Influence of soluble surfactant on wave evolution on falling liquid films

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Abstract. We have investigated the effect of soluble surfactant Triton X-100 on the initial development of waves on vertically falling liquid films. Field method of laser induced fluorescence was used to obtain instantaneous wave patterns forming at different concentrations of the surfactant. These concentrations were chosen on the basis of simple consideration that most pronounced influence of the surfactant on the wave characteristics should be observed when relaxation time of surface tension (dependent on surfactant concentration) is comparable with characteristic time of wavy motion. At low and moderate surfactant concentrations damping of waves is observed, which coincides with the results of other authors. At large surfactant concentration the waves start to grow again, but without initial stage of two dimensional wave development typical of pure liquids. The absence of this initial stage is due to the formation of rivulets on the free surface of films in the presence of the surfactant. The influence of the surfactant concentration on characteristics of rivulets and waves is described.

1. Introduction
Falling liquid films were extensively studied by decades because of their significance in numerous technical applications. Wavy structure of falling films has a significant impact on the operational characteristics of industrial installations. At present, the wavy film flows of pure liquids are studied most fully. The effect of surfactants on the wave characteristics of liquid film flows is investigated much worse, despite the fact that the presence of surfactants is either a necessary condition of the technological process or the result of working liquid contamination.

While the effect of surfactants on the rheology and free surface behavior is actively investigated within the framework of numerous applications of colloid chemistry, the influence of surfactants on the wave hydrodynamics of relatively thick layers formed by falling liquid films is studied insufficiently due to the complexity of the coupled problem of flow hydrodynamics with a free surface and the mass transfer of surfactants. For this reason, the linear stability of film flow in the presence of surfactants in a two-dimensional formulation was mainly studied [1 - 4]. These works, in particular, showed the presence of surfactant concentration waves moving with the film speed and the suppression of the hydrodynamic wave mode compared to the flow of a pure liquid. The influence of surfactants on the wave characteristics is caused both by the dependence of the surface tension on the surfactant concentration and by the Marangoni effect, in which tangential stresses arise on the free surface of the film caused by the variability of the surface tension along the surface.
Experimental results on wave formation in dependence of surfactant concentrations are presented in a few papers, which mainly consider the initial stage of film flow in two-dimensional approach [5 - 7]. The results of these experiments are consistent qualitatively with the results of theoretical analysis. The effect of surfactants on the three-dimensional wave regimes of film flow is not described in the literature due to the complexity of experiments in three-dimensional approach. It should be noted that in the work [8], based on the analysis of photographs of the film flow of surfactants solutions, three-dimensional structural elements such as "nuclei or pockets of disturbance" and "vertical ridges" were distinguished, however, due to the poor quality of published photographs, it is not entirely clear what authors mean by these terms.

To obtain information about the three-dimensional structure of falling liquid films loaded with surfactant, we used the laser induced fluorescence (LIF) method, which is capable to obtain such information with high spatial resolution.

2. Experimental Method
A detailed description of the experimental setup and measurement method is given in [9], so we will only briefly describe them.

The experiments were carried out on a vertical transparent glass plate with dimensions of 20×30 cm at several Reynolds numbers (Re = 18, 40, and 50). Here Re = q/v, q is the specific flow rate of the liquid, and v is its kinematic viscosity. The film flow was formed by a slot distributor. Before entering the slot distributor, the fluid flow rate could be modulated with a given frequency in order to create regular waves in the initial part of the flow. The frequency range (14 - 23 Hz) was chosen because of the lack of interaction of two-dimensional waves for the case of water flow without surfactant.

The measuring of the instant film thickness distribution across the plate was carried out by the LIF method: the fluorescent dye (Rhodamine-G) was dissolved in the working fluid in the amount of 10 mg/l (2*10⁻⁵ M). The working area of the plate with dimensions of 22 cm (downstream) × 15 cm was illuminated by a pulsed laser of green light with a wavelength of 532 nm. The orange color reemitted by the fluorescent dye was recorded through an orange light filter on a digital camera (1008×1024 pixels). The brightness recorded by the camera in different parts of the image is proportional to the local thickness of the liquid film. This thickness is restored according to the algorithm described in [9]. The absence of the effect of dissolved Rhodamine-G on the wave characteristics was checked by additional experiments for several flow regimes with a sequential increase in its concentration up to 30 mg/l.

2.1. Selection of surfactant and its concentration
The choice of the surfactant working concentrations was made using scale considerations, according to which surfactant concentrations are selected based on a comparison of the characteristic time of the wave process Tw and the characteristic relaxation time of the surface tension of the liquid film. The period of regular waves excited with frequency F and the period of the capillary precursor of the waves were considered as maximal and minimal characteristic times of the wave process, so approximate time interval Tw lays between 0.1 s and 0.01 s for the conditions of our experiments. The diffusion scale Td was chosen as the characteristic relaxation time of the surface tension. As it was shown in [10], the surface tension is balanced within 1 - 10 Td even for surfactants with strong interaction in a wide range of concentrations. In accordance with [10], Td = l²/D, where D is the diffusion coefficient of surfactant and l = Γ/C, where Γ is the equilibrium surface concentration of the surfactant at its volume concentration equal to C. Then for the Langmuir adsorption isotherm Γ=Γm∙K∙C/(1+K∙C), where Γm is the maximum surface concentration of surfactant and K is the Langmuir equilibrium adsorption constant. As a result, l=ΓmK/(1+K∙C) and Td=[ΓmK/(1+K∙C)]²/D. Maximum effect of surfactant can be expected when Td ~ Tw. When Td >> Tw, the surfactant can be considered as an insoluble layer on the surface of liquid and when Td << Tw it can be expected that the waves will develop in the same way as for a pure liquid with physical properties modified by the surfactant.
In our experiments we used nonionic surfactant Triton X-100 with a molecular weight of about 625 g. The choice of the surfactant was due to the following circumstances: according to the literature data, the adsorption of this surfactant on the water surface is well described by the Langmuir isotherm and is controlled by diffusion. As a nonionic surfactant, it has a reduced sensitivity to water quality. The adsorption isotherm constants and the diffusion coefficient for Triton X-100 in aqueous solutions are widely represented in the literature. In accordance with [10], the constants necessary for calculating $T_d$ have the following values for Triton X-100: $\Gamma_m = 2.9 \cdot 10^{-6}$ mol/m$^2$, $K = 1.5 \cdot 10^3$ m$^3$/mol, $D = 2.6 \cdot 10^{-10}$ m$^2$/s. Table 1 shows the weight and molar concentrations of Triton X-100 used in the experiments, as well as the $T_d$ calculated for them.

| Table 1. Properties of used surfactant solutions. |
|-----------------------------------------------|
| C, mg/l | C, mol/m$^3$ | C, CMC | $T_d$, s |
|---------|-------------|--------|--------|
| 10      | 0.016       | 0.007  | 116    |
| 20      | 0.032       | 0.014  | 30     |
| 50      | 0.080       | 0.035  | 5      |
| 200     | 0.320       | 1.4    | 0.3    |
| 500     | 0.80        | 3.5    | 0.05   |
| 2000    | 3.20        | 13.8   | 0.003  |

The data on dynamic surface tension (DST), which are relaxation curves of surface tension versus time, are also widely presented in the literature for aqueous solutions of different concentrations of Triton X-100. Comparison of the DST data obtained in [10–14] with the calculated $T_d$ values showed that they match well and differ by no more than 2–3 times in a wide range of concentrations including those laying above critical micelle concentration (CMC). The concentrations of used Triton X-100 solutions expressed in CMC also are shown in the Table 1.

3. Results

When the fluid enters the plate from the slot distributor, its free surface is clean. As the fluid moves away from the film inlet, the surfactant diffuses and absorbs on the free surface. As a result, in the initial part of the flow, the surface tension decreases with distance from the inlet and the shear stress occurs on the free surface which retard fluid. This phenomenon is known as the Marangoni effect. In addition, due to the Marangoni effect, rivulets are formed on the film surface in the initial part of the flow. On the ridges of the rivulets, the velocity of the fluid is higher and the age of the surface is lower, and therefore the surface tension is higher than between them. As a result, in addition to the decelerating shear stress, transverse shear stresses arise, supporting the development of the rivulets. An example of the formation of rivulets is shown in figures 1 and 2.

The amplitude of the rivulets depends on the surfactant concentration and the Reynolds number of the film flow. The characteristic width of the rivulets $\lambda$ is 14–18 mm for Re = 18 and 18–22 mm for Re = 40 and 50. The dependence of the amplitude of the rivulets on the concentration for different flow rates is shown in figure 3. As it can be seen from figure 3, the amplitude of rivulets reaches a maximum at concentrations of about 200–500 mg/l and decreases with increasing film Reynolds number. Note that despite the small relative amplitude of rivulets for all studied cases (A ~ 3–8% of the film thickness), their presence leads to the destruction of two-dimensional waves in the initial part of the flow which leads to the development of three-dimensional waves, bypassing the initial evolution in the form of two-dimensional waves which is typical of the film flow of pure liquids.

As expected, the addition of surfactant stabilizes the flow in a wide range of concentrations. An example of the wave fields at different concentrations of the surfactant is shown in figure 4.

Despite the fact that at high concentrations of surfactant the waves begin to grow downstream, which corresponds to the proposed concept based on $T_d$, the formation of rivulets immediately at the film inlet due to the Marangoni effect distinguishes the flow of surfactant solution from the flow of
pure liquid. In the latter case, as was shown in [15], rivulets are formed only in the process of transition from 2D to 3D waves which occurs much further downstream the inlet.

![Figure 1. LIF images of film flow at Re = 18 and F=0 Hz. a) C =0, b) C=200 mg/l.](image1)

![Figure 2. Transverse section of film at the distance X=50 mm downstream of the film inlet. Re=18, C=200 mg/l.](image2)

![Figure 3. Dependence of the ratio of the rivulet amplitude to the mean film thickness H_m on C.](image3)
Figure 4. LIF images of the wave fields at different concentrations of the surfactant. Re = 40 and F = 19 Hz. The surfactant concentrations are: a) 0 (pure water), b) 10 mg/l, c) 20 mg/l, d) 50 mg/l, e) 200 mg/l and f) 2000 mg/l.

The maximum attenuation of excited waves at all excitation frequencies is observed when the surfactant concentrations are lying in the range between 50 mg/l and 200 mg/l. With a further increase in the concentration, the attenuation of the waves decreases slightly. At the maximum concentration used (2000 mg/l), the waves grow again, but the initial evolution in the form of two-dimensional waves is absent: the waves immediately develop as three-dimensional (3D) ones. Downstream evolution of the waves at different concentrations of the surfactant is shown in figure 5. In this figure the waveforms along a rivulet ridge are shown for the cases of 3D wave evolution.

The wave velocity drops sharply at all excitation frequencies with increasing the surfactant concentration and reaches a minimum values in the concentration region laying between 0.3 and 3 of CMC. Figure 6 shows the dependence of the ratio of the wave velocity (V) to the wave velocity for pure water (V0) on the surfactant concentration at different excitation frequencies.

We assume that the disappearance of the rivulets is possible if during the relaxation time of the surface tension the free surface of the film will move away from the film inlet by a distance much smaller than the width of the rivulets λ. In this case, the flow of the solution will be indistinguishable
from the flow of pure liquid with physical properties the same as those of water modified by added surfactant. However, this assumption requires verification.

**Figure 5.** Downstream evolution of waves at Re=40 and F=14 Hz. C is: a) 0 mg/l (pure water), b) 10 mg/l, c) 500 mg/l, d) 2000 mg/l.

**Figure 6.** Dependence of V/V0 on the surfactant concentration at Re = 40.

In conclusion, we note that the applicability of the LIF method for studying the flow of surfactant solutions requires preliminary testing for each individual surfactant.

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