactants.

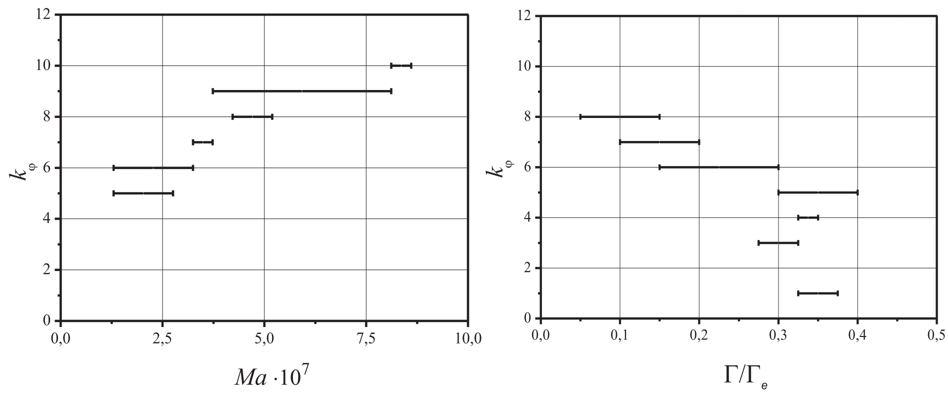

Fig.4 Azimuthal wave number as a function of the Marangoni number (left picture, Γ/Γ_e= 0.15) and the surfactant surface density (right picture, Ma=0.19·10^7)

The plots of azimuthal wave number as a function of the Marangoni number and surface density of the surfactant were constructed based on the results of experiments and are given in (Fig.4). It should also be noted that in the presence of surfactant at the interface there is a threshold value of the Marangoni number, at which a convective flow is initiated. At lower threshold values the flow on the surface is not formed. This threshold value depends strongly on the surface concentration of the surfactant.

Conclusion

The results of experimental studies presented in this paper show that the flow structures observed in some studies [1 - 6], contradict the results predicted theoretically in compliance with the symmetry of the problem. This can be explained by the existence of uncontrolled content of surface-active impurities involved in the formation of the adsorbed layers at the interface. Experiments show that the presence of even small amounts of surfactant molecules on the surface leads to instability of the main flow. The structure of the secondary flow is determined by the geometry of a particular problem. In the case examined in this paper, an axisymmetric flow becomes unstable with respect to multivortex flow, which is periodic in the azimuthal direction. Moreover, the azimuthal wave number depends on the intensity of the flow and content of the surfactant.

The mechanism of the instability of the basic flow is as follows. Initially, a uniform distribution of particles on the surface is disturbed by the arising axially symmetric radial flow, which transports surfactant molecules to the periphery. However, compression of the adsorbed layer of insoluble impurities leads to the appearance of the surface pressure in the layer. Because it is directed against the flow, it slows down the main flow. This results in the formation of a peripheral zone, into which the flow does not penetrate. The boundary of this zone sets new boundary conditions for the flow, instead of conditions previously existing at the solid boundaries of the cuvette. Any violation of the symmetry of the moving boundary leads to breaking of the main flow symmetry due to the presence of feedback between the surface density of surfactant in the selected azimuthal direction and intensity of the main flow in the same direction. The resulting heterogeneity in the distribution of the surfactant in the peripheral layer will increase leading to the instability, whose azimuthal wave number will depend on the control parameters of the problem. Of course, the proposed instability mechanism is hypothetical and should be tested in the theoretical study, which is scheduled for the near future.

Acknowledgements

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