

Thermo-capillary flow in a Hele-Shaw cell as a tool for research of the dynamics of insoluble surfactant monolayer

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Abstract. The occurrence of thermocapillary convection in a Hele-Shaw cell in the presence of the surfactant film on the free surface is experimentally investigated. It is shown that at certain values of the control parameter two different zones are formed on the surface – the zone free from impurities and the stagnant zone. In the first zone, the onset and development of an intense Marangoni convection is observed, while in the stagnant zone the velocity of the motion on the surface is lower by about two orders of magnitude. This study clearly demonstrates that the analysis of the temperature profile provides sufficient information about both the distribution of tangential stresses over the surface and the degree of compression of the surfactant film. In addition, due to a simple linear law of temperature variation on the surface of the stagnant zone, the distribution of the surfactant molecules over the surface can be predicted based on the known equation of state for the film of the examined surfactant. Thus, the application of a set of simple experimental techniques to the examined model problem allowed us to obtain complete information on the state of a complex system consisting of a liquid layer and a surface film of the surfactant, the structure of the volumetric flow, the velocity of the liquid at the surface, the distribution of shear stresses and surfactant molecules over the surface.

1 Introduction

Over the period of the last few decades, capillary flows have been extensively investigated by theoretical and experimental methods. The importance of these studies lies in the fact that there is a wide range of the fundamental and applied problems, in which this class of flows is the main objective of research. Capillary phenomena take place in fluid systems with a phase boundary. One of the most commonly encountered mechanisms of flow initiation on the free boundary is the surface tension gradient. The inhomogeneity of surface tension can be associated with the non-uniformity of temperature, chemical composition or electric potential along the fluid boundary. The arising fluid motions are known under the collective name of the Marangoni flows. The flows are directed against the surface tension gradient.

It is well known that the presence of a surfactant at the fluid-fluid interface can have an essential effect on the stability of hydrodynamic systems and on the structure of the secondary convective flows [1,2]. The presence of surfactant molecules on the free boundary leads to a decrease in the surface tension and changes the rheological characteristics of the boundary. The degree of this influence depends on the surfactant concentration, kinetic properties and thermodynamic conditions. In the limiting case of high concentrations the film of a surfactant can completely immobilize the surface. Also it is obvious that in the opposite case a

highly rarefied gaseous monolayer of the surfactant makes the surface almost perfectly clean. On the other hand, the initiation of the surface flow leads to a redistribution of the surfactant molecules and the appearance of the additional surface stress, which eventually affects the fluid dynamics in the system. In papers [1-4], different aspects of this effect are studied theoretically in the framework of two-dimensional formulation. It is shown that the fluid covered by a surfactant is set to motion when the surface is non-uniformly heated. It should be noted that the cavity was subjected to lateral heating and the numerical simulation was done under a simplified assumption of linear distribution of temperature throughout the whole system [3,4]. A thermocapillary flow serves as a mechanism for transporting the surfactant molecules to the cold side of the cavity. The structure of the convective flow in the cavity is determined by the magnitudes of two parameters. The first one is the elasticity number $E = \Delta\sigma/\Delta\sigma_T$, describes the competition of solutocapillary and thermocapillary effects causing a decrease in surface tension. The second parameter is the surface analogue of the Peclet number $Pe_S = u^*l/D_s$, characterizing the relationship between mass transfer of the surfactant by a thermocapillary flow and by surface diffusion D_s .

When $E > 1$, both the thermocapillary and the solutocapillary stresses compensate each other at all points of the surface. The fluid motion arising at the boundary is almost uniform, because it is balanced by a

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spread of the surfactant due to the surface diffusion. When the Peclet number is small (fast surface diffusion), spreading of the surfactant is practically homogeneous. At a high value of the Peclet number (slow surface diffusion), the surface becomes immobile. At $E < 1$, near the hot side there is a region of the surface that is free from the surfactant. The initiated intensive thermocapillary convection causes the surfactant particles to congregate near the cold wall. As a result, a stagnant zone is formed on the fluid surface and its extension depends on the above mentioned parameters.

Paper [5] is devoted to a numerical simulation of the surfactant behavior on the free surface of a fluid in a two-dimensional rectangular container. As in the previous papers, the fluid was heated on the lateral side. The location of the stagnant point was regulated by changing the elasticity number. The results of simulation qualitatively agree with the analytical results obtained by Homsy [4]. However, the matter of greatest practical interest is a comparison of these results with the experimental data.

The aim of this paper is to study experimentally the behavior of a layer of an insoluble surface-active impurity under the action of a temperature gradient applied to the surface using the formulation that approximates the description given in works [3-4].

2 Experimental setup and technique

The experiments were carried out in a Hele-Shaw cell, which includes three elements-two lateral faces and an n-shaped insert made of a 0.25 cm. glass plate. To minimize the potential sources of contamination, clean parts were tightly pressed together without glue. The finished cuvette was dried and filled with purified water. The cuvette was filled to the brim, so that the free surface of the liquid was flat. Particular attention was paid to cleaning of the water surface. In the experiments we used bidistilled water, which was passed through a deionization filter. The surface of the water in the cuvette was subjected to additional purification, which included the following steps: the cuvette was overfilled with a liquid, and the excess liquid together with the residual impurities was collected from the surface by the pump. Owing to a multi-step cleaning procedure applied to the cuvette, water and water surface, we managed to achieve the "zero-surface" state, i.e. the conditions for complete removal of residual impurities from the free surface. Under weak non-uniform heating, an intensive thermocapillary convection spread over the entire fluid surface, which served as a criterion for estimating the degree of its purity.

A temperature gradient on the surface was generated by radiation from a halogen lamp. A special lens system was used to create the required distribution of the intensity of incident radiation. This method of creating the thermal inhomogeneity on the surface allowed us to avoid distortions of the temperature profile near the lateral walls, which generally occur when using heat

exchangers. Moreover, radiation made it possible to generate in a very short time (of the order of one second) a temperature difference required for heating the lamp spiral. Radiation from a spiral in the form of a rectangle 3x4 mm² was passed through a system of spherical and cylindrical lenses. The result of heating the surface with such a source was the formation of an elongated thermal spot, in which the temperature distribution was close to a linear pattern. The length of the linear portion was about 2 cm. Therefore, the characteristic dimensions of the Hele-Shaw cell were chosen taking into account the characteristics of the heater- the length of the free surface was 2 cm, the depth of the cavity was 0.8 cm, and the width was 0.25 cm. The power source used in the experiment allowed the brightness of the lamp radiation to vary smoothly. The maximum temperature difference on the surface created by radiation depended on the properties of the absorbing medium. Thus, for the surface of strongly contaminated water (which inhibited its mobility) $\Delta T=12^{\circ}\text{C}$, which corresponds to a change in the surface tension by 2 dyn/cm.

To visualize the convective flow, a small amount of light scattering particles were added to the liquid (silver-plated hollow glass spheres of 5-25 μm in diameter with neutral buoyancy). Before use, the particles underwent a multi-step cleaning procedure to avoid contamination of the system by uncontrolled surface-active impurities. The laser knife applied to the system from above provided illumination of the particles in the middle longitudinal area of the working cavity. To measure the velocity in the liquid, the movement of light scattering particles was registered with a video camera. Subsequent processing of the video records allowed us to draw a flow structure and reconstruct the fluid velocity profile depending on the depth.

The temperature distribution of the free surface of the liquid was recorded using the Flir SC5000 thermal imager. The spatial resolution of the temperature measurements was 0.2 mm, the accuracy of the temperature measurement was 0.02°C . This type of video camera is widely used to record the temperature distribution on the free surface of a liquid [6]. Using thermograms of the surface, one can judge the mode of convection in the near-surface layers of the liquid. In particular, the obtained thermograms provided a clear-cut vision of the boundaries of the convective cells. As it will be shown below, the analysis of temperature distributions in our work makes it possible to distinguish between the regions with a clean surface and the surface covered by a surfactant film.

In this work, oleic acid was used as an insoluble surfactant. To obtain a layer of oleic acid, the required amount of its solution in hexane of high purity was applied to the surface using a micropipette. The surface concentration Γ is equal to the number of surfactant molecules per unit area. It is normalized to the concentration of a tightly packed monolayer Γ_e . For oleic acid, $\Gamma_e \approx 7.2 * 10^{-10} \text{ mol / cm}^2$.

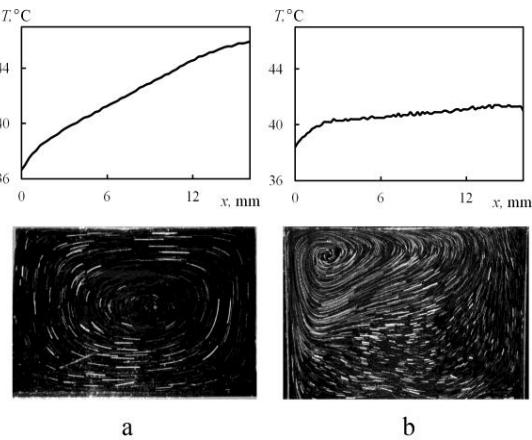


Fig. 1 The flow pattern and surface temperature profile for strongly contaminated (a), and "zero" (b) surfaces

3 Results of experiments

3.1. Comparison of emerging flow patterns and temperature distributions

First of all, the experimental technique was tested on highly contaminated and clean surfaces. Figure 1 presents the results of visualization of the flow structures in the liquid and the distribution of temperature over the surface in these two situations. It is clearly seen that the flow patterns differ significantly. At a large amount of surface active contaminants the characteristic velocities in the cuvette are of about 0.1 millimeter per second, and the velocity field is symmetric with respect to the cell walls (Fig. 1a). It is known that the interface, covered by a layer of a highly concentrated impurity, behaves as a solid and deformable surface, at which the no-slip condition for the tangential velocity component is satisfied. Judging by the flow structure, the specific feature of this situation is the onset of purely thermogravitational convection due to the presence of a temperature gradient along the upper, practically immobile boundary.

In the case of a surfactant-free surface, the velocity of the liquid in the cell is two orders of magnitude higher, and the structure of the motion is strongly asymmetric: the vortex is pressed against the interface, which is characteristic of thermocapillary convection (Fig. 1b). The temperature profiles in both cases are linear (except for a small area located above the descending flow region), but the slope of the curve varies significantly depending on the state of the surface. On a strongly contaminated surface, the temperature drop is much greater. Obviously, this is due to a change in the dominant mechanism of heat exchange along the surface. In the case of immobile or almost immobile surface, this is basically a relatively weak molecular-kinetic mechanism, and in the case of a clean, mobile surface, this is a convective mechanism. In terms of the elasticity number E , the case of strongly contaminated surface corresponds to $E \gg 1$, and the case of cleaned surface to $E \rightarrow 0$.

The most interesting case is $1 > E > 0$ when the thermocapillary effect on the surface exceeds the solutocapillary one. Figure 2 shows the structure of the

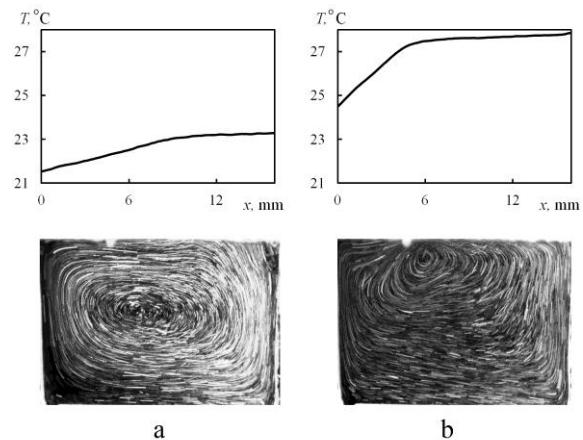


Fig. 2 The flow structure and the surface temperature profile for the cases of smaller (a) and greater (b) temperature differences with the same total amount of surfactants on it.

flow in the liquid and the profiles of temperature at the surface covered by a layer of surfactants at different values of E . A transition from Figure 2a to Figure 2b corresponds to an increase in the temperature difference along the surface (due to increase in the lamp power) with a constant surface density of the surfactant. It is seen that the structure of the flow becomes more complicated. In particular, there is a region where the stream lines running along the surface suddenly duck under it and go deep into the liquid. With reference to the temperature profile, this corresponds to a change in the temperature gradient. In theoretical papers [1,2,4] it was shown that a thermocapillary flow causes a redistribution of impurity concentration on the surface. Transport of the surfactant molecules along the surface stops when inhomogeneity of the surface tension caused by the thermocapillary effect is compensated by heterogeneity of the solutocapillary nature.

Figure 3 schematically shows the surfactant distribution over the surface at different values of the elasticity number. In the absence of a temperature gradient, the impurity particles are uniformly distributed over the surface providing a constant concentration Γ_0 (profile 1). Due to the establishment of a linear temperature profile along the surface, the concentration profile of the redistributed surfactant in the layer will also be linear [1,2,4] (provided that the equation for the state of the surfactant layer is linear), but with an opposite slope (profile 2). An increase in the applied

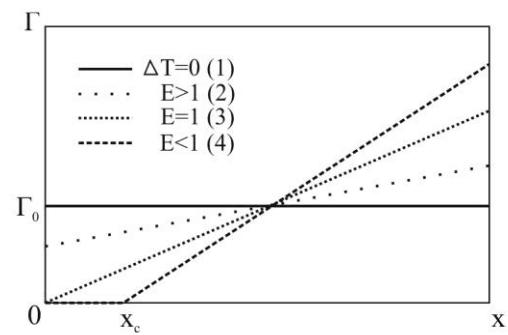


Fig. 3 Draft of the surfactant distribution evolution on the surface with a consequent increase in the temperature difference.

temperature difference leads to the situation when $E=1$, at which the surfactant concentration at the hotter wall reaches zero (profile 3). A further increase in the temperature difference has a dual effect: a part of the surface is cleared from the surfactant, which immediately gives rise to an intense Marangoni convection (profile 4), while the other part is still covered by the surfactant and therefore remains immobile. In such a situation, one should expect the appearance of two surface regions [4] with different boundary conditions for velocity separated by the so-called stagnant point X_c . At the point between the two regions with different heat transfer mechanisms, the slope of the temperature profile changes (see Fig. 2). Thus, the registration of temperature distributions on the free nonuniformly heated surface provides information about both the magnitude of the applied shearing stresses of a thermocapillary nature and the integral characteristic of the flow regime –the location of the stagnant point.

It should be noted that the flow regimes described above, as well as the surface temperature distributions, were stationary, whereas a number of theoretical studies have predicted that in the case of a longitudinal temperature gradient on the surface covered by the surfactant, the oscillatory mode of instability is more dangerous than the monotonous mode [7].

3.2. The study of the equation of state of the surface phase

The results of the experiments show that the size of the stagnant zone occupied by the surfactant layer depends on the temperature difference and the concentration of surfactant molecules on the surface. At a fixed amount of surfactant, an increase in the temperature difference and the corresponding difference in the surface tension $\Delta\sigma$ over the entire length of the surface leads to a displacement of the boundary of the stagnant zone

toward the cold wall. In Figure 4, the location of the stagnation point X_c is plotted as a function of the increment in the surface tension $\Delta\sigma$ along the surface for three different values of the initial surface density of oleic acid molecules. The coordinate of the stagnant point is normalized to the length of the entire surface and the initial concentration Γ_0 is normalized to the concentration of a filled layer of the surfactant Γ_e . It is seen that at low Γ_0 , the location of the stagnant point changes with increasing shear stress according to a linear law, which is replaced by a nonlinear one at high compression rates. The reason for such behavior is the phase transition in the surfactant layer, which manifests itself in the form of a change in the linear equation of state of an ideal gas. The deposited film is characterized by a more complicated relationship. The larger the initial concentration Γ_0 , the less extended is the linear portion of the dependence.

Figure 5 presents the same data, but in a dimensionless form, namely, as a function of the elasticity parameter E . In the work of Carpenter and Homsy [4] mentioned earlier, the formula $X_c=1 - E^{1/2}$ was proposed to relate the position of the stagnant point to the value of the elasticity number. The curve shown in Fig. 5 was calculated by this formula. When making a comparison, one should take into account the fact that for the surfactant the simplest equation of state was accepted in the form of a linear relationship $\Delta\sigma=\gamma\Gamma$, which corresponds to the gaseous state of the layer.

It can be seen that the theoretical relationship does not adequately describes the experimental data even in the region where the surfactant layer remains in the gaseous state upon compression (the first seven points on the experimental curve corresponding to $\Gamma_0=0.1\Gamma_e$). The discrepancies, in our opinion, are associated with an incorrect estimate of the contributions of the convective and heat-conducting mechanisms to the heat transfer processes. Proceeding from the approximation to the theory of lubrication, the authors neglected a weak

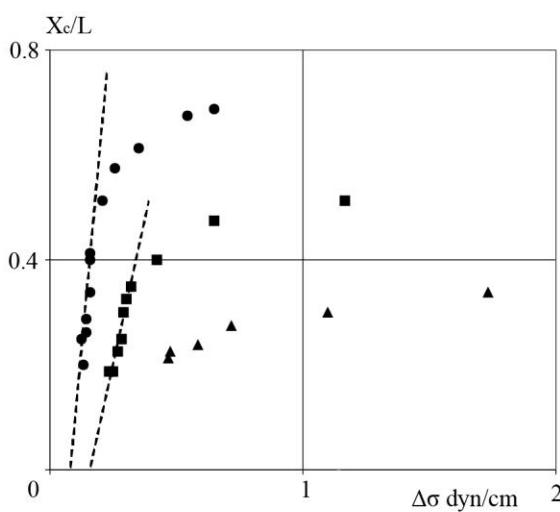


Fig. 4 Graph of the dependence of the dimensionless coordinate of the stagnant point $X_c=f(\Delta\sigma)$ for three different initial concentrations, $\Gamma_0 = 0.1$ (circles), 0.2 (squares) and 0.3 (triangles) of Γ_e .

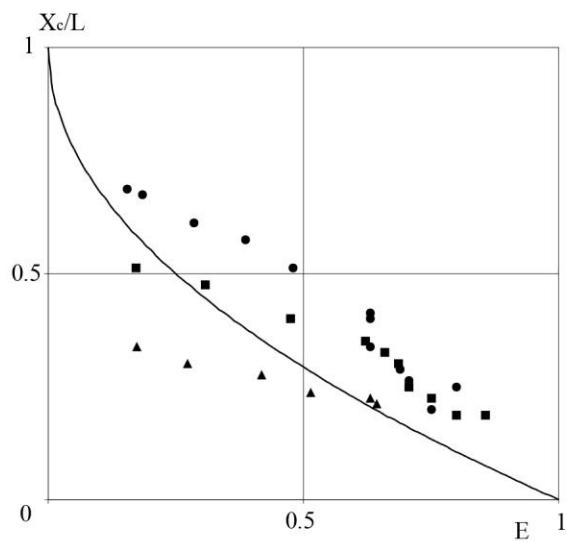


Fig. 5 Graph of the dependence X_c on the elasticity number E for three different initial concentrations, $\Gamma_0 = 0.1$ (circles), 0.2 (squares) and 0.3 (triangles) Γ_e . For comparison, a curve calculated according to the Homsy formula is given.

contribution (as they believe) of convective heat transfer, leaving only the term responsible for the conductive transfer of heat. As a result, the temperature gradient on the surface remains constant even after the formation of the region free from the surfactant. At the same time, the experiments described in this chapter clearly demonstrate a change in the slope of the temperature profile, which is certainly caused by a significant contribution of thermocapillary convection to heat transfer.

4 Conclusion

In this paper, we present a technique for measuring the characteristics of a thermocapillary flow in the presence of surfactants using a thermal imager. For a certain class of problems, this technique allows one to combine measurements of tangential stresses of the thermocapillary nature distributed over the surface and the integral parameter of the flow initiated in the system. It was shown that this parameter determines the characteristics not only of the surface flow but also of the volumetric flow. In this case, there is no need to use light scattering particles, which ensures the achievement of high purity required in such tasks.

We applied this technique to the layers of oleic acid of different concentrations and derived the relationship between the location of the stagnation point and the elasticity number, which is the governing parameter of the problem. The obtained data contradicted the results of theoretical study [4], which obviously implies that some of the assumptions made by its authors are not valid.

The work was supported by the Russian Fund for Basic Research (projects #16-01-00662)

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