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Kinetics of liquid bridges and formation of satellite droplets: Difference between micellar and bi-layer forming solutions

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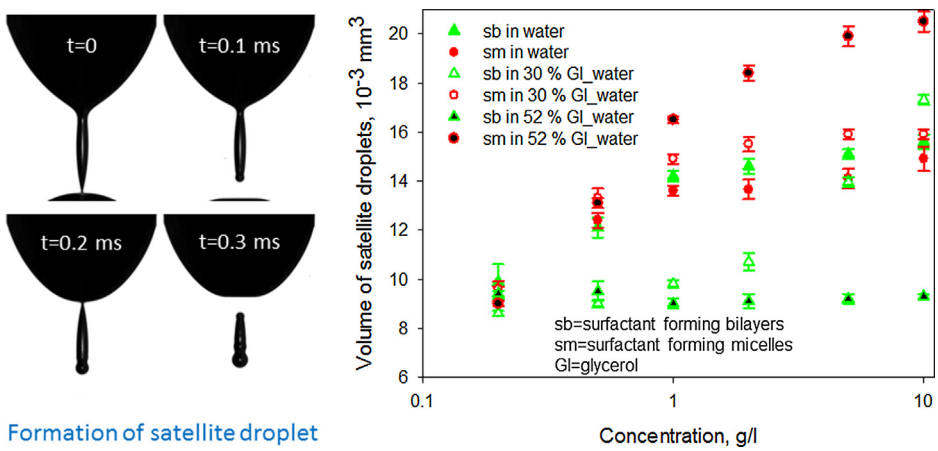
HIGHLIGHTS

- Effective surface tension can decrease as surfactant laden bridge goes to pinch-off.
- Marangoni stresses are the reason for a decrease in effective surface tension.
- A decrease in effective surface tension depends on surfactant equilibration rate.
- Size of satellite droplets increases with decrease of equilibrium surface tension.
- The concentration dependence of the size depends on surfactant equilibration rate.

GRAPHICAL ABSTRACT



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ABSTRACT

The process of drop detachment from a capillary tip and formation of satellite droplets is studied for solutions of trisiloxane surfactants above the critical aggregation concentration. Two of the studied surfactants self-assemble in bilayer based phases, whereas the third forms micelles. The difference in the aggregates formed results in an essential difference in the rate of equilibration between the surface and the bulk solution and in a different behaviour near the pinch-off point. The difference in behaviour becomes pronounced when the viscosity of solutions increases 2–6 times (and therefore diffusion coefficients decrease correspondingly). In particular, when surfactant solutions are prepared in a water/glycerol mixture with a viscosity six times larger than water, the size of satellite droplets formed by the micellar solutions increases more than twice, whereas the size of droplets formed by the bilayer-forming solutions remains almost constant over a range of concentration covering two orders of magnitude. The bilayers forming solutions demonstrate a decrease in the effective surface tension near to pinch-off which can be related to the Marangoni stresses generated by surface flow during the thinning of the capillary bridge connecting the main drop with the liquid in the capillary.

1. Introduction

Drop formation is an essential part of many industrial processes. Surfactants are generally used in these processes to keep

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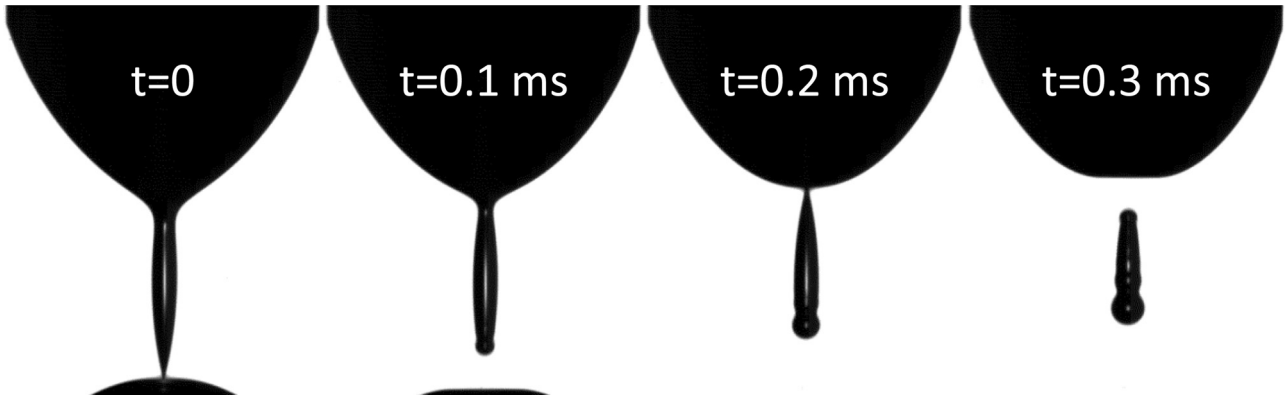

Fig. 1. Formation of a satellite droplet by detachment of a drop of aqueous solution of 10 mM sodium bromide (NaBr) + 0.5 mM hexadecyltrimethylammonium bromide (C_{16}TAB) from the capillary of outer diameter of 1.81 mm.

produced drops stable and prevent their coalescence. Thus, understanding the effect of surfactant properties on drop formation is of great practical importance. The effect of surface tension on the size of a forming drop is well studied and is employed in the drop-weight (drop volume) method of surface tension measurement [1–3]. However, the behaviour of the surfactant laden system in the vicinity of pinch-off, in particular the surfactant distribution at the interface and in the bulk, and the amount of liquid drawn into satellite drops is poorly understood. It should be noted that the formation of satellite droplets is undesirable in many cases, for example in ink-jet printing or spray-drying.

Formation of a satellite droplet is shown in Fig. 1. It is a very quick process in liquids of low viscosity with a typical time between primary (where the main drop detaches) and secondary (close to the capillary) pinch-off of several hundred microseconds. In Fig. 1 the detaching main drop is still seen in the lower part of the frames corresponding to t = 0 and t = 0.1 ms. The size of satellite droplets is determined by the hydrodynamics and the surfactant distribution in the bulk of the solution and on the surface of the liquid bridge connecting the forming drop with the remaining liquid up to the time of secondary pinch-off. It should be stressed that the hydrodynamics and the surfactant distribution strongly influence each other during this process.

The kinetics near pinch-off is determined by the excessive capillary pressure in the thinnest part of the bridge (neck), having the largest mean curvature (1/R2-1/R1) as related to the other parts of the bridge (Fig. 2). The thinning of a capillary bridge accelerates exponentially towards the moment of pinch-off (see Fig. 6 in Section 3.3.1.) because of a capillary bridge instability [4]. The instability is due to the positive feedback between the liquid flow from the neck and the excessive capillary force: a decrease in the neck radius (R2 in Fig. 2) and the corresponding increase of the capillary pressure result in further flow from the neck and a further decrease of the neck radius and increase of the excessive capillary pressure.

Addition of a surfactant reduces the surface tension and therefore surfactant laden bridges have slower kinetics when compared to the pure liquid (see Fig. 6). Excessive capillary pressure expels liquid from the neck and also generates a surface flow which sweeps the surfactant away from the neck (Fig. 2). If there is enough surfactant in the bulk and its transfer to the surface is fast, the loss of surfactant due to the surface convection is replenished quickly from the bulk and the surfactant distribution along the bridge surface is almost uniform. In this case the flow is affected only by the excessive capillary pressure which is proportional to the surface tension.

The situation is more complicated if there is not enough surfactant in the bulk to restore the value of surface tension reached before the instability onset, or the surfactant transfer is slow when

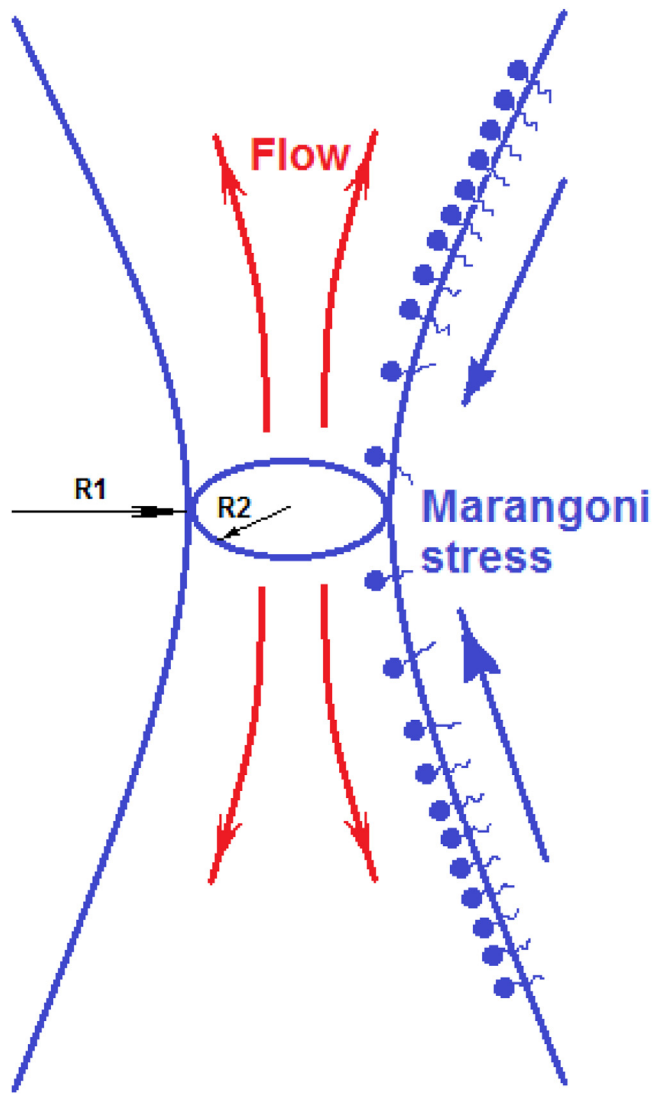

Fig. 2. Sketch of the thinning of a surfactant laden liquid bridge.

compared to its removal by convection. In these cases the surfactant distribution at the surface becomes non-uniform: the surfactant concentration is lower and the surface tension in the neck region is higher than it was before the onset of the instability. This increases the bridge thinning rate beyond that expected for the case of constant surface tension. At the same time, the gradients of surface

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concentration result in surface Marangoni stresses which counteract the liquid flow from the neck (Fig. 2). Taking into account a strong non-linearity and non-stationarity of the processes under consideration and in particular the non-linearity of the relationship between the surface concentration and the surface tension (i.e. surface tension isotherm), either the depletion of surfactant from the neck region or the surface counter flow due to Marangoni stresses can either dominate or eliminate each other.

After the primary pinch-off, the bridge recoils due to momentum conservation and a high capillary pressure at the tip (see Fig. 1) and the recoiling can result in a further surfactant redistribution affecting the secondary pinch-off and therefore the size of the satellite droplet. According to the results of numerical simulations performed under the long-wave approximation [5], Marangoni stresses can cause formation of large satellite droplets for solutions of highly active surfactants at concentrations above the critical micelle concentration (CMC).

From the above discussion, it is obvious that the size of satellite droplets bears essential information about processes close to the pinch-off point. Aside from the practical importance, these processes are of high interest from fundamental point of view even in the case of pure liquids (see Refs. [6,7] for the literature review). The presence of a surfactant makes the problem much more challenging and despite significant efforts in numerical [5,8–10] and experimental [10–13] studies it is still to be understood whether and under which conditions there is depletion of the surfactant from the neck region and how to predict and control the formation and the size of satellite droplets accompanying formation of the primary drops.

It has been shown in our recent study [14] that the effect of surfactant on the kinetics of liquid bridges and the formation of satellite droplets depends considerably on the value of critical aggregation concentration (CAC), which is the CMC when self-assembled structures formed in the bulk are micelles as it was in [14]. Surfactants with high CMC values (above 10 mM under conditions used in [14]) behave like pure liquids. For these solutions the effective surface tension (i.e. the apparent surface tension governing the bridge kinetics) remains constant during the bridge thinning and pinch-off. The size of satellite droplets increases with the increase of surfactant concentration (the decrease of surface tension) and levels off at concentrations above the CMC, when the surface tension also levels off. For surfactants of low CMC (~0.1 mM), the effective surface tension in the vicinity of pinch-off increases at concentrations below CMC, indicating the surfactant depletion from the neck region. The size of satellite droplets increases in the whole range of the concentrations studied in [14], up to 10 CMC, indicating that the surfactant redistribution takes place also above CMC.

The data presented in [14] did not allow a conclusion to be made about the character of surfactant redistribution in low solubility surfactant solutions for concentrations above CMC. However, according to [14], the effective surface tension near to pinch-off calculated from the thinning kinetics of the bridge continued to decrease with the increase of concentration, whereas equilibrium surface tension as well as dynamic surface tension measured immediately before the bridge started to thin remained nearly constant. This can be a manifestation of the depletion of the surfactant from the neck region accompanied by formation of surface tension gradients, provided that the increase in the capillary pressure due to depletion and related acceleration in thinning kinetics is overcome by Marangoni stresses, which slow the kinetics down. Such a possibility was predicted in numerical simulations [5]. The aim of this study is to prove that the observed decrease in the effective surface tension at concentrations above CMC [14], when the values of corresponding dynamic surface tension remain constant, is not an artefact, but it reflects real processes of surfactant redistribution near the pinch-off and can be observed for other surfactants of low solubility.

Another important aspect to be explored is the effect of adsorption kinetics i.e. the rate of equilibration between the surface and the bulk. In fact, moving to smaller CMC values means a slower equilibration at the same concentration normalised by CMC. It was shown in [14] that an up to twofold change in the molecular mass of low molecular mass surfactants does not affect noticeably bridge kinetics and formation of satellite droplets. In the present study, remaining in the field of low molecular mass surfactants, the effect of equilibration rate is addressed by using surfactants forming different self-assembled structures in the bulk at concentrations above CAC. Moreover, further slowing of equilibration rates was achieved by an increase of the viscosity of the solution using surfactant solutions in water/glycerol mixtures. The results are compared with aqueous solutions.

Non-ionic trisiloxane surfactants have been chosen for this study because of their low CAC values and the fact that they give very low value of equilibrium surface tension (20–24 mN/m), overcome slightly only by fluoro-surfactants. The low surface tension is important because it enables larger gradients of surface tension when compared with the surfactants used in [14] which have equilibrium surface tensions above CMC in the range of 32–37 mN/m. Despite their rather similar composition and structure as well as values of CAC and the surface tension at concentrations above CAC, two of the trisiloxane surfactants used self-assemble into bilayer based phases (vesicle, lamellae and sponge phases), whereas the third one forms micelles [15,16]. There is also an essential difference in the wetting properties of these surfactants: those forming bilayer structures are superspreaders [17,18], i.e. they demonstrate complete wetting and very quick spreading on highly hydrophobic substrates, such as polyethylene, whereas the micellar surfactant is not a superspreader. It has been shown [19] that there is an essential difference in the behaviour of superspreaders and non-superspreaders not only in spreading processes, but also in formation and stability of free standing thin liquid films, where no substrate effect is involved. Therefore, a further motivation for this work is to explore whether there is a difference between superspreading and non-superspreading surfactants in the processes of thinning of liquid bridges and formation of satellite drops, i.e. on the length scale of 10–100 μm, which is much larger than the range of films thickness considered in [19], 35–250 nm. This information will contribute to the understanding of superspreading process, in particular to the identification of the length scales at which the properties of surfactants reveal themselves.

2. Experimental

Trisiloxane surfactants were synthesized at Evonik Nutrition & Care GmbH, Germany and are the gift from this company. Dodecane (≥99%) and poly(dimethylsiloxane) (viscosity standard, 1 cSt) were purchased from Sigma-Aldrich. All substances have been used without further purification. The surfactants have a structure presented in Fig. 3, where Cap represents the capping group being either CH_3 or OH. Two surfactants include both ethylene oxide and propylene oxide groups in the hydrophilic part and Cap = OH, whereas the third one has only ethylene oxide groups and Cap = CH_3. In what follows we use a surfactant notation which shows the number of groups of each type. For example, n10m2 corresponds to a surfactant with 10 ethylene oxide and 2 propylene oxide groups. The surfactants n7.5m0 and n6m3 aggregate in bilayer structures and are superspreaders, whereas n10m2 forms micelles and is not a superspreader [16]. The properties of the surfactants are shown in Table 1.

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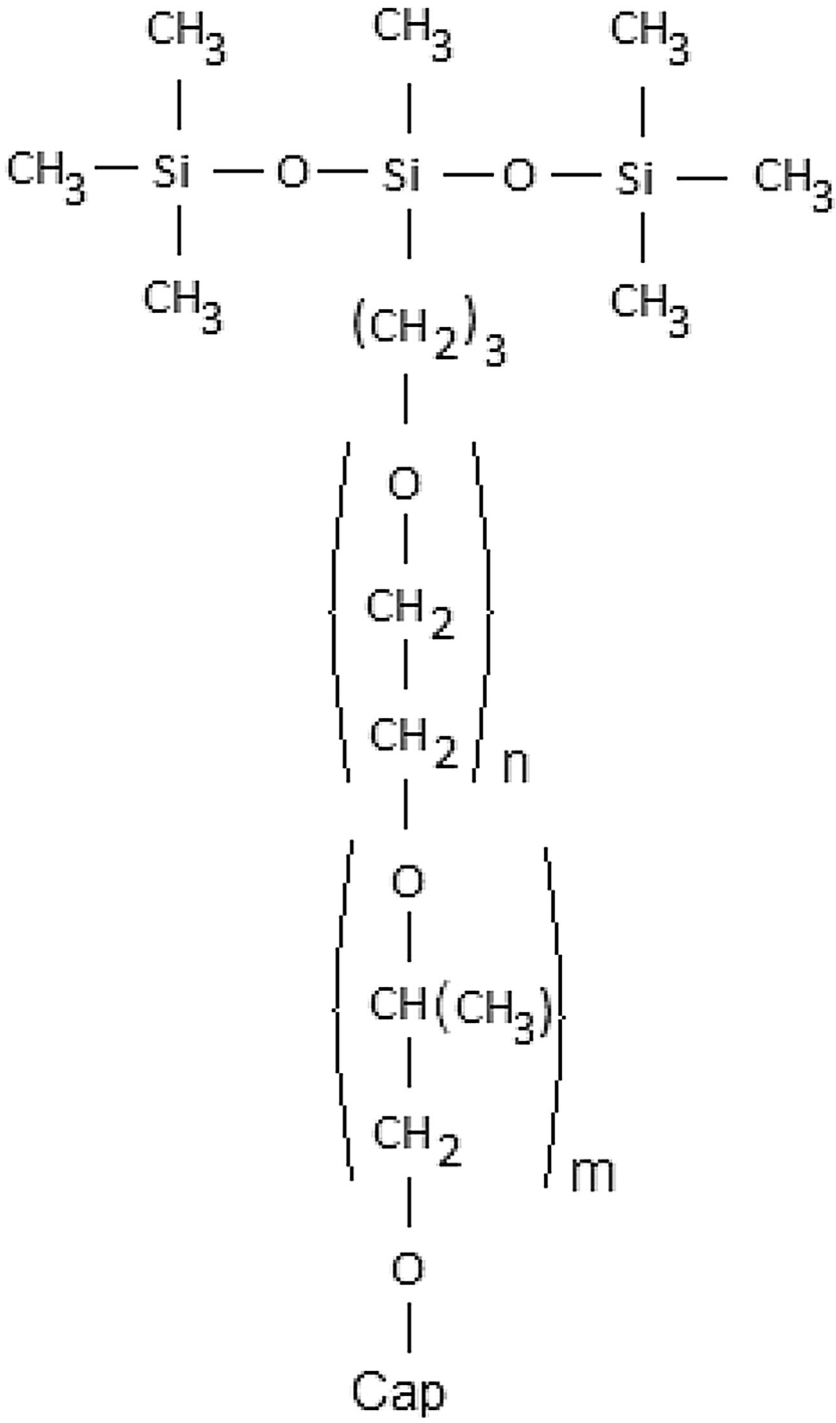


Fig. 3. The structure of trisiloxane surfactants used in the study, Cap represents the capping group being CH_3 or OH.

The values in Table 1 have been obtained from surface tension isotherms measured by a Krüss K100 tensiometer, using Wilhelmy plate. The values of surface tension above CAC have been confirmed also by measurements of dynamic surface tension performed by maximum bubble pressure tensiometer (BPA-1S, Sinterface). These data are in good agreement with the available literature [16,20].

The viscosity of solutions was controlled by addition of glycerol in concentrations of 30 and 52 wt% and measured by a TA instruments Discovery-HR-2 rheometer in flow mode using cone and plate geometry with the angle 2° 0′ 29″ and a truncation of 55 μm.

Table 1
Properties of surfactants under study in aqueous solutions.

Surfactant	n10m2	n6m3	n7.5m0
CAC, g/L (mM)	0.18 (0.21)	0.06 (0.08)	0.1 (0.16)
Surface tension above CAC, mN/m	23.6 ± 0.6	21.8 ± 0.3	20.7 ± 0.3

The surfactant solutions have been prepared in double-distilled water produced by Aquatron A 4000 D, Stuart or in its mixtures with Glycerol, ACS reagent, >99.5%, Sigma-Aldrich, which was used without additional purification. Water-glycerol mixtures have been homogenised on a roller mixer for a duration of at least 6 h. All sur-

Table 2
Properties of water-glycerol mixtures.

Glycerol content, wt%	30	52
Density, g/L	1.07	1.13
Viscosity, mPa·s	2.6	6.0

factant solutions have been homogenised on the same mixer for 30 min. Taking into account that trisiloxane solutions are prone to hydrolysis resulting in a decrease of surface activity [21], all solutions have been used within 8 h of their preparation.

The experimental procedure was the one employed and described in detail in [14]. A drop of surfactant solution was formed at the tip of a capillary with outer diameter D_{out} = 1.81 mm using a micrometre syringe outfit (AGLA, Burroughs Wellcome). As the surface of a newly formed drop is free of surfactant, the drop was left for thermodynamic pre-equilibration to allow the surfactant adsorption to the interface. Pre-equilibration time was normally 30 s, but for solutions of n7.5m0 in water the 20 s interval was also used for comparison. The time was chosen long enough to ensure equilibrium between bulk and surface for most aqueous solutions under study, but short enough for evaporation to be neglected.

The main forces acting on the drop are surface tension and gravity. The maximum possible value of the surface tension force preventing the drop from detachment under gravity is $F_\sigma = \pi D_{out} \sigma$, where D_{out} is the outer diameter of the capillary and σ is the surface tension. F_σ decreases with time during thermodynamic pre-equilibration due to surfactant adsorption. Until the weight of the drop, i.e. the gravity force acting on it, F_g, is smaller than F_σ, the drop is in the mechanical equilibrium on the capillary. The initial volume of the droplet was chosen as large as possible provided that the drop remained under mechanical equilibrium during the time of thermodynamic pre-equilibration.

After pre-equilibration a snapshot of the drop was taken to find the value of the surface tension using software from a DSA100, Krüss, tensiometer and the drop volume was increased slightly to destabilise it in mechanical sense, i.e. after this small increase in the volume the gravity force acting on the drop exceeded the surface tension force and the drop began to detach under action of the force difference ($F_g - F_\sigma$). In the initial stage of the drop detachment process, the extension of the liquid bridge connecting the falling drop to the capillary is due to gravity. After the bridge becomes thin enough the capillary force becomes dominating, governing completely the thinning process in the vicinity of pinch-off [22]. The process of neck thinning and formation of satellite droplet was recorded using a Photron SA5 high-speed video-camera at 10,000 fps.

The kinetics of the bridge thinning and the size of the satellite droplets were found by image processing using ImageJ freeware and Matlab. The presented results are the average from at least three independent measurements.

3. Results and discussion

3.1. Viscosity

Viscosities and densities of water-glycerol mixtures used in this study are given in Table 2 and are in a good agreement with the literature data [23]. Addition of surfactants up to 2 g/L does not significantly change the viscosity. Viscosity increases noticeably only for n7.5m0 at concentrations above 2 g/L (Fig. 4). The maximum increase was observed at glycerol content 30% wt shown in Fig. 4. For the 52% glycerol/water mixture (not shown in Fig. 4) and water (see Fig. 4) the increase did not exceed 50%.

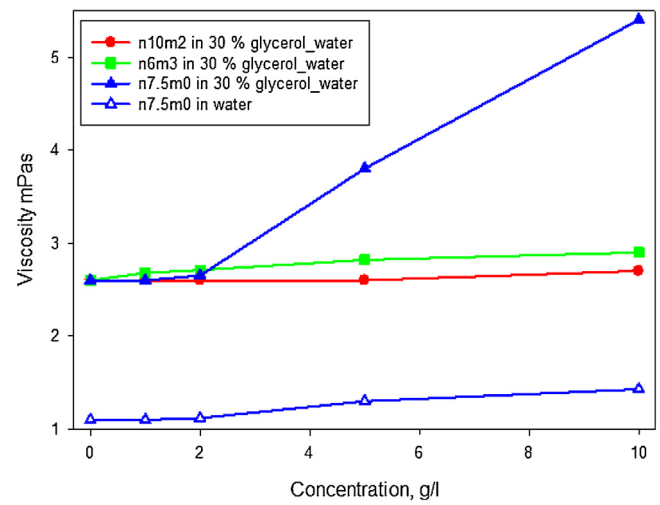


Fig. 4. Dependence of viscosity of surfactant solutions on concentration.

3.2. Dynamic surface tension

During the bridge thinning liquid flows out of it with high velocity. Thus, on the bridge surface near the neck the convective transport of surfactant exceeds considerably its replenishment by surface diffusion. Under such conditions the surfactant transfer from the bulk is the only replenishment mechanism. The bulk flow in the thinning bridge is directed along the surface. In close vicinity of the surface the solution has practically the same normal velocity component as at the surface, i.e. there is a thin boundary layer, where the normal component of the convective flux becomes negligibly small. Therefore the only mechanism of surfactant transfer from the bulk to the surface through this boundary layer is the bulk diffusion. That is why the dynamic surface tension accounting for diffusion controlled equilibration between the bulk and the surface is of great importance for this study.

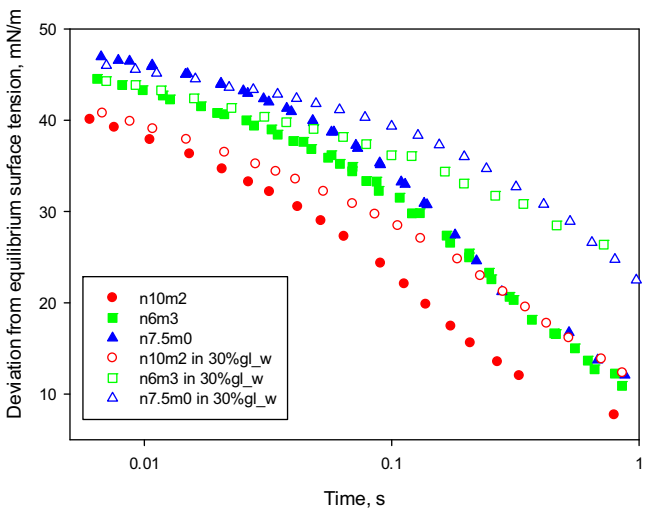
In this study, the solutions with concentrations from 0.2 to 10 g/L were used, all being above the CAC and therefore having similar values of equilibrium surface tension given in Table 1. The difference in the equilibrium surface tension between the surfactants does not exceed 3 mN/m. The results on dynamic surface tension reflecting the rate of surfactant equilibration in dynamic processes are presented in Fig. 5 for two concentrations of 0.5 and 5 g/L. It is seen that the solutions of n10m2 equilibrate much quicker than the solutions of n6m3 and n7.5m0, the last one being the slowest of all studied surfactants. The difference in the kinetics is most probably due to the difference in the size of aggregates formed in solutions at concentrations above CAC. According to [24] the average size of aggregates in aqueous solutions of a surfactant similar in composition to n7.5m0 is ~250 nm, i.e. much larger than that of micelles (normally several nm).

Addition of glycerol results in an increase of solution viscosity (Table 2) and therefore, according to the Stokes-Einstein equation

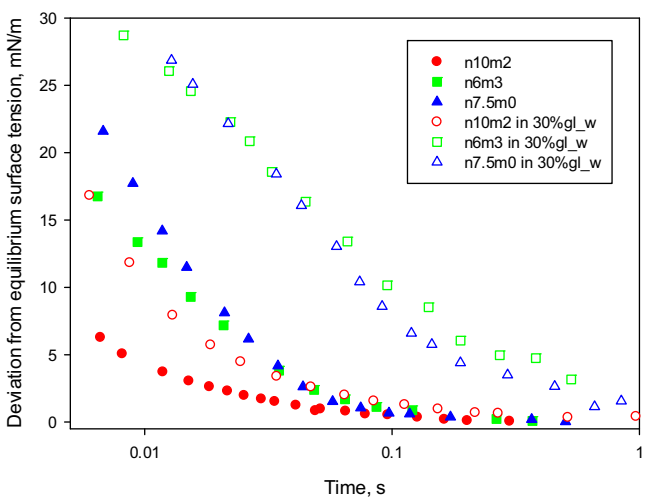
$$D_b = \frac{kT}{6\pi\mu r} \quad (1)$$

in the decrease of diffusion coefficient. In Eq. (1) D_b is the bulk diffusion coefficient, k is the Boltzmann constant, T is the temperature, μ is viscosity and r is the effective radius of the diffusing particle or molecule.

Solutions in 30% water/glycerol mixture have 2.6 times larger viscosity than aqueous solutions. It is seen from Fig. 5 that the adsorption kinetics considerably slows down for solutions of all three surfactants, but the dynamic surface tension of n10m2 solu-



(a)



(b)

Fig. 5. Comparison of dynamic surface tension of surfactant solutions in water and in 30% glycerol/water mixture: (a) – concentration c = 0.5 g/L, (b) – c = 5 g/L. The data on Y-axis are the dynamic surface tension minus equilibrium surface tension for each surfactant.

tions still equilibrate slightly quicker than two other surfactant solutions in water.

3.3. Thinning kinetics

3.3.1. Solutions in pure water

An example of thinning kinetics of a liquid bridge connecting a detaching drop with the liquid in the capillary is shown in Fig. 6. In Fig. 6 zero time corresponds to the pinch-off, and positive values on the x-axis correspond to the time remaining to the pinch-off. This example confirms that the presence of a surfactant considerably slows down the thinning kinetics and the quickest changes in the bridge diameter occur close to the pinch-off point.

In general, the kinetics in the vicinity of pinch-off depends on the capillary pressure and the forces counteracting it. For liquids with low viscosity the main counteracting force is inertia and the kinetics is described by the equation [25]

$$D \sim \left(\frac{\sigma}{\rho}\right)^{1/3} (t_0 - t)^{2/3} \quad (2)$$

where D is the neck diameter, σ is the surface tension, ρ is the liquid density, t is the time and t_0 is the time corresponding to the pinch-off moment. According to Eq. (2) $D^{3/2}$ vs $(t - t_0)$ should be a straight line in the case of inertial kinetics with the slope proportional to $\sqrt{\sigma/\rho}$. At concentrations used in this study, the solution density is independent of surfactant concentration and therefore the slope is proportional to $\sqrt{\sigma}$, where σ is the effective surface tension immediately before the pinch-off. An example of the thinning kinetics near the pinch-off is given in Fig. 7b which demonstrates a good linear fitting for $D^{3/2}$ vs $(t - t_0)$ dependence for the last several milliseconds of the thinning process. In Fig. 7a the data for 30% glycerol/water mixture are presented on the larger time scale to see more clearly the time interval of validity of Eq. (2). It is seen that the validity interval is approximately inside 2.5 ms for the 30% water/glycerol mixture without surfactant (upper curve in Fig. 7a). The same interval was observed for water. The interval of validity extends up to 4 ms for surfactant solutions. Therefore the interval of 2.5 ms was chosen for quantitative analysis to remain in the linear region for all studied compositions.

It is seen from the inset to Fig. 7a that for n6m3 solution of 10 g/L in 30% glycerol/water mixture the slope of the linear region changes close to the pinch-off demonstrating further redistribution of surfactant. Such behaviour was observed also for n7.5m0 at high concentrations even in aqueous solutions, as it can be seen from Fig. 7b. As the difference in the slopes even in the most pronounced case shown in the inset in Fig. 7a is rather small we used the general linear fit on the time interval of 2.5 ms for all studied solutions. The change in the slope near the pinch-off was reported in Ref. [12] for aqueous solutions of SDS, Silwet and Heliosol at concentrations 5 g/L. According to [12] the slope of linear fitting inside 0.6 ms from the pinch-off was larger than the slope inside the time interval 0.6–1.2 ms. This is consistent with the data presented in the inset of Fig. 7a. It should be however noted that the small deviations from the linearity on the time scale of 2.5 ms were observed also for pure liquids, water and 30% glycerol/water mixture.

It should be stressed that Eq. (2) was derived for the case of pure liquids, for which the surface tension is a constant under isothermal conditions. Therefore it does not take into account any non-uniformity of surface tension which is a typical phenomenon for surfactant solutions. The good linear fit in Fig. 7 manifests only that during the last 2–3 milliseconds of thinning the effective (apparent) surface tension, which accounts for the depletion of surfactant from the neck region and the effect of Marangoni stresses, is constant.

If there is a depletion of surfactant from the neck after the drop destabilisation, but the surfactant concentration along the neck changes very slowly (i.e. Marangoni stresses are negligible) then the excessive capillary pressure will be larger than that without the depletion (based on the dynamic surface tension before the drop destabilisation), thinning will be quicker and the effective surface tension calculated from the slopes of linear fitting presented in Fig. 7b will be higher than the dynamic surface tension before destabilisation. Such increase in the surface tension after destabilisation of the drop due to surfactant depletion was found in Ref. [14] for low solubility surfactants at concentrations below the CMC.

If, however, the local concentration gradients are high (for example, the surface tension changes over a very short length scale), the Marangoni stresses will slow down the surface velocity of liquid. There can even be the situation, when the liquid flows out of the neck under capillary pressure in the central (close to the axis) part of the bridge, whereas at the surface it flows in the opposite direction. Thus, Marangoni stresses decrease the total flow from the neck and make thinning slower than would be expected based on the value of dynamic surface tension before destabilization. The slower kinetics means a smaller slope of the lines in Fig. 7b

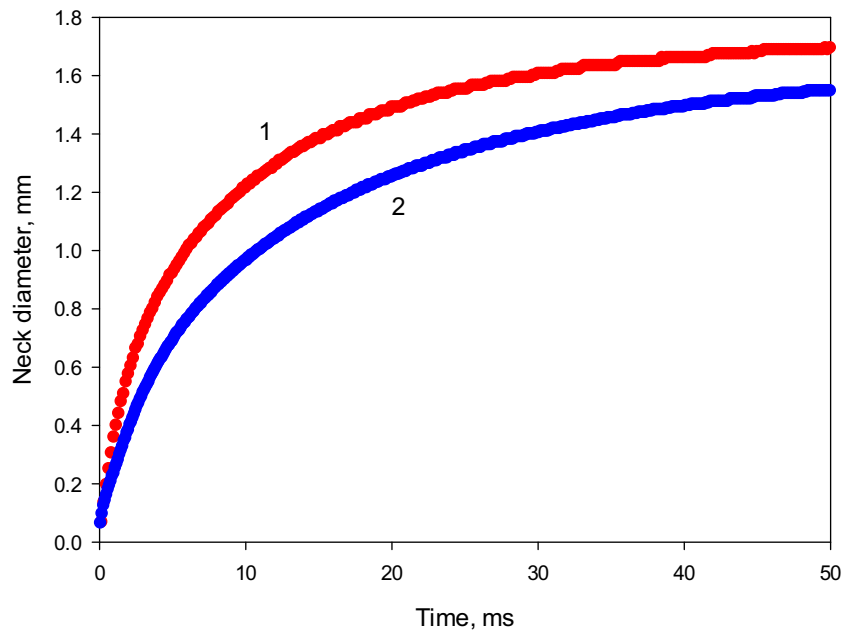


Fig. 6. Thinning kinetics of the neck of bridge: 1 – pure water, 2–0.5 g/L solution of n7.5m0 in water. The abscissa is the time remaining to pinch-off, (t_0-t) in Eq. (2).

and therefore smaller effective (apparent) surface tension. Thus, in the case of surfactant solutions the effective surface tension determined from the slope of $D^{3/2}$ vs $(t-t_0)$ lines does not always reflect the real surface tension in the neck region and should be considered only as an apparent value. This value accounts for the combined action of (possibly different) surface tensions in the various parts of the bridge, which affect the thinning kinetics. That is why, in the case of the dominating effect of Marangoni stresses, the effective surface tension can be smaller than the equilibrium surface tension at the corresponding concentration.

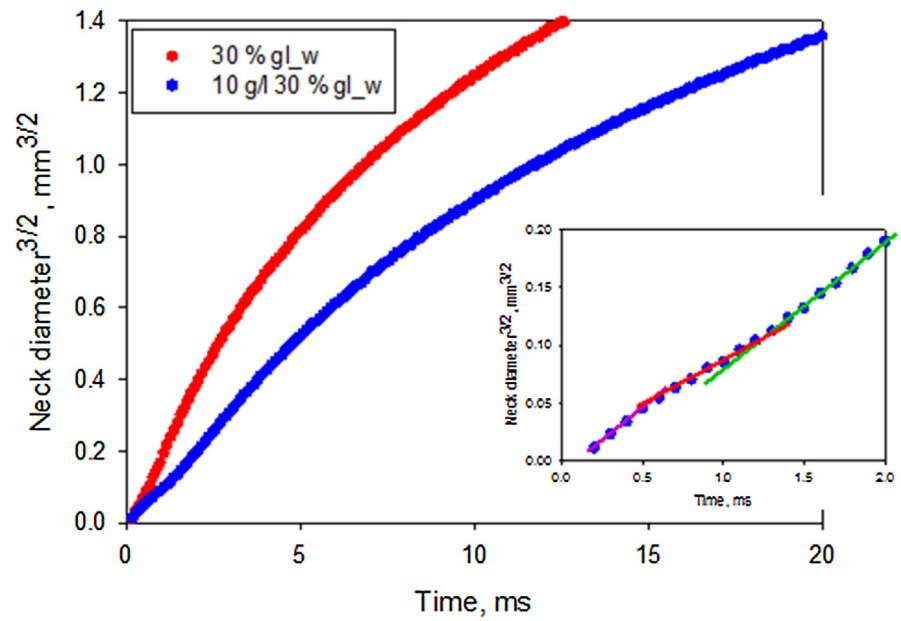
In the experiments presented in Fig. 7b, a drop of surfactant solution was pre-equilibrated during 20 s before destabilisation. From the snapshots taken immediately before destabilisation it was found that for all concentrations except 0.2 g/L the dynamic surface tension remained constant and close to the equilibrium surface tension, being 20.3 ± 0.3 mN/m. Therefore, if there is no surfactant redistribution during the instability development, the slope of lines $D^{3/2}$ vs $(t-t_0)$ should remain the same at concentrations above 0.2 g/L. However the slope demonstrates a small, but noticeable and systematic decrease with the increase in concentration from 0.5 g/L to 10 g/L confirming the surfactant redistribution leading to the change of effective surface tension at pinch-off.

Using Eq. (2) the effective surface tension at pinch-off can be calculated from the slope K_1 of dependence $D^{3/2}$ vs $(t-t_0)$ using as a reference value the slope K_2 for a pure liquid with known surface tension. Water was used as the reference liquid because it has the same density and viscosity as the surfactant solutions. In this case the effective surface tension for a surfactant solution, σ_1, can be calculated as $\sigma_1 = \sigma_2 \left(K_1/K_2\right)^2$, where σ_2 is the surface tension of water. The results of such calculations are shown in Fig. 8. It is seen from Fig. 8 that for the surfactant with the slowest kinetics, n7.5m0, the effective surface tension decreases noticeably with concentration. Such a decrease was observed for both equilibration times of 20 s and 30 s. A much weaker decrease in the effective surface tension was observed for n6m3 for concentrations up to 5 g/L. For the surfactant with fastest equilibration rate, n10m2, it appears that there is a minimum at concentration 1 g/L, but the difference between all obtained values of surface tension for this surfactant is within the range of experimental error.

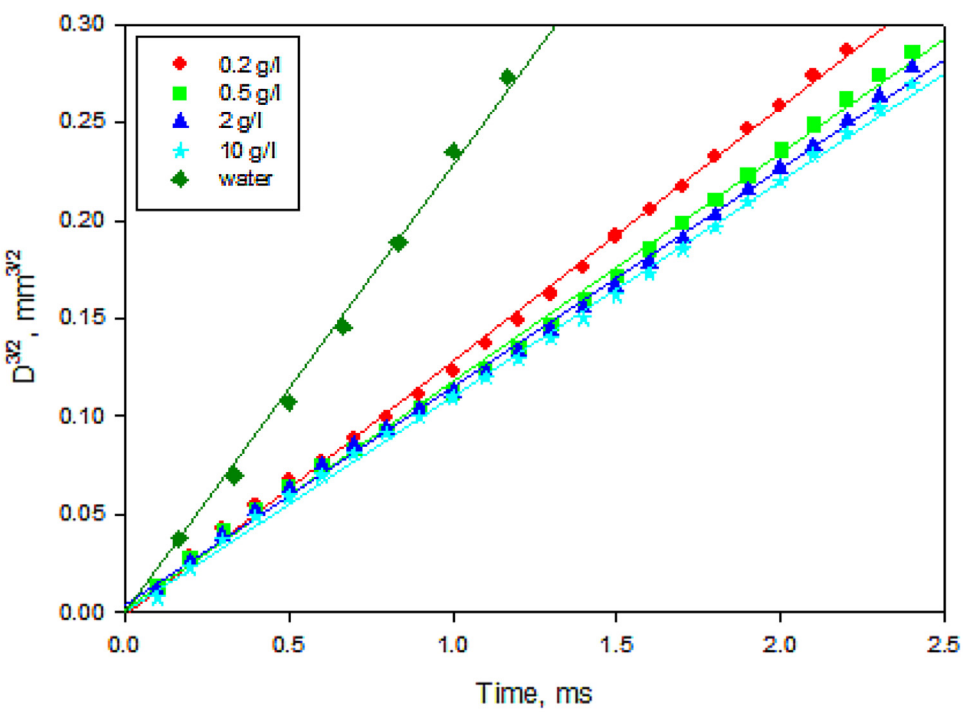
Thus, from the data for surfactant solutions in pure water it can be concluded that for the surfactant with the slowest equilibration rate there is a decrease in the effective surface tension near to pinch-off, although the surface tension before destabilisation of the drop did not change in the range of studied concentrations. The effect becomes less pronounced with the increase of equilibration rate until finally the difference between the values of effective surface tension become insignificant.

It should be stressed that the changes in the effective surface tension presented in Fig. 8 are quite surprising because intuitively one should expect a depletion of the solution in the neck and, therefore, the effective surface tension larger than the equilibrium surface tension. Or, if there is no depletion, the effective surface tension should be similar to the dynamic surface tension before the drop destabilization. As discussed above, the only possible explanation of this result is the stronger effect of the Marangoni stresses on the flow from the neck as compared with the increased capillary pressure due to depletion.

The possible mechanism is related to the non-steady character of the flow during the thinning process. Initially the neck diameter is sufficiently large, of the order of one millimeter, the excessive capillary pressure in the neck is low and therefore the surface stretching rate near the neck due to capillary pressure is also low. Note, that at this stage the effect of gravity is of the same order of magnitude as the effect of capillary pressure ($\rho gh \sim 2\sigma/D$) and therefore the stretching of the bridge as a whole due to gravity also takes place. As all solutions under consideration have concentrations above CAC and there is a considerable source of surfactant in the micelles/vesicles near the surface, most probably the surface tension remains constant during this early stage of thinning. As the neck diameter decreases the effect of gravity becomes negligible and the surface stretching moves entirely to the neck region. With time (depending on surfactant concentration) all micelles/vesicles in close vicinity of the surface are disintegrated to replenish the loss of surfactant due to the previous stretching. After this time the surface concentration at the neck begins to decrease, as time is needed for the new aggregates to come to the surface and the diffusion coefficients are small for micelles and even smaller for vesicles.



(a)



(b)

Fig. 7. Short time kinetics for: (a) – n6m3 in 30% glycerol/water mixture; (b) – n7.5m0 solutions in water (drop was pre-equilibrated during 20 s).

The gradients of surface tension appear at the interface and retard the surface flow. The retardation of the surface flow has a greater influence on the bulk flow as the neck diameter gets smaller. At the end of the thinning process the diameter of the jet squeezed from the neck becomes very small and its power becomes already not sufficient to counteract the surface tension gradients formed on the previous stage. Then the surfactant accumulated at the surface around the neck obtains the possibility to spread back to the neck. In this case also the surfactant partially desorbed in the regions around the neck due to previous local compression here can adsorb back to support the flow directed towards the neck. Such surface flows should obviously reduce the rate of the neck thinning on this stage. Also, the surface flows from the two sides should bring more surfactant to the neck, compressing the adsorption layer on it. Additionally surfactant is supplied to this region from the liquid bulk due to diffusion. Therefore it can be speculated that the surface concen-

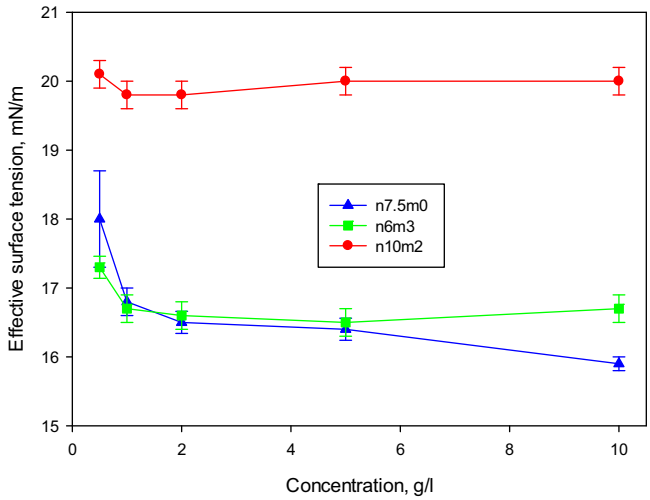


Fig. 8. Dependence of effective surface tension near pinch off for solutions in pure water as calculated from the slope of lines similar to those presented in Fig. 7b .

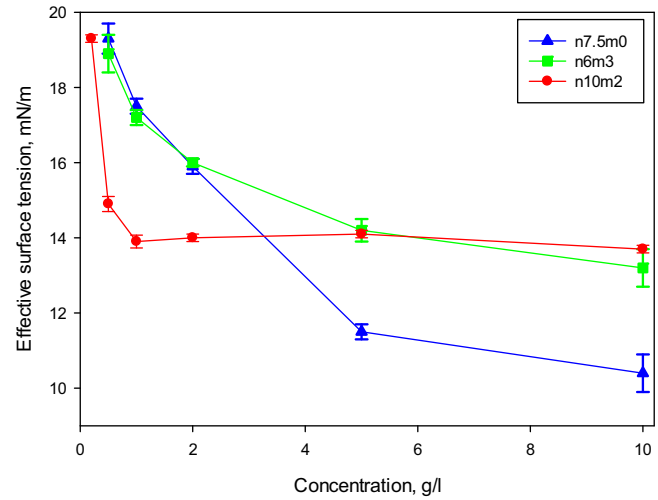


Fig. 9. Dependence of the effective surface tension near pinch off for solutions in 30% glycerol/water mixture as calculated from the slope of lines similar to those presented in Fig. 7b .

tration at the neck becomes equal or, due to flow inertia, even larger than under equilibrium condition. Due to inertia the surface flow cannot stop immediately after the surface tension gradients disappear, creating in this way an additional retardation of the bulk flow from the neck. All these effects should lead to a smaller apparent surface tension value as compared to the dynamic surface tension before the drop destabilization.

The considered here effects strongly resemble the processes causing the auto-oscillations of surface tension when a surfactant is supplied from the point source under free liquid surface [26]. In such systems the strong initial flow also produces a surface tension gradient which on the next stage becomes a source for the back flow, retaining during some time after the reverse gradient of surface tension disappears. The similar surface back flow is possible also in the considered here case of thinning of liquid bridge.

3.3.2. Solutions in water/glycerol mixture

For solutions in both water/glycerol mixtures, inertial kinetics near to pinch-off was still observed despite the higher viscosity. However, by fitting the surface tension of water/glycerol mixtures without surfactant near the pinch-off from the slope of lines similar to those presented in Fig. 7b and with water as a reference liquid, a good agreement with experimentally measured surface tension was found for the 30% glycerol-water mixture, but the calculated value for the 52% glycerol/water mixture was about 4 mN/m smaller than the experimental value. Therefore it can be assumed, that the viscosity of 6 mPa·s possessed by this mixture already slows down the kinetics slightly, affecting the value of effective surface tension. Thus this mixture was used only to follow the effect of viscosity on the size of satellite droplets, but not for quantifying the kinetics.

For solutions of n7.5m0 and n6m3 in 30% glycerol/water mixture there was only a very weak dependence of the dynamic surface tension before destabilisation on the concentration with the difference being around 1 mN/m for concentrations between 0.5 g/L and 10 g/L. The difference in the dynamic surface tension for n10m2 was within the range of the experimental error (±0.3 mN/m) over the same concentration range.

The results on the effective surface tension near pinch-off for solutions in 30% glycerol/water mixtures are presented in Fig. 9. It is clear from Fig. 9 that the decrease in the diffusion coefficient results in much larger changes in the effective surface tension with concentration. In this case, essential changes are observed not only for n7.5m0 but also for n6m3. It should be noted that for solutions of n7.5m0 at concentrations of 5 and especially 10 g/L the effect of viscosity can be partially responsible for the decrease of the effective surface tension, because the viscosity of 10 g/L solution of n7.5m0 in 30% glycerol/water mixture is 5.4 mPa s, i.e. comparable to 52% glycerol/water mixture (6 mPa s). Viscosity of 5 g/L solution of n7.5m0 in 30% glycerol/water mixture is 3.8 mPa s, which is closer to the viscosity of 30% glycerol/water mixture without surfactant (2.6 mPa s) than to that of the 52% glycerol/water mixture and thus the effect of the viscosity for this solution should be much less important.

In the graph for n10m2 on Fig. 9 an additional concentration of 0.2 g/L is also included. The surface tension before destabilisation for this concentration is around 0.6 mN/m higher than that at a concentration of 0.5 g/L, but the change in effective surface tension between 0.2 and 0.5 g/L is 4.4 mN/m displaying that in this concentration range kinetics slow down considerably, most probably due to the Marangoni stresses.

Fig. 6 displays that the fastest decrease in the bridge diameter occurs on the timescale of 10–20 ms before pinch-off. According to Fig. 4 on this time scale there is a noticeable difference in the dynamic surface tension between n7.5m0 and n6m3, especially for the smaller concentration of 0.5 g/L. This is the reason for the difference in the effective surface tension for solutions of these surfactants. The kinetics of n10m2 is much quicker, so there is no manifestation of the Marangoni stresses for this surfactant in water. Even in the 30% glycerol/water mixture, the kinetics of this surfactant on the time scale of 10–20 ms is faster than the kinetics of two other surfactants in water. Therefore, there is no essential decrease in the effective surface tension for solutions of this surfactant in 30% glycerol/water mixtures at concentrations 0.5–10 g/L.

3.4. Satellite droplets

The dependence of the size of satellite droplets on concentration is presented in Fig. 10. For the solutions in pure water (Fig. 10a) there is no essential difference between the surfactants. The size of satellite droplets increases for the whole range of concentrations for all surfactants including n7.5m0, which does not demonstrate any noticeable changes in the effective surface tension near pinch-off.

If we compare the results in Fig. 10a with those presented in [14] for surfactants of close solubility at similar concentrations (Table 3), it is seen that the size of satellite droplets on average increases with a decrease of the equilibrium surface tension.

Table 3
Dependence of sizes of satellite droplets at concentrations 10 cmc on surfactant properties.

Surfactant	C_{16}TAB in 10 mM NaBr[a]	Triton X100[a]	n10m2	n6m3	n7.5m0
CMC, mM	0.1	0.25	0.21	0.08	0.16
Surface tension at CMC, mN/m	37	32	23.6	21.8	20.7
Volume of satellite droplet at c = 10CMC, 10^{-3} mm^3	9.5	12.5	13.7	13.4	14.2

[a] Data from Ref. [14].

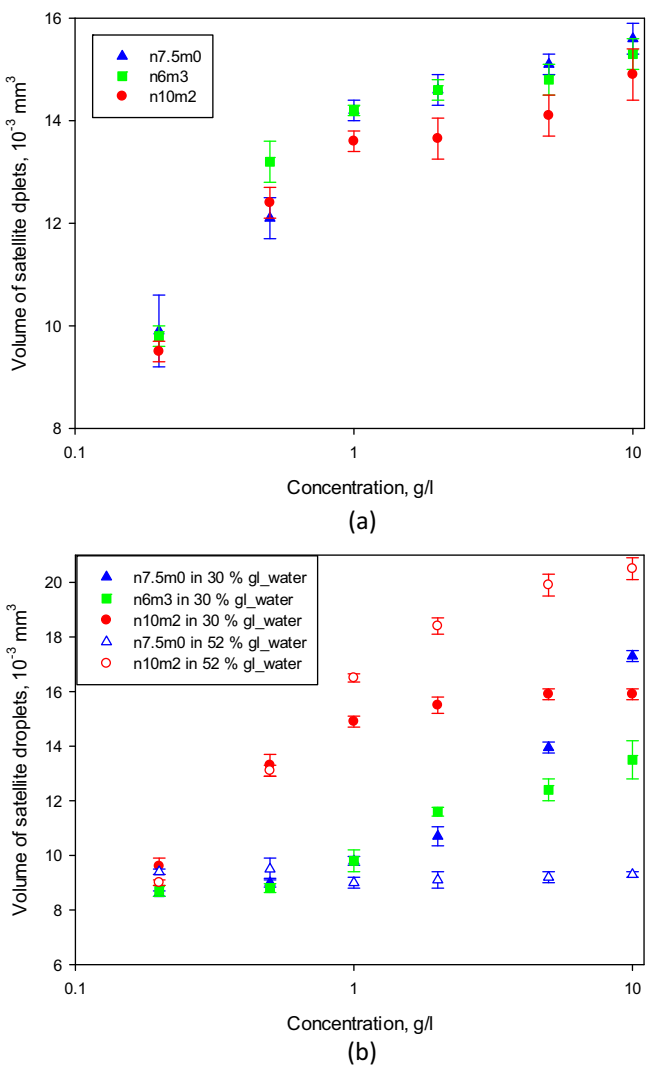


Fig. 10. Dependence of size of satellite droplets on surfactant concentration: (a) – solutions in water, (b) – solutions in glycerol/water mixtures.

For surfactants solutions in water/glycerol mixtures (Fig. 10b) there is an essential difference between micellar and bilayer-forming surfactants. Solutions of n7.5m0 and n6m3 in 30% glycerol/water mixture demonstrating a decrease in the effective surface tension near pinch-off (Fig. 9), demonstrate also a delay in the concentration at which satellites start to grow considerably. There is no such delay for micellar n10m12 solutions. At the further increase of solution viscosity and corresponding slowing down of the adsorption kinetics (the data are not shown) n7.5m0 in 52% glycerol/water mixture does not show any noticeable change in the size of satellite droplets for the whole range of concentrations studied. A small, but continuous increase in the size observed at concentrations above 1 g/L indicates that most probably the satellites size will increase for concentrations exceeding those used in this study. On the contrary, in the solutions of n10m2 in 52% glycerol/water mixture the satellite growth is observed over the whole range of studied concentrations, and the satellites are considerably larger than those in aqueous solutions.

Let us compare the size of satellite droplets presented in Fig. 10a with that formed by pure liquids of similar viscosity and surface tension. The satellite volume is about $10.7 \cdot 10^{-3}$ mm^3 for dodecane (viscosity 1.34 mPa s, surface tension 24.9 mN/m) and $14.2 \cdot 10^{-3}$ mm^3 for poly(dimethylsiloxane) (viscosity 0.82 mPa s, surface tension 17.2 mN/m), i.e. the satellite size increases with the decrease of the surface tension as it was concluded earlier for surfactant solutions. The equilibrium surface tension of surfactants solutions used in this study is 20–23 mN/m. In the absence of any dynamic effects one would expect the satellite size of about $11 \cdot 10^{-3}$ mm^3 for solutions of n10m2 and around $13 \cdot 10^{-3}$ mm^3 for solutions of n7.5m0 and n6m3. However, according to Fig. 10a for the surfactant concentration 0.2 g/L the satellite size is smaller than expected from the estimations based on pure liquids. This can be explained by a higher value of dynamic surface tension for this concentration, especially for bilayer forming surfactants. At the same time, at higher concentrations the satellite size is larger than expected (Fig. 10a). This increase in the size of satellite droplets can be explained by the effect of Marangoni stresses as follows.

The close to symmetrical shape of the liquid bridge (as related to the primary pinch off point) shown in Fig. 2 retains approximately up to 1 ms before pinch-off (see Fig. 11). After that the bridge becomes elongated towards the capillary (see Figs. 1 a and 11). The hydrodynamics during this last millisecond determine to the large extent the size of the satellite droplet. The elongated part of the bridge between primary and secondary neck contains the liquid which will later belong to the satellite drop. Because of the bridge asymmetry the pressure gradient between the (primary) neck and the adjacent parts of the bridge is much larger in the direction of the detaching drop than in the direction of capillary. Therefore the liquid is squeezed from the neck mainly into the large drop, decreasing in this way the size of a prospective satellite drop. If the reverse concentration gradient is formed from the drop side (see Section 3.3.1. for discussion) it redistributes the liquid flux in favour of elongated part of the bridge contributing in this way to the increase of the size of the satellite droplets. The similar processes occur at the secondary neck as well.

Note, the formation of the secondary neck was observed at the pinch-off (at the time resolution of this study 0.1 ms) for pure liquids used in this study, whereas it was 0.2–0.5 ms before the primary pinch-off for the surfactant solutions. The earlier formation of the secondary neck and the corresponding redistribution of the liquid fluxes can also contribute to the increase in the size of the satellite droplets formed by surfactant solutions.

This mechanism can explain also the retarded growth of the satellite droplets for small concentrations of solutions of n7.5m0 and n6m3 in 30% glycerol/water mixture presented in Fig. 10b. According to Fig. 9 the effect of Marangoni stresses is small at small concentrations for these surfactants, therefore the flow redistribution as compared with pure liquid is also small.

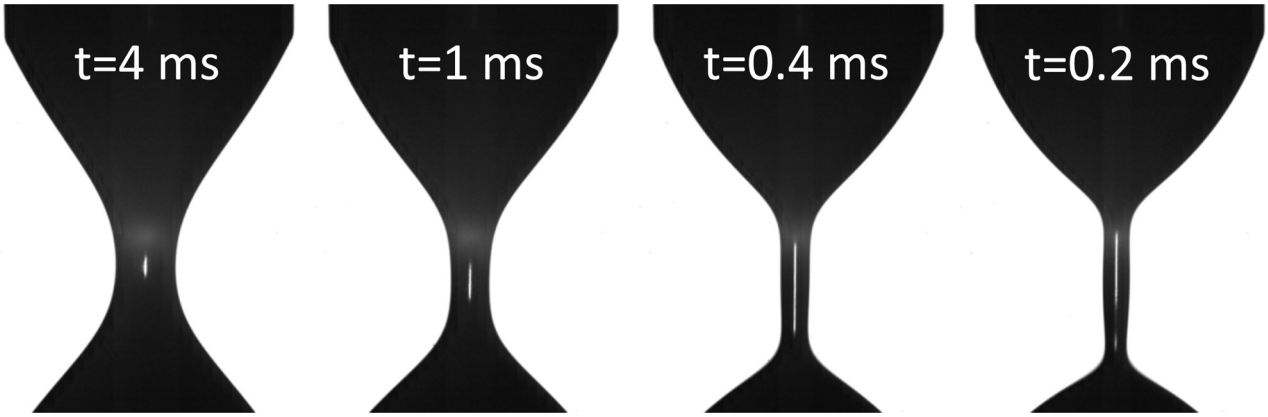


Fig. 11. Changes in the bridge shape close to pinch-off.

4. Conclusions

The performed study has shown that the effective (apparent) surface tension, obtained from the kinetics of thinning of liquid bridges connecting a newly forming drop with the remaining liquid, decreases considerably for the bilayer forming surfactants despite the dynamic surface tension before destabilisation has been kept constant. The effect is very weak for the surfactant forming micelles. The decrease in the effective surface tension becomes more pronouncing at higher viscosities, at which the surfactant equilibration rates slow down.Therefore the phenomenon can be related to the Marangoni stresses arising due to non-uniformity of the surfactant distribution around the pinch-off point.

The size of satellite droplets increases with an increase of concentration for all three surfactants in aqueous solutions. Comparison of the results of this study with the data presented in [14] shows that the size increases also with a decrease of equilibrium surface tension.

When the solutions viscosity increases and the adsorption kinetics slow down because of a decrease of diffusion coefficient, the dependence of the satellite size on concentration changes for solutions forming bilayers. The considerable increase of the size is shifted to the larger concentrations, while at smaller concentrations the size remains nearly constant. For the solutions in 52% glycerol/water mixture the size of satellite droplets remained nearly constant in the whole range of studied concentrations. The shift was not observed for micellar solutions. In this case the satellite size increased in the whole range of the studied concentrations and the maximum size of satellites was observed for solutions in 52% glycerol/water mixtures.

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