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Oscillatory Marangoni convection around the air bubble in a vertical surfactant stratification

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Abstract

The solutocapillary Marangoni convection around a gas bubble in the inhomogeneous binary mixture of miscible fluids with a vertical surfactant concentration gradient was studied experimentally. A new phenomenon, the oscillatory instability of the surfactant mass transfer, near the bubble boundary, was detected and investigated. The interpretation of this effect as an interaction between the surfactant adsorption at the bubble free surface and solutocapillary and buoyancy convective mechanisms is proposed. The experimental data on oscillation period in relation to bubble dimensions, time, liquid layer thickness, physico-chemical fluid parameters and concentration gradients are presented and discussed. ***To cite this article: K. Kostarev et al., C. R. Mecanique 332 (2004).***
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Résumé

Convection de Marangoni oscillante autour d'une bulle d'air dans une stratification verticale surfactante. On présente les résultats d'une étude expérimentale de la convection soluto-capillaire de Marangoni autour d'une bulle d'air dans un mélange inhomogène binaire des fluides miscibles, avec un gradient vertical de concentration surfactante. On a constaté et étudié un phénomène nouveau, une instabilité oscillatoire du transfert de masse surfactant au voisinage de la paroi de la bulle. L'interprétation de cet effet est proposée en termes d'une interaction entre l'adsorption surfactante de la surface libre de la bulle et des mécanismes soluto-capillaires et stabilité convective. Les données expérimentales concernant la relation entre la période des oscillations et les dimensions de la bulle, du temps, de l'épaisseur de la couche liquide, des paramètres physico-chimiques du fluide et des gradients de concentration sont présentées et discutées. ***Pour citer cet article : K. Kostarev et al., C. R. Mecanique 332 (2004).***
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1. Introduction

The convective Marangoni motion is initiated at the liquid/gas interface due to the surface tension inhomogeneity, resulting from its dependence on temperature or (in solutions) on concentration of the dissolved surface-active (surfactant) component. This convection, whether thermocapillary or solutocapillary, is known to play an important role in technological processes involving gas inclusions in a liquid phase, especially in microgravity conditions where the gravitational mechanisms of motion are weakened. In the case where the gas bubbles are inserted in non-uniform liquid, the tangential capillary stresses arise at the bubble interface in the direction of the surface tension increase. These stresses generate an intensive convective flow in the liquid around the bubble. As a result of this flow the bubbles are able to move spontaneously in the direction of the temperature gradient (the phenomenon of thermocapillary migration [1–3]) or of the surfactant concentration gradient (solutocapillary migration [4]).

The surface tension dependence on temperature is the most common reason for its heterogeneity, and therefore it is just the thermocapillary driven Marangoni convection that has been studied intensively. Evidently, similar phenomena may arise both in thermocapillary and solutocapillary flows due to similarity of motion driving mechanisms. However, the fact that the characteristic times of heat and mass diffusion differ generally lends singularity to the character of the Marangoni convection in inhomogeneous mixtures. Moreover, in the solutocapillary case one can watch the action of some additional effects associated with dissolution of the surfactant in a liquid, its transition into a gas phase and adsorption at the interface. This results in the appearance of new phenomena that cannot occur in thermocapillary situation. Experimentally, the concentration studies present much more difficulties compared to thermal ones. Indeed, in the absence of adequate methods for measuring surfactant concentration at the interface, it is impossible to determine precisely the local values of the surface tension. This is the reason why these original solutocapillary phenomena for a long time have been remained unexplored by experiments.

2. Experimental results

In this research, we have experimentally studied the solutocapillary convective flow initiated around an air bubble inserted in a liquid mixture with a vertical concentration stratification. The schematic representation of the experimental setup is given in Fig. 1. The test cuvette represents an interferometric cell in the form of a shallow $90 \times 40 \times 2$ mm parallelepiped cavity framed by two semi-transparent mirror-plated glass walls. Visualization of the concentration distribution in the liquid layer was made by means of the Fizeau interferometer. This gave a system of isolines of the refraction index, which under isothermal conditions varied proportionally to the concentration.
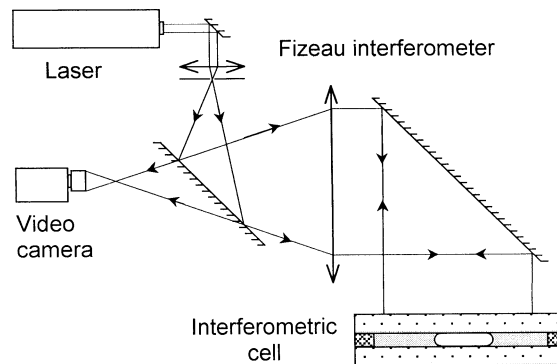

Fig. 1. Experimental setup.

In the first experiment the cuvette was set horizontally and then filled up by a two-layer system of miscible fluids in such a way that a thin layer (∼1 mm height) of a lighter liquid overlaid a heavier one. Due to the small values of the diffusion coefficient the liquids did not mix, only the 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. Note that 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. The initial horizontal concentration gradient in the liquid system was absent.

An air bubble was injected into a two-layered liquid system by a medical syringe. This bubble was pressed by the Archimedean force to the upper cell boundary and therefore stayed motionless. Small bubbles with the diameter less than the cell thickness remained spherical whereas larger bubbles took the form of a flat disk 5–15 mm in diameter squeezed between the horizontal cell walls. Due to the vertical concentration stratification the initiation of the solutocapillary Marangoni convective flow was observed around the bubble surface. A more surface-active liquid was transferred by solutocapillary forces to the opposite pole of the bubble and therefore was accumulated, respectively, in the lower (in experiments with the alcohol) or upper (in experiments with acetic acid) areas of the bubble boundary. The entrapped light or heavy liquid fractions were partly dissolved in the surrounding medium and partly carried back (correspondingly, float up or sink), generating a reverse flow. By analogy with the thermocapillary case, one could expect initiation of the ordinary monotonic convective flow in the form of symmetric vertical vortices. Instead of this flow a non-stationary convection of oscillatory character was discovered. For a time after insertion of the bubble there was neither motion in the surrounding liquid, nor any changes in the concentration field around the bubble (Fig. 2(a)). Evidently the bubble surface only accumulated the surfactant. However, after a time one could observe an abrupt distortion of the concentration isolines (Fig. 2(b)–(d)) caused by ejection of the surfactant from the bubble surface to the surrounding solution. Then this disturbance gradually dissipated (Fig. 2(e)–(f)) as the buoyancy forces restored the vertical density stratification of the mixture.
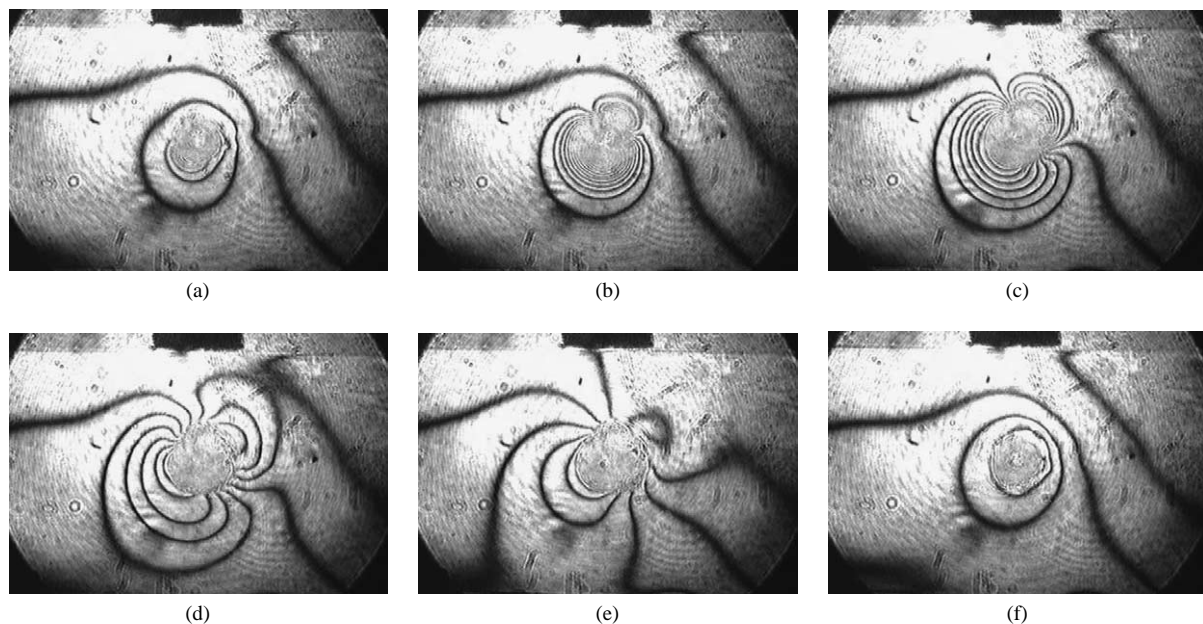

Fig. 2. Interferograms of concentration isolines: (a) $t = 0$ sec; (b) $t = 0.4$ sec; (c) $t = 0.8$ sec; (d) $t = 1.2$ sec; (e) $t = 2.0$ sec; (f) $t = 11.4$ sec.
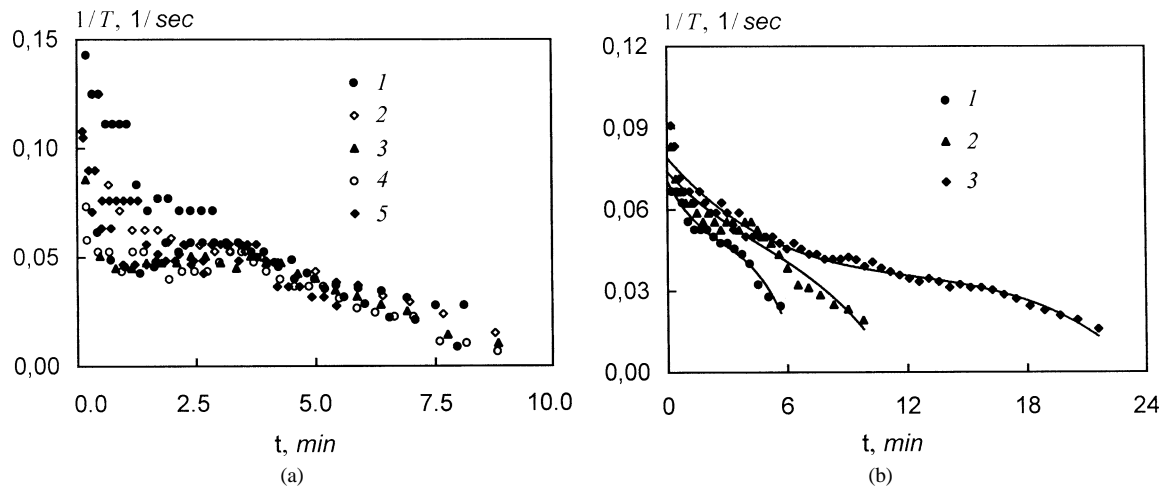
Fig. 3. Variation of oscillation period with time: (a) D: $1 - 15.0$ mm; $2 - 10.7$ mm; $3 - 7.1$ mm; $4 - 5.1$ mm; $5 - 2.4$ mm; (b) $D = 5.0$ mm. Acetic acid concentration: $1 - 20\%$; $2 - 40\%$; $3 - 70\%$.

This process repeated time and again with a fairly good periodicity and could proceed for rather a long time, at least up to the point when the whole liquid around the bubble was mixed to homogeneous medium and the concentration gradient vanished.

The period of these oscillations ranges from some seconds to tens of minutes and can strongly depend on the initial concentration gradient, time, layer thickness, horizontal diameter of the bubble and liquid parameters. Fig. 3(a) shows variation of the oscillation frequency with time in the system composed of water and 40% aqueous acetic acid solution for bubbles of various diameters. It is seen that as the solution is mixed and the vertical concentration gradient decreases, the period of oscillations being initially about 10 sec gradually increases (frequency, respectively, decreases) and 'puffs' of the bubble occur more and more seldom, until after approximately 10 min they cease. However, the graph does not reveal any essential dependence of the oscillation frequency on the bubble diameter. It only slightly decreases with diameter growth, and, besides, smaller bubbles stop 'puffing' in a shorter time. The oscillation frequency is evidently defined mainly by the layer thickness (i.e., interface vertical dimension) and by the concentration gradient. With the increase of the layer thickness the oscillation period slightly goes up, as it also does with the decrease of the initial concentration difference (Fig. 3(b)). What is really specific for the observed oscillations is that, in any case, they decay quite unexpectedly: periodic disturbances of the concentration field may last for a long time with a slowly decreasing period and then come to a sudden stop even though the essential vertical concentration gradient still persists.

To a larger extent the discovered phenomenon depends on the choice of the surfactant and its concentrations. Thus, more pronounced oscillations with fairly large periods (hundreds of seconds and more) were observed in experiments with 15–60% solutions of acetic acid. At smaller surfactant concentrations the oscillations were not recorded at all, whereas at essentially higher concentrations (more than 60%) the oscillations were so frequent that they formed an area of constant surfactant 'boiling' around the bubble. On the contrary, in tests with alcohol solutions, the concentration range, in which essential oscillations were observed, was much narrower, so that in this case 'boiling' was the main mechanism of mass transfer. Period and duration of oscillations are actually defined by the difference in surface tension values rather than by concentration difference. The dependence of the former on the concentration is of nonlinear character. Fig. 4(a) shows the frequency of oscillations versus time for a two-liquid system consisting of 40% and 70% acetic acid solutions. In the present case, due to a smaller difference in the surface tensions of solutions the transfer of the surfactant occurs much slower. Although the initial difference in the surfactant concentration is the same as in the tests with pure water and 30% solution of acetic acid (for comparison,
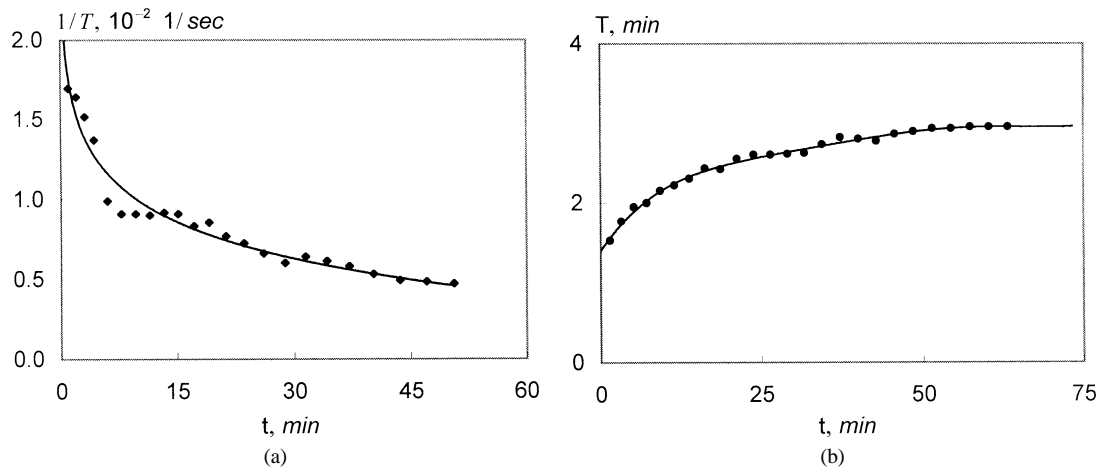
Fig. 4. Variation of oscillation period with time: (a) $D = 3.6$ mm. Acetic acid solutions 40% and 70%; (b) $D = 10.0$ mm. Isopropil alcohol solution 40%.
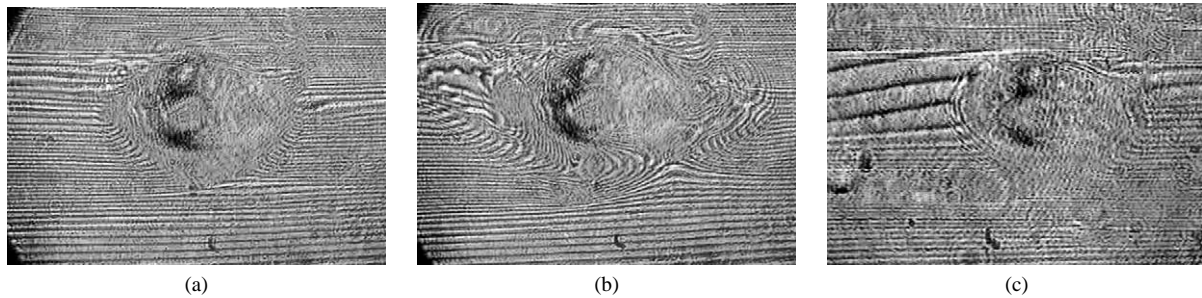

Fig. 5. Interferograms of concentration isolines: (a) $t = 10$ sec; (b) $t = 100$ sec; (c) $t = 60$ min.

see Fig. 3(b)), the period increases to several minutes and so the life-time of these oscillations does, which may last now for several hours. The above data indicate of the threshold character of the observed phenomenon, which is realized only at critical values of some parameters specified both by the problem geometry and by physical characteristics of the examined liquids – mainly surface tension, density and viscosity.

In order to make direct observations of convective flows around the bubble we made another experiment with a vertically oriented liquid layer, in which a steady vertical stratification of surfactant density was achieved by filling it successively with isopropyl alcohol solutions differing in concentration by 10%. As before, the concentration distribution was controlled by the interferometer. The air bubble in the form of a tablet placed edgewise was held motionless in the center of the cuvette with the help of a small wire frame. The frame, which was fixed over the bubble preventing its buoyancy under the action of the Archimedean force, was permeable to fluid and did not hinder mass transfer. The observed interference pattern is given in Fig. 5. Here, as in the experiments with cuvette located horizontally, an oscillatory solutocapillary Marangoni flow was detected in the vicinity of the bubble. It appeared in the form of two periodically arising vortices (Fig. 5(a)) and was caused by ejection of the surfactant from the bubble surface close to its lower pole. Being lighter than the surrounding mixture, the surfactant floated up toward the region near the upper part of the bubble. As soon as the surfactant vortices had floated up, the flow in the fluid ceased and the gravity force restored vertical stratification of the solution concentration, disturbed by surfactant ejection (Fig. 5(b)). Approximately after 90 sec the process was repeated and thus the oscillatory

motion around the bubble could proceed for many hours. Fig. 5(c) presents interference pattern observed one hour after the insertion of the bubble into the mixture. It can be seen that the examined flow has already mixed the solution in a horizontal liquid layer bounded by the bubble poles to a homogeneous state. However the liquid over and under the bubble keeps concentration gradient close to the initial one. Therefore the solution with different concentration touches the bubble poles, which results in constant presence of solutocapillary Marangoni stresses, providing necessary conditions for another round of the short-time Marangoni convection. In Fig. 4(b) the period of vortex generation is plotted as a function of time. It can be readily seen that here, unlike in the situation with a horizontal liquid layer, the period of concentration field disturbances reaches a certain value and then remains practically constant.

3. Discussion

We may suggest the following scenario for initiation of the concentration field oscillations around the bubble. The bubble surface being in contact with the solution more saturated by the surfactant actively adsorbs it. When the surfactant layer locates over the water layer, as in the tests with alcohol solutions (see Fig. 6(a)), the tangential Marangoni capillary forces initiated at the bubble surface generate a flow of the surfactant over the bubble surface towards the opposite pole of the bubble (downward), where it is gradually accumulated and forms a 'pool'. The developed situation is unstable because the surfactant is surrounded by a liquid with higher density, nevertheless the capillary forces hamper its floating by keeping it inside the bubble. However, as soon as the thickness of the accumulated surfactant layer reaches some critical value, the pressure of the liquid becomes higher than the capillary one, and the surfactant is ejected sideways into the surrounding solution. The disturbance wave excited by this ejection distorts the horizontal isolines of the concentration field, which can be seen on the interferograms. The escaped surfactant floats up due to buoyancy force, and the solution restores density stratification closely approaching the initial one. This process is repeated until the surfactant transfer over the bubble surface ceases, either because the external concentration gradient vanishes due to solution mixing, or, alternatively, the surface is saturated with the surfactant. Clearly, the slower are the surfactant transfer over the bubble surface and its accumulation, the larger are the periods of oscillation and the longer is their duration.

In the case when the surfactant layer locates under the water layer (as in the tests with acetic acid) the situation is somewhat different (Fig. 6(b)). The surfactant is also adsorbed at the surface but then slides down the internal side of the bubble interface under the action of gravity force despite counteraction of the upward-directed Marangoni forces. As a result, in the lower part of the bubble there also appears a drop of a pure surfactant still surrounded by the solution of lower density. Finally, the surfactant breaks through into the solution and spreads over the layer bottom.

(a)   (b)
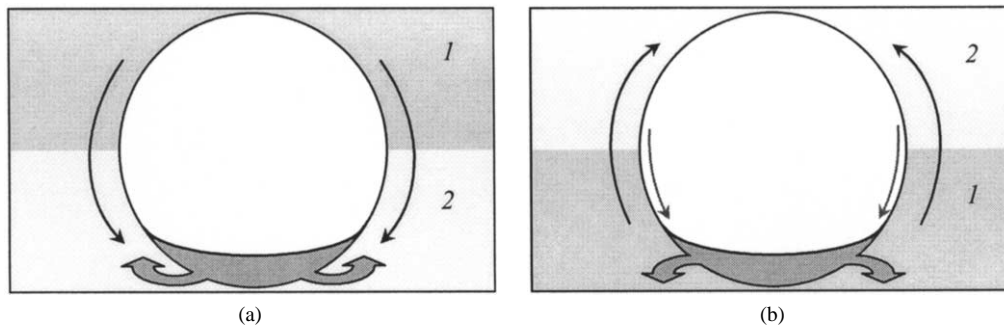
Fig. 6. Solutocapillary Marangoni convection around the air bubble in a vertical surfactant stratification: 1 – surfactant solution; 2 – water.

The proposed model of mass transfer allows us to explain the effects observed in the experiment. In the alcohol solutions the interaction of the unidirectional gravitational and Marangoni capillary forces accelerates the accumulation of the surfactant at the bottom of the bubble. In the solutions of acetic acid the Marangoni forces, on the contrary, retards the surfactant transfer thus causing an essential increase in the oscillation period. Moreover, the rising alcohol continuously mixes up the solution stratification, whereas the falling acetic acid practically does not affect the central part of the solution layer. As a result, in this case the initial surfactant stratification is retained for much longer time, and therefore the oscillations duration considerably increases. The described phenomenon is observed exclusively in the solutocapillary-caused Marangoni convection. In the case of thermocapillary convection around the bubble in vertical temperature gradient such an oscillatory instability is not initiated because of the absence of heat adsorption at the surface and also because of the small characteristic times of heat diffusion. Owing to a large value of temperature conductivity, thermal disturbance of the liquid transported over the surface rapidly dissipates and the instability does not have enough time to arise.

Acknowledgements

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