ORIGINAL ARTICLE

Instability of the Interface Due to Surfactant Diffusion in the System of Immiscible Liquids

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Abstract

The loss of stability of the horizontal interface in a two-layer system of immiscible liquids with a diffusing component was investigated experimentally. To this end, the evolution of the system, which was based on a mixture of chlorobenzene and benzene (lower layer) and water or an aqueous solution of sodium chloride (upper layer) was examined. At the beginning of the experiment, the diffusing component (acetic acid), which was a surface-active substance (surfactant), was located in the lower layer of the system. Since the initial densities of the base fluids were close to or equal to the acid density, all further density changes in the system were only the result of the contraction effect. The prepared liquids filled the vertical Hele-Shaw cell and were separated by a movable partition. The removal of the partition led to the development of the diffusion process of acid, which turned to be the reason for the loss of stability of the system provoking the deformation of the inter-phase boundary and the detachment of droplets from it. The dependences of changes in density and interfacial tension at the point of maximum deflection of the boundary on time and initial acid concentration in the lower layer were determined. For case of discontinuity of the interfacial surface a neutral curve was obtained. The analysis of the system behavior revealed a stabilizing role of the solutal Marangoni convection.

Keywords Inter-phase boundary · Taylor instability · Diffusion · Surface-active substance · Marangoni convection

Introduction

The Rayleigh-Taylor instability of a two-layer liquid system, in which the density of the upper liquid is higher than the density of the lower one, has long been a classical subject of studies in hydrodynamics (Strutt and Rayleigh 1883; Fermi and von Neumann 1953). Despite a longstanding history of research in this field, there is an increasing interest in it, especially in the field of chemohydrodynamics, covering a block of problems about the interaction between the flows and the neutralization reaction caused by its exothermicity and the appearance of the reaction product (Bratsun 2014; Bratsun et al. 2016; Mokbel et al. 2017). Here, a major focus is on

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the case, in which the reaction is caused by the diffusion of a reagent into the second reagent through their interface. If the reagent and / or the reaction product exhibit surface-active properties, then the diffusion and reaction provoke the occurrence of a capillary motion. If, in addition, this also increases the density of the upper reagent, the whole process is accompanied by the development of the Rayleigh-Taylor instability, which can be considered as a mechanism responsible for the mass transfer enhancement (Asad et al. 2010). In most cases, the instability shows itself as a periodic system of "fingers", propagating from the interface (Ying and Eckert 2007, Eckert et al. 2012) and preventing the frontal development of the reaction. There has been a number of works suggesting that the position of the inter-phase boundary and the associated reaction front should be stabilized with the use of orthogonal vibrations. The possibility of positive effect was supported by the calculations of V. Volpert made for the polymerization front and the reaction front in liquids (Allali et al. 2001; Allali et al. 2010), but was not verified experimentally. In our view, for a successful solution of this problem, first it is necessary to study the stability of the liquid system in the absence of vibrations and chemical reaction, replacing one

of the reactants with a solution of the reaction product or a salt having similar composition. Only after describing the evolution of such a system and plotting the corresponding neutral curve we can study the behavior of the system of reacting components, and proceed to the statement and consideration of the relevant vibration problem.

Experimental Procedure

The behavior of initially stable two-layer system of immiscible liquids with horizontal interface was examined experimentally. The selected system comprised a mixture of benzene and chlorobenzene (lower layer) and water or aqueous solution of sodium chloride (upper layer) (Fig. 1). The instability of the interface in this system occurs as a result of diffusion of acetic acid, initially located in the lower layer. The acid was miscible in all proportions both in the mixture and in water, also the addition of the acid resulted in lowering of the surface tension at the interface. The specific feature of the examined system is that the initial density of the mixture and the aqueous solution was close to the density of the acid. In such a system, a change in density during diffusion is caused by the effect of contraction, which is a non-additive change in the volume of the mixture as a result of a change in the intermolecular distance of its components associated with the variation of their concentration.

Let us determine the other peculiarities of the selected system. First, the effect of contraction in the system is such that the diffusion of acid leads to a local increase in the density of liquids on each side of the interface. Second, a change in the
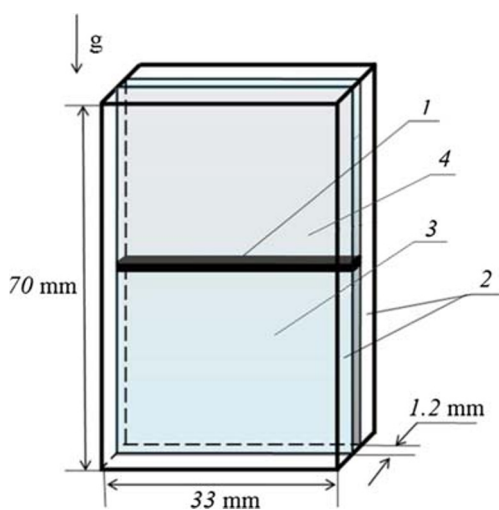
densities is of the non-proportional nature - in an aqueous solution, this change is at least an order of magnitude greater than in a benzene-based mixture (where the variation of acid concentration has practically no effect on the mixture density). Therefore the density of the upper layer increases faster than that of the lower layer, which is the reason for the development of instability. Thirdly, the diffusion of acid is accompanied by the formation of an opaque emulsion on each sides of the interface. On the one side, the emulsion droplets can be used as light-scattering particles for flow visualization, and on the other side, in the case when the concentration of the droplets becomes very high, the analysis of arising concentration fields is impossible.

In the experiment, a vertical Hele-Show cell measuring $70 \times 33 \times 1.2$ mm^3 was filled with two liquids, which before beginning of the test were separated by a horizontal partition, the removal of which led to the formation of the inter-phase boundary, through which the acid penetrated into the upper layer (Fig. 1).

The emerging concentration fields of acetic acid were visualized by a Fizeau interferometer fitted with an external resonator (Fig. 2). In the experiment, we used benzene mixtures with an initial mass concentration of acid $C_0 \leq 35\%$. In this range, the refractive index of aqueous solutions of acid monotonously changed with increase of its concentration. As a result, for the cell thickness of 1.2 mm the transition from one interference fringe to another was associated with a change in the acid concentration from 0.45% (at C ~ 0%) to 0.35% (at C ~ 30%). For acid in the benzenes mixture, a similar transition corresponded to a change in the concentration of acid by 0.14%.

It should be noted that the use of interferometry in real time allows us to study the dynamics of concentration fields, as well as to visualize the structure of the flows and to track their evolution (due to small values of the diffusion coefficient, concentration turns to be "frozen" into the bulk of moving fluid).

The experiments were performed at ambient temperature of $24 \pm 1°C$.

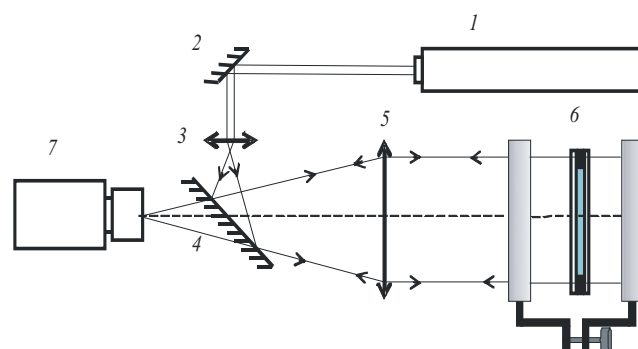Fig. 1 The scheme of the cuvette: *1* – movable partition; *2* – plane-parallel glasses contacting liquids; *3* – initial mixture of benzene, chlorobenzene and acetic acid, *4* – water or aqueous solution of sodium chloride

Fig. 2 The scheme of the experimental setup: *1* – helium-neon laser; *2* – rotating mirror; *3* – micro lens; *4* – a semitransparent mirror; *5* – lens collimator; *6* – a cuvette with external resonator; *7* – digital video camera

Results

After removal of the partition, a free-convective motion is initiated in the lower layer of the system as a result of diffusion: the mixture "depleted" by acid moves downward in the form of jets displacing the liquid with the initial concentration of acid C_0 (and initial density) toward the interface. On the contrary, the solution in the upper layer is enriched with acid, which leads to the formation of stable stratifications of density and concentration. In such a system (with free inter-phase boundary and a heavy liquid overlying a light one) any deformation of the latter can only increase, because the densest solution sinks into the resulting boundary deflection, and an increase in the acid concentration leads to a local decrease in the interfacial tension σ. Note that there are three main mechanisms that specify the shape of the examined interface: gravity, interfacial tension, and capillary convection. The effect of gravity as a deforming force is associated with the creation of density gradient directed downwards. Its influence is opposed by the interfacial tension, since the deformation of the interface leads to an increase in area of the latter and, accordingly, to an increase in its potential energy.

Furthermore, the fact that a diffusing component is a surfactant, leads to the formation of the longitudinal gradient of its concentration along the deformed interface and, consequently, the interfacial tension. The gradient of the latter causes the capillary flow from the point of the maximum deflection of the interface to the side walls of the cavity, preventing thus the interface deformation (due to the appearance of the vertical component of the motion). If the last two mechanisms are incapable of resisting the effect of gravity, then the deformation of the inter-phase boundary increases, which at large values of C_0 leads in the course of time to a break of its continuity and the formation of droplets submerging into the lower fluid layer.

There are two more factors, which are specified by the parameters and configuration of the cuvette and play a significant part in the deformation of the interface. One of them is associated with the effect of wetting the cuvette walls by the liquids of the system. Due to a small thickness of the cell, the wall menisci extend across the entire surface of the inter-phase boundary and prevent it from being deformed. Their effect on the interface can be estimated by varying the distance between the lateral walls of the cell. However, the tests showed that a two-fold increase in the distance between the walls had a negligible effect on the results, so that a further increase in the cell thickness was hampered by a growth of the emulsion concentration and the number of the interference fringes beyond the resolution threshold of the setup.

The second factor is the incompressibility of the fluid, which results in a decrease in the volume of the lower layer during surfactant diffusion. The observed decrease can be compensated by supplying the bottom layer with an additional volume of liquid with a free or solid, yet easily deformable surface. However, under vibrations such an approach leads to the occurrence of oscillatory flows (Ivanova and Kozlov 2002), which are disagreeable events in studying the stability of the interface. In the absence of compensation for the volume variation during surfactant diffusion, the interphase boundary must either additionally deform without changing the position of the line of its contact with the cell walls, or move along them as an entity (a similar phenomenon was observed in a similar situation in (Birikh et al. 2018)). Since the objective of the work is to create a database for a subsequent vibration problem, we should accept both effects with due regard of their action in the analysis of the obtained results.

The evolution of the liquid system with $C_0 = 20\%$ in such conditions is shown in Fig. 3, which presents a series of interferograms of the central part of the cell. The liquid of the upper layer is an aqueous solution of sodium chloride. It should be noted that in the majority of other tests the amount of emulsion formed in the mixture was considerably lower than in the above mention situation. Later, this made it possible to visualize the distribution of acid concentration near the interface.

As the experiment shows, three scenarios of the interface deformation can be realized depending on the initial acid concentration in the lower layer. The evolution of liquid system according the first scenario is observed at small values of C_0 ($C_0 \leq 9\%$). At such concentrations the growth of the deflection, which is similar to that shown in Fig. 3a, slows down quickly and then ceases due to: (i) a decrease in the concentration difference across the interface, (ii) an increase in the rate of acid diffusion into the upper layer liquid due to an increase in concentration at its lower boundary, (iii) an accelerated growth of the intensity of Marangoni convection that stirs the boundary layers of the solution, due to a rapid change in   in the region of small C_0.

The second scenario is realized in the range of $9 \leq C_0 \leq 18\%$. The increase in the deflection as a whole (similar to Fig. 3b) is followed by an outrunning growth of its central part (Fig. 3c), the formation of the neck (Fig. 3d) and subsequent droplet detachment. Since a drop is formed from the solution with a maximum concentration of a heavier acid, its separation is associated with the elimination of a significant part of the local excess density, which leads to a partial restoration of the original deflection configuration (Fig. 3e-3f). Third scenario takes place if only after separation of the first drop the cycle of formation and detachment of the droplet is repeated one or more times. As a rule, this effect is observed at $C_0 > 18\%$.

Each of the scenarios described above is associated with the corresponding characteristic evolution of the acid concentration in the region of maximum interface deformation which is defined as the region of the maximum displacement of the interface from its initial (horizontal) position (Fig. 4). In
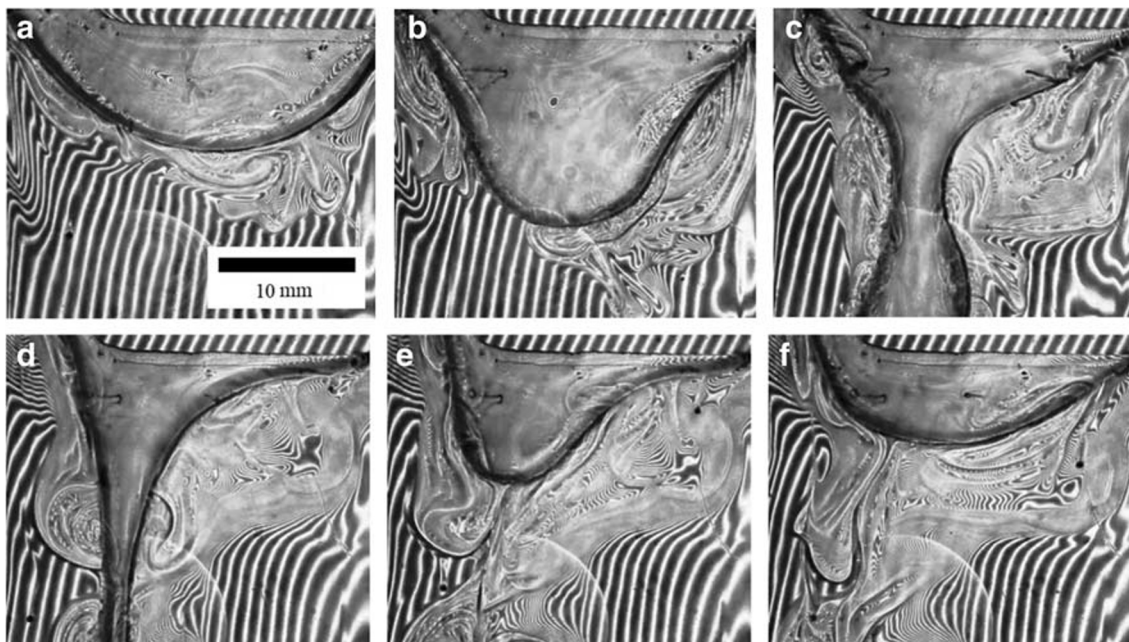
Fig. 3 Variation in the shape of the interface in the system of liquids with $C_0 = 20\%$ at different times from the beginning of experiment t, s: 5 (**a**), 270 (**b**), 330 (**c**), 360 (**d**), 415 (**e**), 440 (**f**). The liquid of the upper layer is an aqueous solution of sodium chloride with $C_{01} = 7.2\%$

particular, shaded symbols on the curves shown in Fig. 4b and Fig. 4c, correspond to the moments of detachment of the drop from the surface.

It should be noted that during the realization of third scenario (see Fig. 4c), the first of the drops is formed at the time of removal of the partition, when due to a small area of contact between the liquids and the intensive diffusion, one can observe a sharp "protrusion" of the interphase boundary into the lower layer. The arising small-scale vortex capillary motion overlaps the region of this "protrusion" and leads to the formation of a neck followed by a detachment of the drop, despite the fact that the values of the liquid density and the interfacial tension are close to the initial values.

Using the known dependences $\rho = f(C)$ (Nikolsky 1965) and $\sigma = f(C)$ (Abranzon et al. 1979), we can determine the relation between the interfacial tension and the attainable fluid

density in the region of maximum deflection of the interface at the time of droplet detachment for different fluids in the upper layer and values of C_0 in the lower layer (Fig. 5). At first sight, the obtained dependence has a paradoxical appearance, since the separation of a drop at smaller values of the interfacial tension requires the larger change of a density. The situation becomes more understandable if we recall that the Marangoni convection is a stabilizing factor of the interface equilibrium. As was mentioned above, the intensity of this type of convection is proportional to the difference in the interfacial tension between the region of maximum deflection and the near-wall zone, in which the tension remains close to the initial value for a long time.

To determine the conditions of the interface stability, we introduce the Marangoni number $\mathrm{Ma} = \frac{\Delta\sigma h}{\rho\nu D}$ and the Rayleigh number $R = g\,\Delta\rho\,h^3/\,\nu D\rho$, where g is the gravity acceleration,
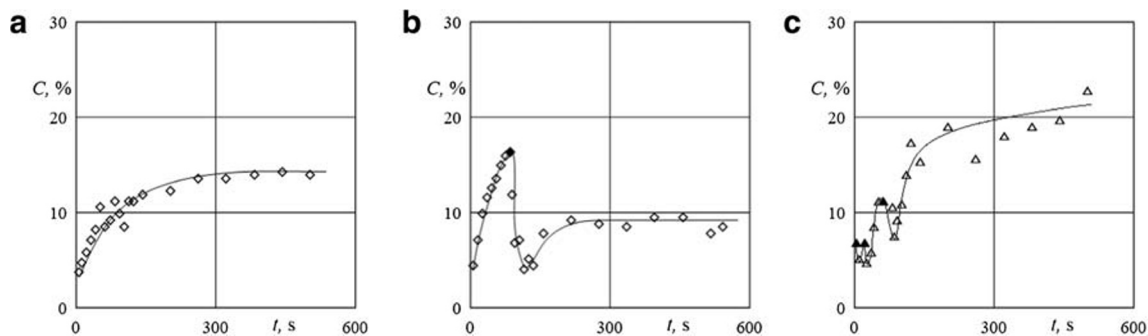

Fig. 4 Time variation of the acetic acid concentration in the region of the maximal deformation. The liquid of the upper layer is an aqueous solution of sodium chloride with $C_{01} = 7.2\%$. The initial concentration of acid in benzene mixture C_0, %: 7 (**a**), 10 (**b**), 20 (**c**)
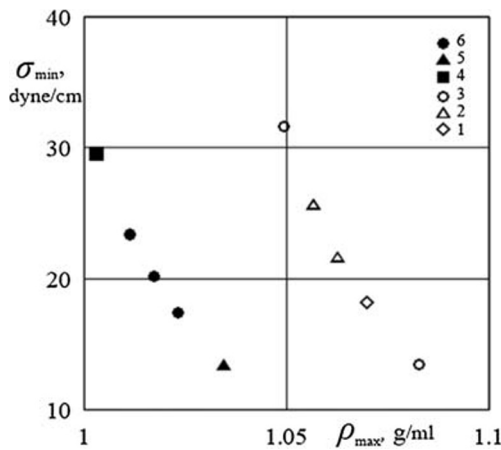
Fig. 5 The relation between the interfacial tension and the density of the acetic acid solution in the region of maximum deformation of the interface at the time of drop detachment. The upper layer is a solution of NaCl, C_0,%: 10 (1), 20 (2), 25 (3); the upper layer is distilled water, C_0,%: 15 (4), 20 (5), 25 (6)

ρ is the initial density of the upper layer fluid, $\Delta\rho$ is the increase of density in the region of maximum deflection of the interface, Δ is the interface tension difference between the region of maximum deflection of the interface and the near-wall zone where the initial values of σ is kept, a is the thickness of Hele-Show cell, h is the initial height of the upper layer of fluid, ν is its initial kinematic viscosity, D is the coefficient of the acid diffusion into upper layer fluid at C_0. Figure 6 shows the relation between Ma and R numbers at the moment of drop detachment.

A negative value of R can be attributed to the fact that the direction of the density gradient coincides with the vector of gravity. In Fig. 6 it is marked the areas of parameters at which the diffusion process either leads to the development of the interface instability or fails to do this.

It is worthy of note that the stability map of the inter-phase boundary can be constructed on the basis of the
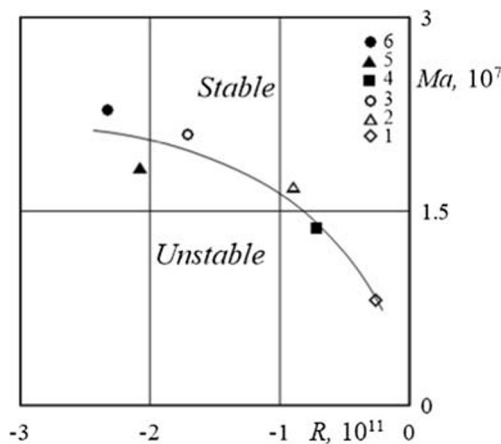

Fig. 6 The relation between the Marangoni and Rayleigh numbers at the time of drop detachment. The upper layer is a solution of NaCl, C_0,%: 10 (1), 20 (2), 25 (3); the upper layer is distilled water, C_0,%: 15 (4), 20 (5), 25 (6)

physicochemical parameters of the fluid of the upper layer only, i.e., without taking into account the characteristics of the lower layer. Apparently, this situation is a consequence of the fact that in the process of acid diffusion only the properties of the upper layer liquid change, while the properties of the lower layer fluid in the vicinity of the inter-phase boundary are maintained almost unchanged due to weak buoyancy convection. The low intensity of this convection in turn is a direct consequence of the initial leveling of the base fluid densities with respect to the density of the diffusing component and the weak contraction of the benzene mixture.

Conclusions

In summary, the experiment, which was performed using the Fizeau interferometer, made it possible to visualize the distribution of concentration of a diffusing surfactant and describe its evolutionary dynamics in the region of maximum deformation of the horizontal liquid-liquid interface. A number of relations between different physicochemical parameters of a system of liquids at the time of droplet separation were obtained. A stability map for a two-layer system was constructed using the Rayleigh and Marangoni numbers as the coordinates. It was shown that the main contribution to the integrity of the inter-phase boundary was made by the Marangoni convection, which occurs due to the surface tension difference between the region of maximum deflection and the least deformed near-wall areas of the interface. The obtained results form a database sufficient for a successful implementation of the vibration experiment on stabilization of the interface position during a chemical reaction. This experiment can be very interesting from the viewpoint of a subsequent usage of its results in space materials science, since the development of the reaction front instability is often observed under conditions of maximum suppression of the gravitational effects (Ying et al. 2007).

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