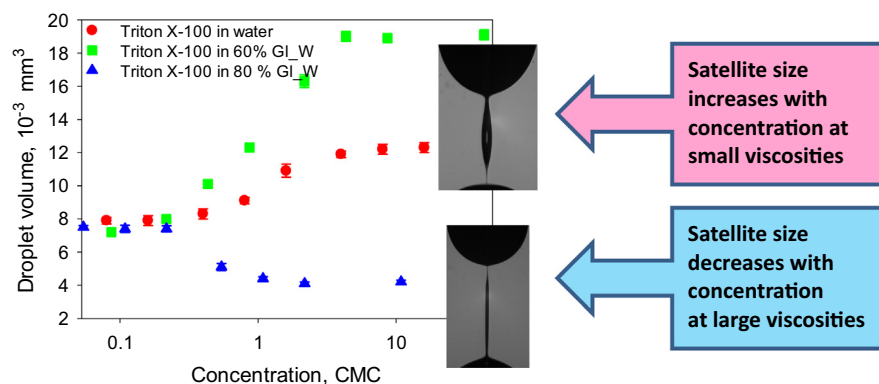Regular Article

Effect of soluble surfactants on pinch-off of moderately viscous drops and satellite size

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GRAPHICAL ABSTRACT

Satellite size increases with concentration at small viscosities

Satellite size decreases with concentration at large viscosities

ARTICLE INFO

ABSTRACT

Hypothesis: Surfactant redistribution in a liquid bridge close to drop detachment depends on competition between the bridge deformation rate and surfactant equilibration rate. Surfactant effect can be different in situations when diffusion coefficient changes independently of thinning kinetics or in line with it. Using moderately viscous liquids should allow both situations to be explored experimentally.

Experiments: Formation of liquid drops at the tip of capillary is studied experimentally for silicone oils and for surfactant-laden and surfactant-free water/glycerol mixtures of moderate viscosity with particular attention to the kinetics of liquid bridge close to pinch-off and formation of satellite droplets.

Findings: Effect of surfactant depends on the dynamic regime of the bridge thinning. In the presence of surfactant, inertial kinetics slows down close to pinch-off demonstrating effective surface tension smaller than dynamic surface tension. An acceleration of thinning kinetics caused by depletion of surfactant from the liquid bridge was observed in viscous and visco-inertial regimes. The size of satellite droplets has a maximum versus viscosity; increasing with surfactant concentration at smaller viscosities and decreasing with an increase of surfactant concentration at largest studied viscosity, where inversion of the pinch-off point was observed for surfactant solutions.

1. Introduction

Liquid drops are ubiquitous in everyday life and applications are numerous, including medicine, food, pharmaceutical, agricultural

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Nomenclature

A_I	proportionality constant in scaling law for inertial kinetics of bridge thinning, Eq. (2)	t_0	time of pinch-off
A_V	proportionality constant in scaling law for viscous kinetics of bridge thinning, Eq. (4)	μ	dynamic viscosity of liquid
		ρ	density of liquid
A_{VI}	proportionality constant in scaling law for visco-inertial kinetics of bridge thinning, Eq. (1)	σ	surface tension
		σ_0	surface tension of surfactant-free liquid
CMC	critical micelle concentration	σ_d	dynamic surface tension of surfactant solution at the time of drop destabilisation
g	acceleration due to gravity		
h_m	neck radius	σ_e	effective surface tension, i.e. surface tension found from fitting the experimental data using one of the Eqs. (1), (2) or (4)
I	inertial regime		
L_v	viscous length scale $L_v = \frac{\mu^2}{\rho\sigma}$		
Oh	Ohnesorge number $Oh = \sqrt{\frac{L_v}{R}} = \frac{\mu}{\sqrt{\rho\sigma R}}$	σ_{ef}	effective surface tension found from the fitting by Eq. (2) of experimental data for faster inertial kinetics found for surfactant solutions
R	radius of capillary		
R_d	drop radius	σ_{es}	effective surface tension found from the fitting by Eq. (2) of experimental data for slower inertial kinetics found for surfactant solutions
Re_L	local Reynolds number		
t	time		
V	viscous regime	σ_{eq}	equilibrium surface tension of surfactant solution
VI	visco-inertial regime		
v	drop volume		

and fine chemicals industries, 2-D and 3-D printing, and cooling [1–5]. For most applications, control of drop size and size distribution as well as elimination of normally undesirable satellite droplets is of great importance. Predictive control is only possible on the basis of thorough understanding of the complex physics underlying drop formation. Considerable scientific attention has been given to the processes close to the pinch-off point, where a liquid bridge connecting the forming drop to the feeding liquid breaks up [6,7]. This is a singularity point where the capillary pressure, being the driving force of bridge thinning, and the liquid velocity diverge as the radius of the neck of the bridge goes to zero.

Surfactants are used in most industrial drop formation processes as a part of formulation and/or as drop stabilisers [8,9]. Addition of surfactant lowers the interfacial tension and therefore results in a decrease of the drop size, a fact used for a long time to measure interfacial tension by the drop weight/drop volume method [10–13]. As a rule, drop formation in industrial applications is rapid, with characteristic times being in the second and even sub-second range. Adsorption and redistribution of surfactant under such highly dynamic conditions affects the drop formation process and drop size distribution. That is why understanding the surfactant dynamics during the drop formation process is of high importance.

Especially strong dynamic effects are expected in the vicinity of pinch-off, when liquid is expelled from the thinning liquid bridge at high velocity. Due to continuity the flow is transferred to the interface where it sweeps the surfactant away from the thinnest part of the bridge (neck) as shown in Fig. 1. As the velocity is directed along the bridge, the replenishment of the surfactant occurs mostly by diffusion from the bulk. Therefore, the resulting surfactant distribution is determined by the rate of the bridge thinning, availability of surfactant in the bulk phase and the surfactant diffusion coefficient. On the other hand, non-uniform surfactant distribution at the interface will result in Marangoni stresses (Fig. 1) which slow down the bridge thinning. The complicated surfactant redistribution takes place also immediately after pinch-off. The bridge recoil [14,15] can result in the local increase of the surfactant concentration and generation of Marangoni stresses accelerating or slowing down the secondary pinch-off and therefore affecting the size of the satellite drop.
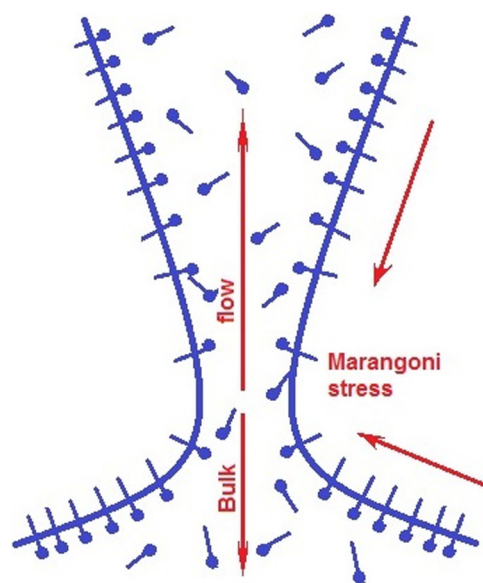

Fig. 1. Sketch of thinning liquid bridge at formation of surfactant-laden drop.

Most theoretical/numerical studies on surfactant-laden liquid bridges have been carried out using insoluble surfactants [16–18]. Although these studies do not account for surfactant exchange between the liquid bulk and the interface, many of the obtained results are of general importance, in particular predicted depletion of surfactant from the liquid bridge. It has been shown that a liquid bridge stretched between two discs which are slowly moved apart can be stabilised by Marangoni stresses caused by non-uniform surfactant distribution under conditions of high liquid viscosity and low surface diffusion coefficient [16]. Study on the break-up of viscous liquid threads covered by insoluble surfactant in the long wavelength approximation has shown that the self-similar solution for the kinetics of a surfactant-free liquid bridge close to the pinch-off is still valid [17]. The results of numerical simulations for bridges covered by an insoluble surfactant were validated by using spread monolayers of octadecanol [18].

Surfactant depletion from the liquid bridge was also found in the numerical studies on the breakup of viscous liquid threads [19] and liquid bridges [20] containing a soluble surfactant. The study presented in Ref. [19] has also shown that Marangoni stresses caused by surfactant redistribution in the thinning liquid bridge can result in the formation of very large satellite droplets. This prediction was confirmed in an experimental study [21] where the size of satellite drops increased by up to 3 times when surfactant was added. Faster than expected kinetics of bridge thinning was observed in several experimental studies [19,22–24] and explained by depletion of surfactant from the thinnest part of the bridge resulting in a local increase of capillary pressure. Conversely, slower than expected kinetics of bridge thinning were reported [21] for solutions of slowly equilibrating surfactants. This retardation was explained by the strong effect of Marangoni stresses.

Thus, analysis of available literature shows that the redistribution of surfactant affects strongly the kinetics of liquid bridges near the pinch-off and the size of satellite droplets, but it is difficult to predict the direction of this effect and relate it to surfactant properties. Obviously, the effect of surfactant redistribution should depend strongly on the rate of surfactant transfer to the interface, which is confirmed by slowing down the bridge thinning for solutions of slowly equilibrated surfactants [21]. Therefore, the aim of this study is to understand the interplay between the rate of replenishment of adsorbed surfactant (depending on surfactant concentration and diffusion coefficient) and the rate of surface deformation (depending on liquid viscosity and surface tension) and its effect on the kinetics of liquid bridges and the size of satellite droplets.

Glycerol/water mixtures of different concentrations were used as a solvent in this study, enabling variation of the surfactant diffusion coefficient. An increase of the glycerol content results in an increase of mixture viscosity [25] and a corresponding decrease of the diffusion coefficient. Considering that for small enough viscosities, the kinetics of thinning is independent of viscosity one can change the surfactant replenishment rate by keeping constant the rate of bridge thinning, i.e. the rate of surface deformation. At higher viscosities the rate of bridge thinning is inversely proportional to viscosity, i.e. it changes in line with the diffusion coefficient. The crossover between these regimes is determined by the Ohnesorge number $Oh = \frac{\mu}{\sqrt{\rho \sigma R}}$, where μ is the dynamic viscosity of liquid, ρ is the density of liquid, σ is the surface tension and R is the radius of capillary where the drop is formed. The main challenge of this approach is to distinguish between the effects of surfactant dynamics and changes in hydrodynamic regimes which occur due to changes in viscosity and surface tension of solution.

Near pinch-off, the kinetics of thinning of a liquid bridge composed by pure liquid are governed by self-similarity solutions based on the intrinsic time scale related to the material properties of the liquid [6,7]. A general solution for an incompressible Newtonian liquid surrounded by a dynamically passive fluid taking into account capillarity, viscosity and inertia was first proposed by Eggers [26] considering the motion of axisymmetric column of liquid with a free surface having constant density, viscosity and surface tension. Solution of Navier-Stokes and continuity equations with appropriate boundary conditions was obtained by expansion of pressure and velocity fields in power series on radial co-ordinate and keeping only the terms of lowest order [26]. This solution is denoted in this paper as the visco-inertial, VI, regime. The neck radius near pinch-off, h_m, in VI regime decreases linearly with time t as [26].

$$h_m = A_{VI} \frac{\sigma}{\mu} (t_0 - t) \tag{1}$$

where t_0 is the time corresponding to pinch-off and A_{VI} = 0.0304 [26]. Eq. (1) describes the neck kinetics very close to the pinch-off,

whereas at a larger time scale different solutions can be valid due to different force balances [27–29]. If the external length scale related to the problem is much larger than the viscous length scale $L_v = \frac{\mu^2}{\rho \sigma}$, then $Oh \ll 1$ and viscous forces can be neglected in comparison to inertia and capillarity. This is denoted henceforth as the inertial, I, regime. The neck evolution close to pinch-off in the inertial regime according to Keller and Miksis [30] is described as

$$h_m = A_I \left(\frac{\sigma}{\rho} \right)^{1/3} (t_0 - t)^{2/3} \tag{2}$$

with A_I being in the range 0.63–0.7 [7,29]. Eq. (2) was derived for a model of a breaking sheet of liquid initially composed by two wedges in assumption of potential flow. Transition between I (Eq. (2)) and VI (Eq. (1)) regimes occurs when the local Reynolds number, $Re_L(t)$, based on the length and velocity characteristic for thinning liquid bridge becomes of the order of unity. This gives the neck radius at transition [27–29]

$$h_{m, I \to VI} \sim L_v = \frac{\mu^2}{\rho \sigma} \sim R Oh^2 \tag{3}$$

The transition can be observed only if L_v is large enough to be detected. In particular, for water $L_v \sim 10$ nm and therefore only inertial kinetics of neck thinning can be observed on experimentally accessible length scales.

If $Oh \gg 1$ then the similarity solution neglecting inertia, corresponding to viscous regime, V, appears first. The solution for the neck kinetics in this regime was first derived by Papageorgiou [31] using asymptotic expansions similar to Ref. [26] to Stokes equation under slender jet approximation and is given as

$$h_m = A_V \frac{\sigma}{\mu} (t_0 - t) \tag{4}$$

with A_V = 0.0709 [31]. The transition from the viscous to visco-inertial regime should be observed [28,29] at

$$h_{m, V \to VI} \sim R Oh^{-40/13} \sim R \frac{(\rho \sigma R)^{20/13}}{\mu^{40/13}} \tag{5}$$

Surprisingly, despite thorough previous experimental studies on drop formation and kinetics of liquid bridges, studies on regime transitions are rather scarce and for $Oh < 1$ rather contradictory. Whereas expected for $Oh < 1$ $I \to VI$ transition was observed [32] for glycerol/water mixture at Oh = 0.163, $V \to VI$ transition was found instead at $0.1 < Oh < 1$ [22,33,34]. The values of h_m at transition found in Refs. [22,33] were much smaller than expected from either Eqs. (3) or (5) and h_m was found independent of viscosity in Ref. [34]. The complexity of transitions between regimes was further explored in Ref. [28] using both numerical and experimental studies. It was demonstrated [28] that bridge thinning at $Oh < 1$ can proceed through additional transition viscous regime through the route of I → V → VI. The low Oh viscous regime was also found in numerical simulations using multiscale finite element method [29].

The above review shows that the establishing of the exact regime limits in the range of $0.01 < Oh < 0.4$ covered by this study is not straightforward. Therefore before introducing surfactant, the experimental study for pure liquids was carried out to separate the effect of surfactant dynamics.

2. Experimental

The surfactants, dodecyltrimethylammonium bromide (C$_{12}$TAB), Across organics, 99%, hexadecyltrimethylammonium bromide (C$_{16}$TAB), Sigma, BioXtra, ≥99%, and Triton X-100, sigma-Aldrich, laboratory grade, as well as glycerol, Alfa Aesar,

ultrapure, HPLC grade and silicone oils 1 mPa s, 5, 10, 50 cSt, Aldrich were used as purchased. Double-distilled water was produced by Aquatron water still A4000D, Stuart. Glycerol/ water mixtures, (Gl_W), were homogenised on a roller mixer for at least 6 h. The same time was used for homogenisation of surfactant solutions. Surfactants were used in the range of concentrations 0.1–10 critical micellar concentration (CMC) related to solutions in pure water.

To study kinetics of a liquid bridge, first a stable drop of a surfactant solution was formed manually using a micrometre syringe outfit (AGLA, Burroughs Wellcome) on the tip of a capillary with outer radius R = 0.905 mm and was left for thermodynamic equilibration for 30 s. During this time surfactant was adsorbing at the drop surface and surface tension decreased from that of pure glycerol/water mixture to the dynamic surface tension on the corresponding time scale. The time of equilibration, 30 s, was chosen as a compromise between the desired long enough time to obtain a surface tension essentially lower than that of water/glycerol mixture without surfactant and the necessity to avoid a noticeable evaporation of water which would result in an increase of relative glycerol concentration and in the increase of viscosity, as well as in the increase of surfactant bulk concentration. The drop was illuminated by a cold light source KL5125, A. Krüss Optronic.

The (mechanical) stability of the drop is determined by the balance of gravity and surface tension force and is described by the Bond number, $Bo = \frac{\Delta \rho g R_d^2}{\sigma}$, where $\Delta \rho$ is the density difference between the liquid in the drop and ambient fluid ($\Delta \rho \sim \rho$, if the ambient fluid is air), g is the acceleration due to gravity and R_d is the drop radius. Therefore, assuming that the drop detachment occurs at the same Bo, the size of detaching drops should decrease with decreasing surface tension. The size of the drop was chosen in such a way that it remained mechanically stable after 30 s despite the decreasing surface tension, but was close enough to the stability limit after that time.

After 30 s for selected solutions a snapshot of the drop was taken using a high speed video-camera Photron SA5 equipped with Navitar, 2X F-mount objective. From this image the dynamic surface tension at t = 30 s was found using the software DSA100, Krüss. Additionally dynamic surface tension for all surfactant solutions was measured using maximum bubble pressure tensiometer BPA-1S, Sinterface and results of two methods were compared. This surface tension is called further the dynamic surface tension at the instability onset, σ_d. It depends on the surfactant studied and its value varies between that of water/glycerol mixture without surfactant, σ_0 and the equilibrium surface tension for the considered surfactant concentration, σ_{eq}, i.e. $\sigma_0 \geq \sigma_d \geq \sigma_{eq}$.

After 30 s the volume of the droplet was increased slightly until the drop became mechanically unstable and detached from the capillary. The experiments have been performed under the conditions of a close to zero flow rate, so that the kinetics of thinning is independent of the flow rate [13], i.e. independent of the Weber number, $We = \frac{\rho u^2 R}{\sigma}$ <<1, where u is the liquid velocity. The process of thinning and breakage of the liquid bridge as well as formation of the satellite droplets was recorded using the high-speed video-camera at 7000–10000 frames per second with spatial resolution up to 4 μm/pixel.

The kinetics of the bridge thinning and the size of the satellite droplets were determined by the image processing using the ImageJ free software and Matlab. Kinetics were analysed to find the transition between regimes depending on viscosity and dynamic surface tension σ_d. The presented results are the average from at least three measurements with experimental error being inside 6%.

The equilibrium surface tension was measured using the tensiometers PAT-1 Sinterface (drop shape analysis) and K100, Krüss (Du Noüy ring). Values of critical micelle concentration of surfactants in glycerol/water mixtures were found from intersection of linear part of isotherm near CMC and the line of constant surface tension above CMC (see Supporting material, S. 1 for isotherms in 60% glycerol/40% water mixture). All surfactants were used at concentrations below and above CMC.

The viscosity was measured by a TA instruments Discovery-HR-2 rheometer in flow mode using cone and plate geometry with the angle 2^O 0′ 29″ and a truncation of 55 μm. Density was measured by weighting 10 mL of liquid dosed by Eppendorf pipette.

3. Results and discussion

3.1. Materials characterisation

The values of CMC are presented in Table 1 together with values of surface tension above CMC. For all studied surfactants CMC increase with the increase of glycerol percentage in the mixtures in line with the literature [37,38]. The value of CMC for C_{16}TAB in 80% GL_W is not presented in Table 1, because of complications in measuring equilibrium surface tension for this composition. C_{16}TAB in aqueous solutions has quite high Krafft temperature, around 23 °C for solution in water [39] and according to our observations confirmed by the literature data [37,40] it increases with an increase of glycerol percentage in the mixture. To avoid crystallization, solutions of C_{16}TAB were prepared at 40–50 °C and were used afterwards in drop formation experiments. During the experiment, the solution cooled to room temperature, but because of the short timeframe of the experiment no crystallization was observed. As measurement of equilibrium surface tension takes a long time (hours), for solutions of C_{16}TAB in 80% GL_W crystallization began during these measurements and therefore it was impossible to obtain correct results.

Examples of dynamic surface tension for surfactant solutions used in this study are presented in Fig. 2 and S. 2. Comparison results for dynamic and equilibrium surface tension shows that for Triton X-100 in 60% Gl_W at concentrations below 1.25 mM, dynamic surface tension at the instability onset (t = 30 s) $\sigma_d > \sigma_{eq}$, but starting from 1.25 mM $\sigma_d = \sigma_{eq}$. For solutions C_{16}TAB and C_{12}TAB in 60% Gl_W, as well as C_{12}TAB in 52% Gl_W some solutions at concentration below CMC and all solutions above CMC are in thermodynamic equilibrium before destabilisation. Dynamic surface tension of C_{12}TAB in 80% Gl_W (S. 2) is slightly higher than equilibrium one in the whole range of the studied concentration $\sigma_d > \sigma_{eq}$. The same is true for solutions of Triton X-100 (and supposedly C_{16}TAB) in 80% Gl_W, but the difference between σ_d and σ_{eq} is larger. Note, there is a good agreement between the values of dynamic surface tension measured by maximum bubble pressure instrument and σ_d found from fitting of drop shape before destabilisation (see S. 2 for comparison).

Physical properties of liquids used in this study are given in Table 1. The data for glycerol/water mixtures are in good agreement with the literature [25]. Viscosity of surfactant-laden glycerol/water mixtures is independent of concentration of C_{16}TAB and Triton X-100 over the whole studied range. Viscosity of C_{12}TAB solutions remains constant up to concentration 75 mM and increases at higher concentrations.

The theoretical description of drop formation under gravity conditions, which does not take into account surfactant dynamics includes three dimensionless numbers: Bo, We and Oh [36]. As discussed above, the present study is performed under conditions of We ~ 0, therefore it is not considered in the following analysis. The effect of gravity can be neglected at length scales smaller than the gravitational capillary length $L_g = \sqrt{2\sigma/\rho g}$ [35], which for the liquids considered in this study is in mm range. Therefore gravity can be neglected while considering pinch-off kinetics in sub-mm

Table 1
Physical properties of studied liquids.

Liquid	Density, ρ, kg/m^3	Dynamic viscosity, μ, mPa·s	CMC, mM	Equilibrium surface tension, σ_e, mN/m	Ohnesorge number, Oh
Oh < 0.1					
Surfactant-free liquids					
52% G_W	1133	6		68.5	0.023
Silicone oil 5 cSt	920	5		19.0	0.037
60% G_W	1158	11		67.2	0.041
65% G_W	1162	16		67.0	0.060
Silicone oil 10 cSt	930	9		20.0	0.072
71% G_W	1185	25		66.8	0.093
Surfactant solutions					
52% G_W + C$_{12}$TAB	1133	6	16.0	37.0	0.031
60% G_W + C$_{12}$TAB	1158	11	17.0	37.0	0.056
60% G_W + C$_{16}$TAB	1158	11	1.8	36.5	0.056
60% G_W + TX-100	1158	11	0.6	31.5	0.061
Oh > 0.1					
Surfactant-free liquids					
80% Gl_W	1210	58		65.3	0.217
83% Gl_W	1213	78		65.2	0.292
85% Gl_W	1223	103		65.0	0.384
Silicone oil 50 cSt	960	48		21.0	0.355
Surfactant solutions					
80% Gl_W + C$_{12}$TAB	1210	58	30.0	37.0	0.288
80% Gl_W + C$_{16}$TAB	1210	58		36.0	0.292
80% Gl_W + TX-100	1210	58	2.3	32.1	0.309
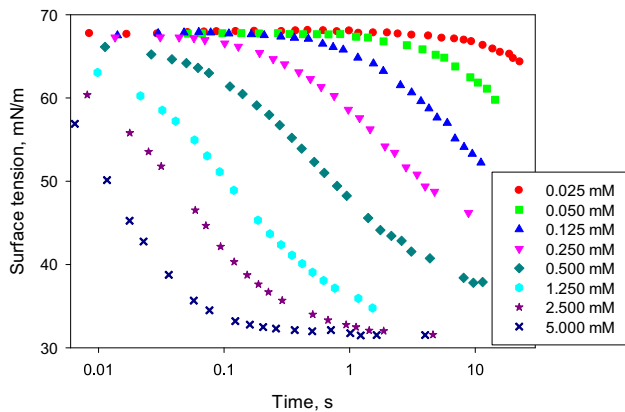
Fig. 2. Dynamic surface tension of Triton X-100 in 60% Gl_W.
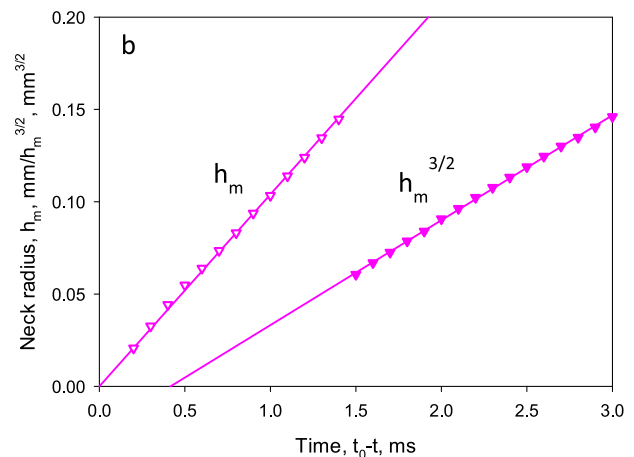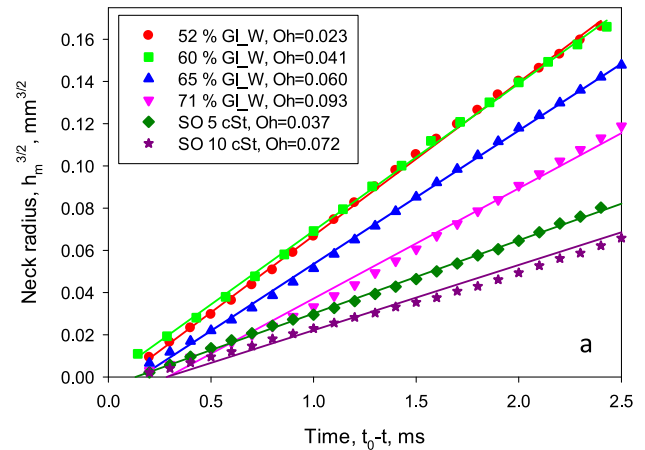
Fig. 3. Short time kinetics of the neck thinning for surfactant-free liquids with 0.02 < Oh < 0.1: a – fitting according to the inertial kinetics; b – regime transition for the mixture of 71% glycerol and 29% of water: filled symbols correspond to inertial kinetics with $h_m^{3/2} \sim t$, empty symbols correspond to viscous kinetics with $h_m \sim t$.

range. The only dimensionless number which is relevant to the kinetics of liquid bridges (if surfactant dynamics is excluded) is the Ohnesorge number, Oh. Therefore, any deviations in kinetics at Oh = const have to be ascribed to the influence of surfactant dynamics. At the same time Bo has an essential effect not only on the drop size, but also on the length of liquid bridge at pinch-off and therefore it can affect the size of satellite droplets [15,36]. As surfactant presence affects both, Oh and Bo and it is difficult to distinguish between contributions of each number as well as choose the proper value of surface tension under conditions of continuous surfactant redistribution, the size of satellite droplets will be considered as a function of well-defined material parameters, such as viscosity and surfactant concentration.

3.2. Kinetics of liquid bridges, Ohnesorge number Oh<0.1

3.2.1. Surfactant-free liquids

Fig. 3 shows the short time kinetics for surfactant-free liquids under condition Oh < 0.1. The data for the mixtures containing 52 and 60% of glycerol as well as silicone oil 5 cSt demonstrate a perfectly linear dependence of $h_m^{3/2}$ on t predicted by Eq. (2) (Fig. 3a) for the available time resolution of $t > 0.1$ ms. For the mixture of 65% glycerol and 35% of water the linear fitting is still quite good,

although deviation from the linearity is noticeable at $t \leq 0.5$ ms and neck radius $h_m < 80$ μm. For the most viscous mixture of 71% glycerol and 29% of water considerable deviation from the linearity

is obvious from Fig. 3a, indicating the regime transition. Indeed, as shown in Fig. 3b in close vicinity of pinch-off, neck radius becomes proportional to time (empty symbols). Regime transitions in Fig. 3 occur at about 20 times larger neck radius than predicted by Eq. (3). Therefore, it can be assumed that the observed transition is to the transient viscous regime predicted in Refs. [28,29]. It should be noted that the linear fit in Fig. 3a for liquids at $Oh < 0.06$ does not go exactly through the origin of the co-ordinate system as expected from Eq. (2). The reason of that is the contribution of V/VI kinetics at $t < 0.1$ ms and the error in determination of break-up time, which is 0.1 ms.

Comparison of the proportionality constant A_I in Eq. (2) with the experimental data revealed some discrepancy, although not very large. Moreover, according to the experimental data A_I is not a constant but decreases slowly with the increase of Oh (see Supporting materials, S. 3). The reason for that may be a small violation of the condition $Oh \ll 1$ for the studied range of Ohnesorge numbers.

3.2.2. Surfactant solutions

Addition of surfactant lowers surface tension and therefore slows down the bridge thinning process, but additional effects can arise from the surfactant redistribution caused by interfacial flow and interface deformation during the thinning. Previously, inertial kinetics was studied mostly for surfactants dissolved in water. In this case depletion of surfactants from the thinning bridge resulted in faster than expected kinetics [23,24].

When viscosity of aqueous phase increases due to addition of glycerol, equilibrium properties of surfactant solutions change very slowly (see Table 1). As shown above at $Oh < 0.06$ the bridge thinning kinetics remain inertial, i.e. independent of viscosity. At the same time the diffusion coefficient decreases with an increase of viscosity as $1/\mu$ according to the well-known Stokes-Einstein equation. Therefore, if surfactant is swept from the neck by the surface flow accompanying the bridge thinning, its replenishment will occur much slower in water/glycerol mixtures.

According to the data in Table 1 for solutions of $C_{12}TAB$ in 52% Gl_W as well as that for solutions $C_{12}TAB$ and $C_{16}TAB$ in 60% Gl_W, $Oh < 0.060$. Therefore for all these solutions only inertial kinetics is expected without transition to viscous or visco-inertial kinetics inside the studied time interval. Data on the short time kinetics for $C_{12}TAB$ solutions in 52% Gl_W are shown in Fig. 4, where 52% glycerol/water mixture and 5 cSt silicone oil are used as the reference liquids. The neck thinning for surfactant solution is slower than that of surfactant-free 52% GL-W mixture due to decrease of surface tension in accordance with Eq. (2). Remarkably however,
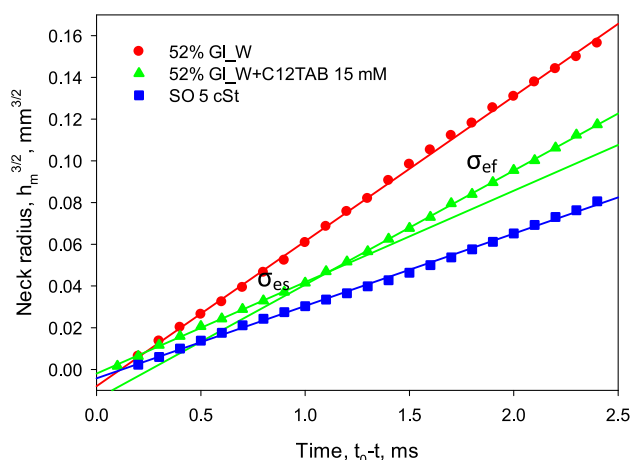

Fig. 4. Short time kinetics of the neck thinning for solution 15 mM of $C_{12}TAB$ in 52% Gl_W as compared with pure liquids.

thinning further slows down close to the pinch-off. The similar behaviour demonstrated all solutions of $C_{12}TAB$ in 52% Gl_W, $C_{12}TAB$ and $C_{16}TAB$ in 60% Gl_W at concentrations both below and above CMC, except the lowest concentrations, where surface tension was close to that of surfactant-free mixture. The solution of $C_{12}TAB$ in 52% GL_W was chosen for Fig. 4 because in this case the value of Oh is even smaller than that of 60% glycerol/40% water mixture, $Oh = 0.041$, the later demonstrating no deviation from inertial kinetics (Fig. 3a).

Note, the deceleration shown in Fig. 4 is not an artefact caused by the surface overturning near the pinch-off [35,36]. Indeed such overturning can obscure the pinch-off region [35] and prevent observation of real neck, when only the part of the bridge with larger radii is visible. Although according to numerical analysis [41] overturning should occur at $Oh < 0.0746$, which is in the range considered in this work, image analysis shows that for the liquids considered in this study overturning was not observed inside the available time resolution. The image sequence showing the absence of the surface overturning phenomenon for the solution of 15 mM of $C_{12}TAB$ up to pinch-off is given in Supporting materials (S. 4). Besides, the slowing down was not observed for pure liquids in the similar range of Oh, with either faster (water glycerol mixture) or slower (silicone oil) thinning kinetics than considered surfactant solutions (see Fig. 3a).

Using Eq. (2) effective surface tension responsible for the bridge thinning for surfactant solution can be easily calculated using slopes of $h_m^{3/2}$ vs t dependence, denoted K_s for the slower I regime and K_f for faster I regime, and known surface tension of surfactant-free liquid. Note, the effective surface tension is not equal to the real dynamic surface tension at the neck. It is apparent value accounting for the effect of surfactant redistribution. First, for the pure liquids with constant surface tension the excessive capillary pressure in the neck is completely determined by the changes in the surface curvature, whereas for surfactant solutions the excessive capillary pressure can also be influenced by the different values of dynamic surface tension in different parts of the bridge (see Fig. 1) caused by surface flow and different equilibration rates. Second contribution to the effective surface tension is from Marangoni flow, which is directed to the neck (Fig. 1) and therefore slows down the thinning kinetics resulting in decrease of effective (apparent) surface tension.

Results of such calculations show that the effective surface tension at faster bridge thinning, σ_{ef}, is similar to the dynamic surface tension before drop destabilisation $\sigma_{ef} = \sigma_d$. The effective surface tension at slower bridge thinning, σ_{es}, is smaller than both σ_d and σ_{eq} (see S. 5 for details). Note, previously acceleration of inertial thinning due to surfactant depletion close to pinch-off was reported for surfactant solutions in water [23,24]. Slower than expected kinetics of bridge thinning, i.e. effective surface tension $\sigma_e < \sigma_d$ was observed for solution of surfactant forming vesicles in water and also for micellar solutions of trisiloxane surfactants in 30% glycerol/70% water mixtures [21], however there was no transition from faster to slower kinetics on the timescale of observation. The results of the present study show that the slowing down kinetics of thinning of surfactant-laden liquid bridges is a general phenomenon not restricted to the certain type of surfactant or to concentrations above CMC. The only condition for this phenomenon to be observed is the slow kinetics of surfactant transfer during the fast inertial bridge thinning. Comparison of results of this study to Ref. [21] suggests that the transition time depends on liquid viscosity.

Maximum Ohnesorge number for Triton X-100 solutions in 60% Gl_W, $Oh = 0.061$ is slightly larger than $Oh = 0.060$ for 65% Gl_W mixture. Therefore for solutions with $\sigma_d = \sigma_{min,eq}$ one can expect $I \rightarrow V$ transition at $t \sim 0.5$ ms. According to Fig. 2 condition $\sigma_d = \sigma_{min,eq}$ is fulfilled for Triton X-100 concentration 1.25 mM. Fig. 5

confirms $I \rightarrow V$ transition, but it also shows transition to slower inertial regime beforehand. For surfactant concentration 0.125 mM Fig. 2 gives $\sigma_d \sim 47$ mN/m $> \sigma_{eq} = 42.8$ mN/m and $Oh = 0.050$. Therefore for this solution only fast to slow inertial regime transition was observed without $I \rightarrow V$ transition (see S. 6).

The rate of thinning at slow inertial regime depends on surfactant properties and viscosity. The ratio K_s/K_f of slopes $D^{3/2}$ vs t is smaller for solution of $C_{12}TAB$ in more viscous 60% Gl-W mixture than in less viscous 52% Gl_W. For all studied solutions K_s/K_f decreases with an increase of concentration at concentrations below CMC and slowly increases/levels off at concentrations above CMC (see S. 7). No transition to slow regime (i.e. $K_s/K_f = 1$) was found for the smallest studied concentration of $C_{12}TAB$ in 52% Gl_W and for concentrations 0.09 and 0.18 mM (0.05 and 0.1 CMC) of $C_{16}TAB$ in 60% Gl_W.

The values of K_s/K_f are closer to unity for solutions of $C_{12}TAB$ in 52% GL_W than for solutions in 60% Gl_W. Therefore, it can be expected that transition should disappear at further decrease of glycerol content. This assumption is in agreement with Ref. [23], where no slowing down was observed for $C_{12}TAB$ solutions in water and effective surface tension, σ_e, found from the slope of inertial thinning was the same as σ_d.

The transition point between fast and slow inertial regime moves away from pinch-off time with the increase of surfactant concentration (see S. 8). Therefore at certain concentration this point can move beyond the timescale of inertial kinetics and only slow inertial kinetics with effective surface tension considerably smaller than σ_d will be observed. Most probably this case was addressed in Ref. [21] for solutions of trisiloxane surfactants at concentrations above CMC.

It was assumed [21] that the slow inertial kinetics is the result of retardation of bridge thinning due to Marangoni flow caused by the initial surfactant depletion from it (see Ref. [21] for details). If bridge is very thin, i.e. surface to volume ratio is high then the effect of the Marangoni flow on the bulk flow can be very strong. Of course depletion itself should result in faster thinning. But the possible scenario is that the Marangoni flow persists even when surfactant concentration is already restored by this flow and bulk diffusion, because of inertia of liquid. Note, this effect should be more pronounced with the increase of the bulk viscosity, as in this case penetration of the surface flow in the bulk should be stronger. This is in line with the results on $C_{12}TAB$ in 52% Gl_W and 60% Gl_W.

Slowing down of the bridge thinning near pinch-off was found in numerical simulations for viscous regime in the presence of insoluble surfactan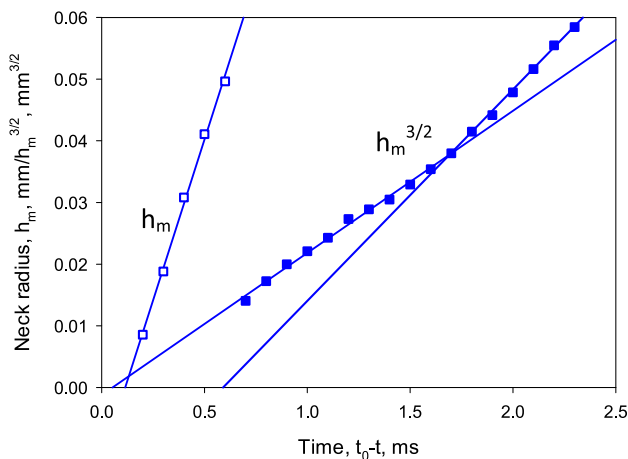t [42], as well as in the presence of soluble surfactant at detachment of buoyant drop in viscous liquid [43]. According to Ref. [44] in the case of high surfactant activity and therefore strong Marangoni stresses, surfactant can be redistributed in such way that maximum of capillary pressure occurs in the location outside the neck causing slower thinning in the present neck location. This mechanism can be relevant also for the case of inertial thinning considered in the present study. Moreover, according to numerical simulations [29] the maximum of axial velocity is outside the neck what should affect the surfactant redistribution.

As the whole bridge elongates, the axial position of the neck moves down during the thinning process. This movement accelerates close to the pinch-off moment (Fig. 6), when the primary pinch-off point moves close to the detaching drop. This movement affects the surfactant and velocity distribution in the bridge and can be responsible for the slower kinetics. It is noticeable that the kinetics slowing down is observed in the same time range as acceleration in neck position movement (sf Fig. 4 and Fig. 6).

3.3. Kinetics of liquid bridges, Ohnesorge number $0.2 < Oh < 0.4$

3.3.1. Surfactant-free liquids

The increase of viscosity and corresponding increase of Oh results in appearance of transition to visco-inertial regime at the time scale of observations, i.e. the neck thinning for surfactant-free liquids in the range of $0.2 < Oh < 0.4$ follows the route $I \rightarrow V \rightarrow VI$ (Fig. 7). For 80% glycerol/20% water mixture, $Oh = 0.22$, value of neck radius at $V \rightarrow VI$ transition obtained in our study are in good agreement with Eq. (3) and numerical results presented in Ref. [28]. The same transitions were observed for other surfactant-free liquids at $0.2 < Oh < 0.4$ presented in Table 1, with transition time increasing with the increase of Ohnesorge number. Proportionality constants for inertial kinetics, Eq. (2), A_I, found from slopes of $h_m^{3/2}$ vs t fitting for surfactant free liquids with $0.2 < Oh < 0.4$ are in good agreement with data for $Oh < 0.1$ (see S. 1). Proportionality constants for both Eq. (1) and Eq. (4) are in reasonably good agreement with theoretical values (see S. 9).

3.3.2. Surfactant solutions

The Ohnesorge numbers of surfactant solutions in 80% GL_W included in Table 1 are in the range $0.2 < Oh < 0.4$ therefore their behaviour should be similar to that presented in Fig. 7. This behaviour was observed for all studied solutions of $C_{12}TAB$ in 80% Gl_W
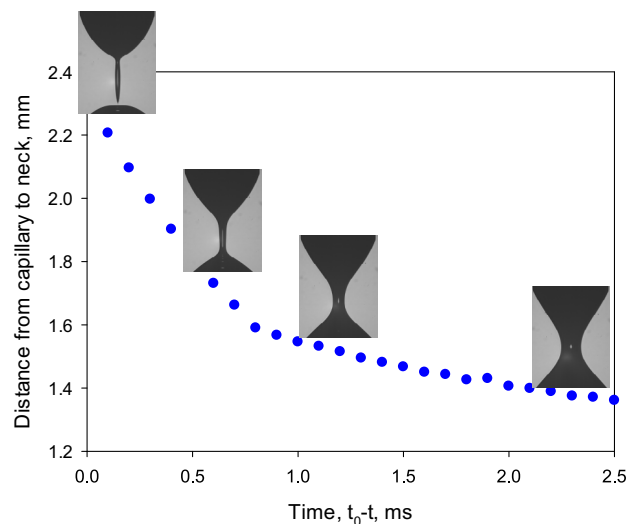

Fig. 5. Thinning kinetics for 1.25 mM solutions of Triton X-100 in 60% Gl_W: filled symbols correspond to inertial kinetics with $h_m^{3/2} \sim t$, empty symbols correspond to viscous kinetics with $h_m \sim t$.

Fig. 6. Change in the neck position at approaching the pinch-off for solution of 15 mM $C_{12}TAB$ in 52% Gl_W.
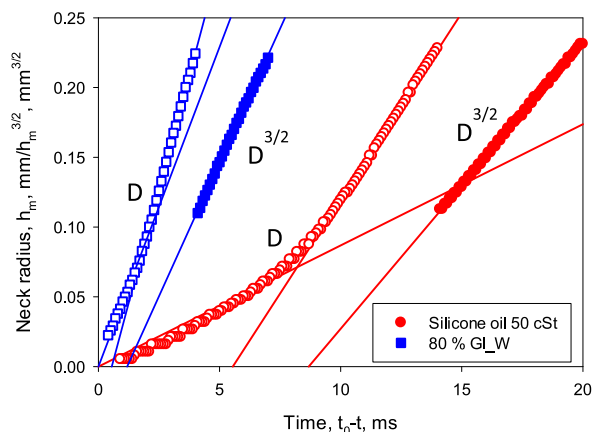
Fig. 7. Kinetics of thinning of liquid bridges 80% Gl_W, Oh = 0.22 and silicone oil 50 cSt, Oh = 0.36: filled symbols correspond to inertial kinetics with $h_m^{3/2} \sim t$, empty symbols correspond to viscous and visco-inertial kinetics with $h_m \sim t$.

Fig. 8. Inverted primary pinch-off for 1.25 mM of Triton X-100 in 80% Gl_W.

(see S. 10). The values of the effective surface tension, σ_e, found from the slopes of viscous regime kinetics are in good agreement with the dynamic surface tension at the instability onset, σ_d, (see S. 11). The high scatter of the data for visco-inertial regime did not allow the reliable quantitative estimation of the effective surface tension for this regime, however qualitatively it can be concluded that the effective surface tension is higher than dynamic surface tension at concentrations below CMC (due to the depletion of surfactant) and close to dynamic surface tension at concentrations above CMC.

The behaviour becomes more complicated for surfactants with smaller values of CMC, Triton X-100 and $C_{16}TAB$. First of all, for these surfactants the inversion of primary pinch-off point was observed. At small surfactant concentrations pinch-off occurred near the main drop, but at larger concentrations (1.25 mM for Triton X-100 and 4.5 mM for $C_{16}TAB$) the primary pinch-off occurred already near the capillary (Fig. 8). Note, for surfactant-free liquids the primary pinch-off always occurs near the main drop [15,44], because of the larger curvature of the neck in the lower part of the bridge connected to the main drop and therefore larger capillary pressure here [15]. As it can be seen from Fig. 8, in the case of the reversed pinch-off the curvature is larger at in the top part of the bridge already at 2 ms before pinch-off. The possible reason for this can be surfactant redistribution with larger concentration being at the bottom of the bridge. To the best of our knowledge the experimental observation of inversion of the pinch-off point at drop formation caused by the presence of surfactant was not reported before. Such inversion was predicted in numerical simulations on a bridge stretched between two disks for both a surfactant-free bridge and a bridge covered by an insoluble surfactant [16]. In this case inversion occurred above a certain threshold value of stretching velocity. Suppressing of the pinch-off near the main drop as compared to the pinch-off near the capillary was also predicted in numerical simulations on detachment of surfactant-laden buoyant drop in viscous liquid [43].

The contribution of surfactant to the kinetic of the liquid bridge for Triton X-100 and $C_{16}TAB$ noticeably depends on concentration (see S. 12 for an example). The general trend is that effective surface tension increases at regime transitions $I \rightarrow V \rightarrow VI$ indicating depletion of surfactant from the thinning bridge. This is true also for the case of an inverted pinch-off point. For large concentrations the effective surface tension calculated for the inertial regime is smaller than the dynamic surface tension at the instability onset, $\sigma_e < \sigma_d$, in line with observations for Oh < 0.1, whereas at small concentrations $\sig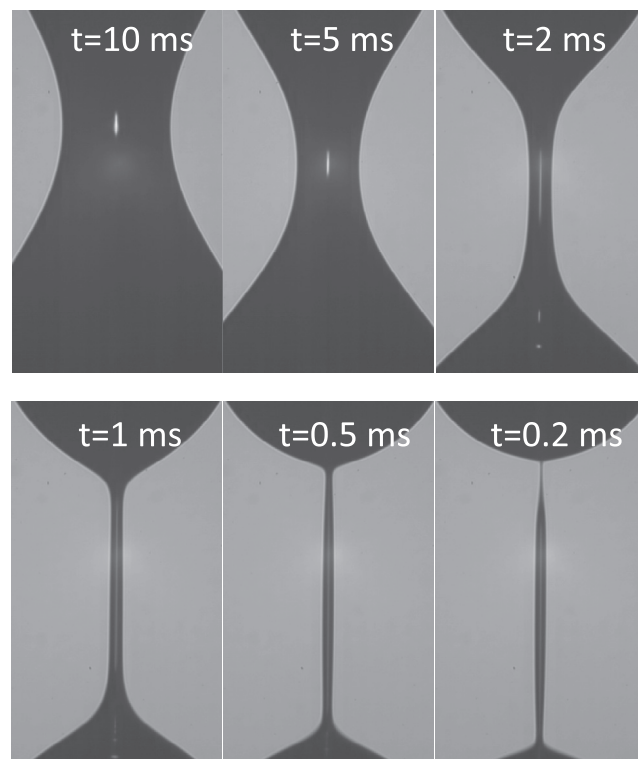ma_e > \sigma_d$. Therefore it can be concluded, taking into account also the results of Refs. [21,23] that surfactant can both accelerate and slow down inertial kinetics depending on concentration and diffusion coefficient. An increase of surfactant concentration and decrease of diffusion coefficient will eventually result in slower kinetics compared to the expected from the dynamic surface tension.

Effective surface tension in viscous and visco-inertial regimes for Triton X-100 and $C_{16}TAB$ is larger than σ_d, which is in agreement with results presented in Ref. [22]. At small surfactant concentrations effective surface tension is even larger than σ_{eq}, i.e. surfactant-laden bridge thins faster than surfactant-free one. As this acceleration was observed for all solutions at small concentrations including solutions of $C_{12}TAB$, we think this acceleration is not an artefact, but the problem needs more thorough study at a higher resolution in time and space. We can only speculate that surfactant presence may in some cases delay $V \rightarrow VI$ transition and what we observe is another transient viscous regime instead of visco-inertial one.

The behaviour of a surfactant at inertial and viscous thinning is different because of the velocity of inertial thinning is independent of liquid viscosity, but surfactant diffusion coefficient decreases with an increase of viscosity, whereas in viscous regime both the velocity of thinning and surfactant diffusion coefficient are reversely proportional to viscosity.

3.4. Satellite droplets

For all studied liquids, detachment of the main drop was accompanied by formation of a satellite droplet. For surfactant-free water/glycerol mixtures the maximum size of satellite droplets was observed at glycerol concentration 60%. Comparing this value with the results presented in Figs. 3 and 7 it can be concluded that the size of the satellite drops start to decrease when $I \rightarrow V$ transition occurs on the time scale ~0.5 ms and decreases further with development of transitional viscous regime.

For surfactant solutions the satellite size depends of both surfactant concentration and liquid viscosity (Fig. 9). The maximum on viscosity for surfactant solutions is observed for 60% glycerol/40% water mixture similarly to surfactant-free liquids. For solutions in 60% Gl_W the satellite size increases with the decrease of surfactant CMC. For $C_{12}TAB$ solutions (Fig. 9a) the size of satellite droplets increases with concentration and then levels off at concentrations around 1–2 CMC independently of solution viscosity. Similar behaviour was observed for $C_{16}TAB$ and Triton X-100 solutions (Fig. 9b) in water [15,23] and in 60% Gl_W, however concentration when satellites size levels off increases for these solutions with a decrease in the CMC values.

For solutions in 80% Gl_W a decrease of the satellite size with surfactant concentration was observed for $C_{16}TAB$ and Triton X-100 solutions (Fig. 9b). For Triton X-100 noticeable decrease in size occurs at the same concentration 1.25 mM (0.54 CMC) when the inversion of the pinch-off point was observed, however for $C_{16}TAB$ the decrease in the satellite size occurs at smaller concentration (1.8 mM) than the inversion of the pinch-off point (4.5 mM). Therefore the decrease in the satellite size is not a direct consequence of the inverted pinch-off, although it is obvious that both phenomena are governed by the surfactant redistribution close to the pinch-off as these phenomena do not occur in pure liquids in the same range of Ohnesorge numbers or for solutions of high CMC surfactant $C_{12}TAB$. In particular, the increase in the size of the satellite droplets correspond to the case when $\sigma_e \leq \sigma_d$, whereas the decrease is found when $\sigma_e > \sigma_d$.
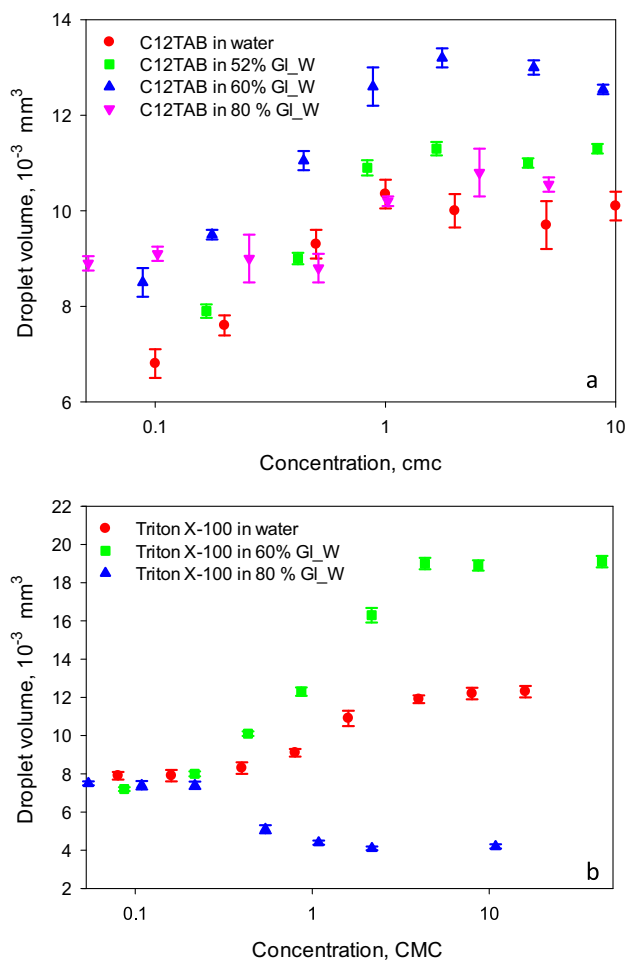

Fig. 9. Size of satellite drops formed by aqueous solutions of $C_{12}TAB$ (a) and Triton X-100 (b). Data for solutions in water are taken from Ref. [23].

4. Conclusions

Formation and detachment of surfactant-free and surfactant-laden drops from the tip of a capillary was studied under conditions of moderate Ohnesorge number $0.01 < Oh < 0.4$. Particular attention was paid to the kinetics of thinning of the bridge connecting the detaching drop to the capillary close to the pinch-off time and the size of satellite droplets accompanying the formation of the main drop. Surfactant dynamic effects on drop formation were probed for two different situations: (i) when surfactant diffusion coefficient changes independently of thinning kinetics or (ii) when it changes in line with thinning kinetics.

To isolate the effect of surfactant, regime transitions at thinning the liquid bridge were studied first for pure liquids. At $Oh < 0.06$ only inertial kinetics of the bridge thinning was observed. For surfactant-laden liquids the kinetics, while remaining in the inertial regime, slowed down close to the pinch-off, most probably due to retardation of the liquid outflow from the bridge neck by Marangoni stresses. The time from the moment of pinch-off to the change from the fast to the slow inertial regime increased with surfactant concentration. In previous studies of surfactant dynamics, inertial bridge thinning was probed only under conditions of considerably lower Ohnesorge numbers. For solutions in water, $Oh < 0.01$, acceleration of bridge kinetics due to surfactant depletion was found for convenient surfactants [23,24], whereas slower kinetics was found for surfactant forming vesicles at concentrations above CMC [21]. Slower kinetics for micellar solutions in glycerol/water mixture was found at $Oh = 0.018$ [21], which is in good agreement with finding of the present study.

At $0.2 < Oh < 0.4$ the kinetics followed the route I → V → VI in line with predictions made in the literature for pure liquids [28,29]. Surfactant solutions followed the same route as surfactant-free liquids with the effective surface tension increasing along the route I → V → VI. It was higher than dynamic surface tension in visco-inertial regime for the most studied solutions. Increase in effective surface tension in visco-inertial regime due to surfactant depletion is in agreement with the existing literature [22].

At high concentrations of $C_{16}TAB$ and Triton X-100 in 80% glycerol/20% water mixtures, the inversion of the primary pinch-off point was observed: the primary pinch-off occurred near the capillary followed by secondary pinch-off close to the main drop. Kinetics of thinning of the bridge at primary pinch-off did not depend on its position. Inversion of pinch-off due to the presence of surfactant was not observed till now experimentally, but has been predicted in numerical simulations [16,43]. Experimentally such inversion was observed only in the presence of electric field [44].

The size of the satellite drops has a maximum for 60% glycerol/40% water mixture independently of surfactant presence. The size decreases when larger part of thinning process occurs in viscous/visco-inertial regime. For solutions of low CMC surfactants, $C_{16}TAB$ and Triton X-100, in 80% glycerol/20% water mixture the size of satellite droplets decreased with the increase of surfactant concentration, whereas for all other compositions satellite size increased with the increase of surfactant concentration until levelling off at concentrations above CMC. In this case the size of satellite drops decreases with the increase of CMC. Increase of satellite size with surfactant concentration at small viscosities is in agreement with the literature [15,23].

To make the results more relevant to industrial emulsification and spraying processes the study should be extended to include effect of flow rate (Weber number). Increasing the flow rate decreases the time of drop formation and should make surfactant dynamic effects even more pronounced. The approach proposed

in this work of uncoupling changes in diffusion coefficient due to viscosity change and liquid flow dynamics is also very promising for revealing the effect of surfactant dynamic on spreading and in particular for explaining superspreading mechanism, where the surfactant dynamics is assumed to be of importance [45].

Acknowledgements

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jcis.2018.01.039.

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