Experimental study of the effect of various surfactants on the wave characteristics of the film flow

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Abstract. In this paper we present the results of experimental investigation of the effect of ionic surfactants (sodium dodecyl sulfate and cetrimonium bromide) at various concentrations on the vertical film flow in the range of Reynolds numbers $10 < \text{Re} < 50$. The laser-induced fluorescence technique was used for instant film thickness measurements. The results are compared with data obtained for non-ionic Triton X-100. For all surfactants the rivulets formation and the dumping of wave motion are observed. The difference in the action of ionic and non-ionic surfactants on wave motion is revealed. Such deviations indicate that for ionic surfactants the surface tension relaxation process (at least in the case of film flows) is not fully described by diffusion processes, but has a more complex nature.

1. Introduction

At the present, the effect of surfactants on the wave characteristics of liquid films flow is considered in a small number of works. This is primarily due to the complexity of the coupled problem of hydrodynamics of flows with a free surface and the mass transfer of surfactants. Therefore, researches are mainly limited to considering two-dimensional cases. For example, the linear stability of film flow in the presence of surfactants in a two-dimensional formulation was studied in [1–4]. In these works, it was shown that the hydrodynamic wave mode is suppressed in comparison with the flow of a pure liquid and that surfactant concentration waves move with the speed of the film. It was also shown that the influence of surfactants on the wave characteristics is due to both the dependence of the surface tension on the surfactant concentration and 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.

A few experimental works concerning surfactant concentration influence on the wave formation mainly considered 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 stabilization effect of surfactants on the wave regimes was considered in [8], where appearance of some three-dimensional structures in the initial stage of film flow was mentioned. Recent experimental study of influence of soluble surfactant on the initial development of waves on vertically falling liquid films [9] revealed formation of rivulets and appearance of three-dimensional waves in the initial part of the flow. The study [9] was limited to the initial stage of the flow only. The subsequent evolution of appeared structures and development of 3D wave regimes for film flows with different concentrations of Triton X-100 in water were studied in [10] for film Reynolds numbers (Re) up to 95. Here $\text{Re} = \frac{q}{\nu}$, where $q$ is the specific flow rate and $\nu$ is the kinematic viscosity of the working fluid. The used long test section (140 cm) and high-speed laser-induced fluorescence (LIF) technique allowed authors of [10] to reveal, at some surfactant
concentrations, the achievement of developed 3D wave regimes. It was shown that the characteristics of waves in such regimes differ from those for case of pure water. Some details of the differences between 3D waves and developed 3D wave regimes in the cases of film flow of pure water and water with surfactant was discussed in [11]. For example, an analysis of the velocity fields under 3D waves at the beginning stage of their evolution revealed a weaker flows along the capillary precursor in the case of flow of water with surfactant. It was concluded that the discrepancies in developed 3D wave regimes for water with surfactant and pure water was associated differences of the wave characteristics at the initial stage of wave evolution.

It should be noted that mentioned above recent studies of wave characteristics [9 – 11] was concerned only one non-ionic surfactant Triton X-100. Therefore, the main goal of this work is experimental investigation of the different surfactant effect on the wave characteristics at the initial stage of the film flow. Since the properties of waves immediately after the film inlet strongly affect the subsequent development of the film flow.

2. Experimental conditions and measurement technique

In the present work we used the same as in [9] experimental setup and measurement technique, so we will only briefly describe them. The experimental conditions were chosen close to those of [9] in order to simplify the comparison of the wave characteristics.

The experiments were carried out on vertical transparent glass plate with the dimensions 20 cm in transversal and 30 cm in vertical directions in the range of film flow Reynolds number 10 < \( Re < 50 \). Here \( Re = \frac{q}{\nu} \), where \( q \) is the specific flow rate and \( \nu \) is the kinematic viscosity of the working fluid. 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 \( F \) in order to create regular waves in the initial part of the flow.

The method of laser induced fluorescence (LIF) was used to measure instantaneous local film thickness \( h \) on the area of size 20 cm in transversal and 25 cm in vertical directions with spatial resolution of 0.25 mm/pix. The LIF method is based on the reconstruction of local film thickness in accordance with local light intensity emitted by a small amount of fluorescent dye dissolved in working liquid. In our experiments working liquids were doped with small amounts, about 10 – 30 mg/l, of fluorescent dye Rhodamine 6G. The prepared solutions of the dye absorb green and emit orange light. A pulsed green laser with a wavelength of 532 nm was used to illuminate the working area. The reemitted orange light of Rhodamine 6G was recorded by a low-noise CCD camera with a step filter that cut off the exciting laser light. The total error in the determination of film thickness for all investigated regimes of film flow was estimated to be not more than 5%.

The choice of the surfactant working concentrations in water (as in [9 – 11]) was made using scale considerations, according to which surfactant concentrations are selected based on a comparison of the characteristic time of the wave process \( T_w \) and the characteristic relaxation time of the surface tension of the liquid film. The period of wave repetition rate 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 \( T_w \) lays between 0.1 s and 0.01 s for the conditions of our experiments. The diffusion scale \( T_d \) was chosen as the characteristic relaxation time of the surface tension. As it was shown in [12], the surface tension is balanced within 1 – 10 \( T_d \) even for surfactants with strong interaction in a wide range of concentrations. Maximum effect of surfactant can be expected when \( T_d \sim T_w \). When \( T_d > T_w \), the surfactant can be considered as an insoluble layer on the surface of liquid and when \( T_d < T_w \) 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.
Unlike works [9–11], in presented experiments, we used aqueous solutions of ionic surfactants: anionic sodium dodecyl sulfate (SDS) and cationic cetrimonium bromide (CTAB). Surfactant concentration C in water was in the range of $10 < C < 2000$ mg/l. This corresponds to the calculated according [12] diffusion scale $T_d$ lies in the range $15 – 0.001$ sec (for more details see [9]). These data agree with presented in literature ([12–18]) data on dynamic surface tension.

As it turned out, anionic surfactants such as SDS quench the fluorescence of Rhodamine 6G. This leads to a decrease in the brightness of the recorded images, which, as a consequence, leads to an increase in the error of the film thickness measurements. Moreover, at some SDS concentrations, the quenching is so strong that recording the wave pattern is impossible even for a qualitative analysis. Some quantitative measurements can be performed with satisfactory accuracy only for some small concentrations of SDS in water. To reduce the quenching effect of SDS, a solution of NaCl in water can be used instead of pure water (for example, see figure 1). Sufficient quality (brightness) of the registered images is obtained using a 0,5M NaCl solution in water. Therefore the main quantitative results were obtained for solutions of SDS in water with addition of NaCl at the indicated concentration. It should be noted that adding of NaCl sufficiently change the properties of mixtures concerning dynamic of surface tension [18].

3. Results

For the film flow of solutions of ionic surfactants SDS and CTAB as well as for non-ionic Triton X-100, the formation of rivulets is observed for all investigated surfactant concentrations. Apparently, the formation of rivulets is the common feature of film flows of surfactant solutions. This effect is related to the Marangoni force, which occurs due to the difference in the local coefficient of surface tension. Initially, after leaving the slot distributor and forming film flow, the liquids surface is clean. As the liquid moves away from the beginning of the flow, the surfactant diffuses and is absorbed onto the free surface. So the surface tension decreases with the distance from the distributor and the shear stress occurs on the free surface which retard liquid. In addition, the perturbations of the film thickness arising because of instability of the flow increase with the formation of rivulets due to the

![Figure 1](image1.png)

**Figure 1.** LIF images $Re = 50$, $F = 14$ Hz, SDS with concentration $C = 2000$ mg/l dissolved in pure water – a) and water with NaCl – b).

![Figure 2](image2.png)

**Figure 2.** An example of rivulet formation at $Re = 14$ and SDS concentration $C = 2000$ mg/l in water with NaCl. a) LIF image. The bar at the bottom of image is 2 cm long. b) Cross section of the reconstructed from the image a) film thickness at a distance 50 mm downstream of the film inlet. A – amplitude and $\lambda$ – characteristic width of rivulets.
difference in local surface tension in the region of such inhomogeneities. So, on the crests of rivulets, the velocity of liquid 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 retarding shear stress, transverse shear stresses are generated to support the development of the rivulets. An example of the formation of rivulets is shown in figure 2.

The rivulets characteristics depend on both Re and the surfactant concentration, for each tested surfactant. In contrast of Triton X-100 the amplitudes of rivulets $A$ divided by the average film thickness $H_m$ for CTAB and SDS deviate slightly and lie mostly in the 1 – 6% range for almost all cases (see figures 3 and 4). The first exception is the case of CTAB solution flow at $Re = 10$ (points 4 in figure 3). In this case the dependency on concentration is similar to that observed for the Triton X-100: the curve have pronounced maximum value and lower values at minimal and maximal concentrations. It should be noted that, in general, rivulets are more pronounced at low Re values and, therefore, the relative amplitude is higher at low Re (compare, for example, the position of marks 1 (circles) in figures 3 and 4). Apparently, it is because the forces supplying rivulets are stronger due to the lower flow velocity.

For the case of film flow of Triton X-100, the maximum amplitudes of rivulets are observed at range of concentrations at which maximum dumping of wave motion occurs. For CTAB and SDS amplitude of rivulets cannot be reliably related with level of dumping, because for all investigated concentrations a significant attenuation of wave motion is observed. Also, the width of the rivulets for all investigated cases (including Triton X-100) is in the range of 13 – 22 mm and practically does not depend on the flow rate.

![Figure 3](image1.png)  
**Figure 3.** Rivulets amplitudes $A$ divided by the average film thickness $H_m$, depending on concentrations of CTAB in water. 1 – Re = 15, 2 – Re = 40, 3 – Re = 50, 4 – Re = 10.

![Figure 4](image2.png)  
**Figure 4.** Rivulets amplitudes divided by the average film thickness, depending on concentrations of SDS in water with added NaCl. 1 – Re = 14, 2 – Re = 40, 3 – Re = 50.
The second deviation beyond small values of rivulets amplitude is the case of a flow of SDS with concentration $200\times10^0$ mg/l in 0.5 M NaCl solution in water (figure 4). This deviation, as well as the absence of waves at high concentrations of CTAB and SDS, are unexpected, since for maximum concentrations the estimated values of characteristic relaxation time of the surface tension are small ($T_d \sim 1$ ms, which is about three time less than for Triton X-100), and one can expect behavior as for pure liquid with surface tension modified by additives, as it was observed for Triton X-100 [9 – 11] (figure 5 d)).

The difference in wave patterns for cases of SDS and Triton X-100 flows is demonstrated in figure 5 c) and d). As can be seen, in the case of SDS flow (figure 5 c)), the damping of modulated waves is observed and in the case of natural flow (without modulation) no waves are observed on the surface (figure 2 a)).

Another interesting point is the flows of SDS and Triton X-100 with $C = 500$ mg/l. When there is no wave modulation, no waves are observed on the surface and the rivulets have significantly different characteristics. But for the case of modulated waves propagation, the observed wave patterns look the same (figure 5 a) and b)), despite the fact that the estimated value of the surface tension relaxation time for SDS ($T_d \sim 9$ ms) significantly differs from that for Triton X-100 ($\sim 50$ ms).

This facts indicate that for ionic surfactants the surface tension relaxation process is not fully described by diffusion processes, but has a more complex nature.

**4. Conclusion**

The effect of ionic surfactants (SDS and CTAB) at various concentrations (in range of $10 \sim 2000$ mg/l) on the vertical film flow in the range of Reynolds numbers $10 < \text{Re} < 50$ was experimentally studied using the LIF technique. As in the case of the film flow of non-ionic Triton X-100, in the initial part of the flow the formation of rivulets is observed due to the Marangoni force caused by inhomogeneities in the local values of surface tension. The formation of rivulets at the beginning of the flow leads to the growth of 3D waves bypassing the stage of evolution in the form of 2D waves. Apparently, this effect coupled with the dumping of wave motion is an universal scenario for the evolution of the film flow of surfactant solutions.
Whereas the width of rivulets is almost independent on Re and surfactant concentrations, their amplitude correlates with the flow conditions. For example, the rivulets amplitude is higher at low Re. Apparently, it is because the forces supplying rivulets are stronger due to the lower flow velocity.

The absence of the waves on the surface for a film flow at high concentrations of CTAB and SDS is unexpected, since in these cases the estimated value of the surface tension relaxation time ($T_d \sim 1$ms) is less than the characteristic time of the wave process for all investigated Re. Moreover, at such a concentration of non-ionic Triton X-100 in water, the $T_d$ value is three times higher, and waves appear on the surface. Also the unexpected attenuation of the generated by periodic flow rate modulation waves at high concentrations of ionic surfactants is observed.

Such deviations indicate that for ionic surfactants the surface tension relaxation process is not fully described by diffusion processes (at least in the case of film flows), but has a more complex nature. And additional detailed studies are needed to reveal correct regularity.

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