Flow Development at the Surfaces of Bubbles and Droplets in Gradient Solutions of a Surface-Active Liquid

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Abstract—The development of solutocapillary flows at the surfaces of air bubbles and chlorobenzene droplets was experimentally studied in nonuniform aqueous solutions of ethanol and isopropanol, which have a low surface tension and, hence, exhibit surface-active properties with respect to water. The experiments demonstrated the retardation of the onset of the development of the Marangoni concentration-induced convection relative to the moment of the contact between an inflowing surfactant (alcohol) and the surface. The critical concentration gradients (the Marangoni diffusion numbers) necessary for the initiation of mass transfer of a liquid along the interface were determined as dependent on the rate of inflow of a tongue of a more concentrated solution and the initial alcohol concentration around the bubble.

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INTRODUCTION

Marangoni tangential capillary forces directed at an increase in the surface tension are known to arise at the surfaces of gas bubbles or insoluble liquid droplets placed in a liquid medium with temperature or surfactant concentration gradients. These forces initiate convective flows in the bulk liquid by involving near-surface layers in motion. Such convection (thermocapillarly or solutocapillary, respectively) plays an important role in the heat-and-mass transfer and hydrodynamics of multiphase media and substantially affects many technological processes.

It is interesting that, despite similar motive forces, solutocapillary flows differ strongly from thermocapillary ones. First of all, these differences are related to long characteristic times of the diffusion of impurities and, consequently, much higher Prandtl and Marangoni diffusion numbers. As a result, the concentration nonuniformities remain preserved in liquids much longer than the thermal ones; hence, the duration and intensity of the action of capillary forces at an interface appear to be many times enhanced. Second, the mechanism of surfactant transfer to interfaces (adsorption) differs from the mechanism of temperature generation at an interface. Interfaces have inertial properties so that the convective transfer and surface diffusion of surfactants may occur along them. The above factors result in solutocapillary phenomena, which have no thermocapillary analogs. Among such effects is the development of self-oscillating concentration-induced flows.

The development of oscillating regimes of concentration-induced convection was experimentally observed for the first time around imobile air bubbles placed in a thin horizontal layer of a liquid with a vertical gradient of surface tension [1–2]. The experiments were performed with a 2-mm-high cavity filled with a bilayer system of miscible liquids, one of which was surface-active with respect to the other (methanol-water, water–acetic acid). Plane-parallel glasses with a semitransparent mirror coating served as the upper and lower walls of the cavity, which enabled us to visualize the horizontal distribution of the surfactant concentration in the liquids as a system of isolines of refractive indices with a Fizeau interferometer. Intense periodical short-time perturbations of the concentration field were found around bubbles. The period of these oscillations varied from several seconds to tens of minutes depending on time, initial surfactant concentration gradient, the properties of the liquids, layer thickness, and bubble diameter. As the vertical concentration gradient decreased, the oscillations occurred more and more rarely, and then suddenly ceased. It was assumed that regular ejections of excess surfactant accumulated near one of the poles of the bubble due to a solutocapillary flow at its surface into the surrounding solution caused the observed intensification of the mass transfer. However, the structure of the perturbations per se could hardly be experimentally studied in terms of a three-dimensional problem.

In order to clarify the reasons for the development of the oscillations, the dynamics of the surfactant concentration distribution and the structure of the convective motion around a bubble in a thin vertical layer of a stratified liquid was studied [3, 4]. For this purpose, an experimental Hele–Shaw cell was mounted vertically on its narrow side, and the observations were performed from the lateral wide sides. The cell was filled...
with aqueous solutions of acetic acid or isopropanol characterized by a stable stratification of surfactant concentration. A 20–30-µl air bubble was placed into a liquid, where it took the shape of a short horizontal cylinder 4–6 mm in diameter with a free side surface. The bubble was prevented from rising under the action of the buoyancy force by a special wire frame, which did not hinder the development of the Marangoni convection.

Using the interference method, it was established that the cause of flow oscillations near the bubble is the competition of two concentration-induced convection mechanisms (capillary and gravitational) of mass transfer having different characteristic times. The time dependences of the oscillation period were studied at different average solution concentrations, surfactant concentration gradients, and the Marangoni and Grashof numbers. It was shown that the relationship between the dimensionless oscillation frequency and the Marangoni number is independent of time, the nature of dissolved liquids, and the direction of concentration gradients.

The described oscillations of concentration-induced flows were not observed for free surfaces of gas bubbles alone. Similar oscillation regimes of the convection were found in the vicinity of interfaces between immiscible liquids in the experiments with chlorobenzene droplets in stratified aqueous isopropanol solutions [5]. Unlike the case of the bubbles, a concentration flow influencing the period and duration of the oscillations was formed inside the droplets as a result of surfactant diffusion from the solution into them. The study of concentration fields made it possible to describe the basic stages of the surfactant absorption by the droplets and the development of flows inside them, as well as to demonstrate the correlation between the maximum gradients of the surfactant concentrations outside and inside the droplets.

In subsequent studies [6], a thin vertical layer of a liquid was confined on top and bottom by solid inserts forming an extended horizontal channel with a rectangular cross section. An air bubble that completely blanked the channel and, therefore, had only a small part of its side surface free, was placed in the channel. This type of cavity shape allowed us to compare the experimental results and the data of subsequent numerical simulation. The experiments were carried out at different initial distributions of the surfactant concentration in the channel; methanol, ethanol, and isopropanol were used as surfactants. The active interaction of two different convection mechanisms of mass transfer was observed similar to that described in [5]. The first mechanism represented intense Marangoni convection, which transferred the surfactants along the free bubble surface and damped rapidly due to the equalization of the surface surfactant concentration as a result of stirring the solution near the bubble. The second mechanism was related to the action of the buoyancy force, which gave rise to the formation of a relatively slow global flow of a liquid inside the cavity as a result of rising of a solution with a high surfactant concentration. This advective flow restored the disturbed stratification of the solution at the bubble surface; then, an intense capillary flow was observed again. The time dependences of the oscillation period and vertical concentration gradient were studied and the critical Marangoni and Grashof numbers at which the oscillation regime of the convective motion was established were determined.

The aforementioned problem was also solved numerically using a convection model with a diffusion transfer of a surfactant to the bubble surface (without the formation of a surface phase) [7]. A rectangular cavity extended in a horizontal direction, with one of its vertical walls modeling a bubble surface impenetrable to a surfactant, was considered. An initial horizontal gradient of the surfactant concentration was preset in the cavity. The calculations showed that, at large Schmidt numbers (~105), the self-oscillating regimes of concentration flows could be established in the cavity. Again against the background of slow gravitational convection, short-term peaks of the Marangoni convection were observed with an intensity exceeding the former by one order of magnitude. The experiments and numerical calculations were in rather good agreement with respect to the convective motion structure and oscillation periods.

The experimental study of the flow structure and the concentration fields near a bubble in a narrow channel [6–8] showed an interesting phenomenon of a retardation in the onset of the Marangoni flow relative to the moment of the contact between a bubble free surface and a nonuniform flow of a surfactant. This retardation could result from the formation of an initial island of a new surface phase of a surfactant, which is necessary for the development of the capillary motion.

The goal of this work was to clarify the conditions and the critical surfactant concentration gradient necessary for the development of a solutocapillary motion that, in turn, would enable us to estimate the actual role of adsorption and to formulate a theoretical model adequately describing the mass transfer of surfactants along interfaces.

**EXPERIMENTAL**

Figure 1 shows the scheme of the experimental setup. A cavity having the shape of an extended horizontal channel with a rectangular cross section 2 mm high and 1.2 mm thick located between two vertical glasses with a semitransparent mirror coating (Fig. 1a) used for visual observation was filled with working liquids (water or uniform aqueous ethanol or isopropanol solutions). Because of the small thickness of the liquid