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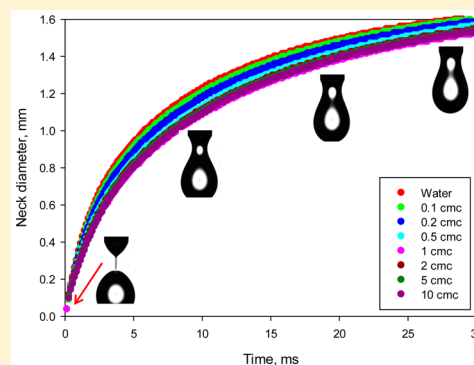
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## Effect of Soluble Surfactants on the Kinetics of Thinning of Liquid Bridges during Drops Formation and on Size of Satellite Droplets

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**ABSTRACT:** The results of an experimental study on thinning and breakage of liquid bridges during detachment of a drop from the tip of a capillary are presented for a series of surfactant solutions (including cationic, anionic, and nonionic surfactants) over a broad range of molecular masses, values of critical micelle concentration, and concentrations. The used experimental protocol revealed that the kinetics of the bridge thinning depends much more on the dynamics of adsorption at the surface of the drop before it destabilizes, rather than on the depletion of surfactant from the surface of the thinning bridge due to its stretching as the instability develops. The kinetics of the bridge thinning and the size of satellite droplets formed after the bridge breakage depend considerably on the surfactant concentration and the value of critical micelle concentration. It is proposed that the dynamic surface tension on the time scale of the drop formation can be used as an effective surface tension for the description of the bridge kinetics over the broad range of experimental conditions used.



### INTRODUCTION

Drop formation is omnipresent in nature and industry. For many applications, such as emulsification, inkjet printing, including DNA and protein microarray fabrication, and microfluidics, the size of drops, their surface composition, and presence of small satellite droplets are of vital importance. Thinning and breakage of the liquid bridge connecting the newly forming droplet with the reservoir of liquid is an essential part of the process, determining the properties of the final product.

In this study the process of drop formation is considered under the conditions of close to zero flow rate under gravity. In this case the main forces acting are gravity and surface tension. The relative effect of these forces is described by the Bond number,  $Bo = \Delta\rho g L^2 / \sigma$ , where  $\Delta\rho$  is the density difference between the liquid in the drop and surrounding fluid,  $g$  is the acceleration due to gravity,  $\sigma$  is the surface tension, and  $L$  is the characteristic length, the best choice of which is the drop radius. From the definition of the Bond number it is obvious that the decrease of the liquid surface tension should result in a smaller size of drops detached from the capillary, providing that the detachment occurs at the same value of  $Bo$ .

When a liquid drop is gradually formed at the tip of a capillary in the presence of gravity, first, at small drop volumes, a force balance exists between the gravity and the vertical component of surface tension. With an increase of volume of the drop the gravity force increases, the drop elongates, the angle between the vertical axis and the surface of the drop decreases, and the vertical component of surface tension increases balancing gravity. The maximum attainable surface tension force is equal to  $2\pi R\sigma$ , where  $R$  is the capillary radius. After the weight of drop exceeds this threshold value, instability

sets in and the liquid bridge connecting the drop with the liquid in the capillary elongates and becomes thinner until it finally ruptures. There are two driving forces governing this process: gravity stretching of the filament dominates in the initial stage of instability and the excessive capillary pressure,  $P_c = 2\sigma/D$ , in the thinnest part of the bridge, denoted here as the neck, governs the dynamics near the pinch-off point.<sup>1</sup> Here  $D$  is the neck diameter.

Using various theoretical approaches, such as linear and weakly nonlinear stability analysis, approximate solutions based on one-dimensional equations and self-similarity in the vicinity of pinch-off point, and numerical simulations, the problem of thinning of liquid bridges is well understood in the case of pure (surfactant-free) liquids.<sup>2–8</sup> The theoretical results demonstrate good agreement with numerous experimental studies.<sup>9–12</sup> A comprehensive review on the mechanism and regularities of thinning of liquid bridges composed of pure liquids is given in refs 13 and 14. It has been shown that far from the pinch-off point the thickness of the neck decreases exponentially with time.<sup>6</sup> Near the pinch-off point, the neck kinetics is described by self-similar solutions which are dependent on the properties of the liquid, in particular on the correlation between inertial and viscous forces.<sup>2–4</sup>

One of the essential parameters affecting the thinning kinetics is surface tension because it determines the instability onset and the capillary pressure in the neck. This parameter affects also the limiting length of the bridge, formation of satellite droplets, and their size.<sup>5</sup> The surface tension is a constant for pure liquids, but it can change considerably with

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time for surfactant solutions during the growth and detachment of the drop. When a new surface is created, it is initially free of surfactant molecules and demonstrates a surface tension equal to that of pure solvent. The gradual adsorption of surfactant results in a decrease of surface tension with time. The dynamic surface tension depends on many factors, the most important being the concentration of surfactant monomers and self-assembled structures, such as micelles, vesicles, etc., in the bulk of solution, the corresponding diffusion coefficients, the rate of disintegration of the self-assembled structures if present, and the convective flows inside the liquid phase.<sup>15,16</sup> Moreover, in the case of surfactant solutions, the local (in space) values of the surface tension during elongation and thinning of the liquid bridge can be different giving rise to surface tension gradients and Marangoni flows. This causes considerable complications as the effect of the surfactant on the kinetics of liquid bridges is therefore not limited to a simple lowering of the surface tension to the equilibrium value. This requires a comprehensive theoretical and experimental study. Despite the great practical importance of this problem, the literature on kinetics of surfactant-laden bridges is not as plentiful as that for pure liquids and the behavior of real systems is not yet completely understood.

Theoretical studies on liquid bridges covered by insoluble surfactants<sup>17–19</sup> have shown that the presence of a surfactant stabilizes a cylindrical liquid filament by two mechanisms: (i) lowering interfacial tension and (ii) Marangoni stresses which suppress deformation of the interface. The stabilization reveals itself in a longer time and bridge length before pinch-off. This conclusion was supported by an experimental study on bridges with the surface covered by an insoluble surfactant.<sup>10</sup> A noticeable difference between the behavior of surfactant-laden and surfactant-free liquid bridges has been found in ref 10 only at a high initial surface coverage. The relative contribution of the stabilizing mechanisms depends on the surfactant concentration, diffusion coefficient, and stretching velocity. Capillary pressure expels liquid from the neck region. Convective surface flow sweeps the surfactant away from the neck. If the surface diffusion toward the neck is not quick enough and cannot restore the equilibrium, then the neck region becomes surfactant free and the capillary pressure driving the neck thinning is equal to that of the pure liquid. However, in this case the surface concentration gradients become important and stabilization due to Marangoni stresses takes place.<sup>17–19</sup>

The bridges containing insoluble surfactants are very convenient model systems, but in most industrial applications soluble surfactants at high concentrations are used. In this case the behavior becomes even more complicated, because the surfactant transfer from the bulk can replenish its loss from the neck surface as well as diminish the surface concentration gradients. It is also important in the case of a soluble surfactant that the adsorption of the surfactant onto the surface of growing and detaching droplet is a slow diffusion-controlled process, and therefore the dynamic surface tension can deviate considerably from the equilibrium value.<sup>20</sup> According to ref 21, for example, the dynamic surface tension of an aqueous solution of hexadecyltrimethylammonium bromide, one of the surfactants used in the present study, at a concentration slightly above the cmc reaches equilibrium value only at a time exceeding 10 s. The equilibration time increases with a decrease of concentration.<sup>21</sup>

A theoretical study of the effect of surfactant solubility was started in refs 22 and 23. A comprehensive numerical study was performed in ref 24. It has been shown that both stabilization mechanisms found for the case of insoluble surfactants also work for the soluble surfactants; however, their importance is determined not only by the surfactant concentration and activity but also by the presence of micelles which act as surfactant reservoirs. It was predicted in ref 24 that Marangoni stresses can cause formation of large satellite droplets at high surfactant concentrations. There are, however, very few experimental studies on formation of surfactant-laden drops<sup>25–29</sup> when compared with studies of (pure) liquids without surfactants. The main attention in these studies is paid to the difference in the behavior between surfactant-laden and surfactant-free bridges and comparison of the behavior at concentrations below and above the critical micelle concentration (cmc).

A review of the current literature shows an absence of a systematic experimental study on kinetics of surfactant-laden liquid bridges enabling a comparison of the influence of the surfactant properties and concentrations. Moreover, the question about the relative contributions to the thinning kinetics of the dynamic surface tension during the stable regime and the depletion of the surfactant from the neck region after instability onset has not been considered. The aforementioned problems are very important from both fundamental and practical points of view. From the fundamental side the problem is related to the understanding of surfactant behavior in liquid colloidal systems under the conditions of considerable surface deformations, which is directly connected to the problems of surfactant enhanced spreading<sup>30</sup> and stability of foams.<sup>31</sup> From the practical side, the understanding of the effect of a soluble surfactant on the thinning of liquid bridges enables the prediction and control of size and composition of formed drops and, in particular, the formation and size of satellite droplets. In what follows the effect of surfactant concentration and cmc value on the kinetics of thinning of surfactant-laden liquid bridges and the size of satellite droplets is considered for the case of aqueous solutions of low viscosity in air. The study is performed for three types of surfactants: cationic, anionic, and nonionic.

## ■ EXPERIMENTAL SECTION

The surfactants decyltrimethylammonium bromide (C<sub>10</sub>TAB, Acros Organics, 99%), dodecyltrimethylammonium bromide (C<sub>12</sub>TAB, Acros Organics, 99%), hexadecyltrimethylammonium bromide (C<sub>16</sub>TAB, Sigma, BioXtra, ≥99%), sodium lauryl ether sulfate (SLES, TexaponN701, Cognis UK Ltd.), and poly(ethylene glycol) octylphenyl ether with average number of ethylene oxide groups 9.5 (Triton X-100, laboratory grade, Sigma-Aldrich) as well as sodium bromide (Sigma, BioUltra, ≥99.5%), sodium chloride (BioXtra, ≥99.5%), and dodecane (Sigma-Aldrich, ≥99%) were used as purchased. All solutions were prepared in double-distilled water produced by Aquatron A 4000 D, Stuart.

The experiments were performed as follows. A stable drop of the solution under study was formed manually using a micrometre syringe outfit (AGLA, Burroughs Wellcome) on the tip of a capillary with outer diameter 1.81 mm. The drop was illuminated with back light using a cold light source KLS125, Krüss Optronic. The size of the drop depended on the surfactant used and its concentration. The drop was left for 30 s for equilibration (partial or complete depending on the surfactant). 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 and to exceed noticeably the time of several seconds necessary to destabilize the

**Table 1. Critical Micelle Concentrations (cmc) of Studied Surfactants in Aqueous Solutions**

surfactant cmc, mM	C <sub>10</sub> TAB	C <sub>12</sub> TAB	C <sub>16</sub> TAB	C <sub>16</sub> TAB + 0.01 M NaBr	SLES + 0.1 M NaCl	Triton X-100
	60	15	0.9	0.1	0.1	0.25

drop) and the necessity to avoid a noticeable evaporation of water which would result in an increase of the bulk concentration. Besides, the time should be short enough to see the effect of deviation of the dynamic surface tension from the equilibrium value at least for some of the studied solutions.

After 30 s a snapshot of the drop was taken using a high-speed video camera (Photron SA3 or SA5) equipped with Navatar, 2X F-mount objective. From this image the dynamic surface tension at  $t = 30$  s was found using the software DSA100, Krüss. This surface tension is called further the dynamic surface tension at the instability onset,  $\sigma_{30}$ . It depends on the surfactant studied, and its value is smaller than that of pure water,  $\sigma_0$ , but larger than or sometimes equal to the equilibrium value,  $\sigma_{eq}$ , i.e.,  $\sigma_0 > \sigma_{30} \geq \sigma_{eq}$ .

After 30 s of equilibration the volume of the droplet was increased slightly until the drop became unstable and detached from the capillary. The experiments have been performed under the conditions of a close to zero flow rate (Weber number,  $We = \rho u^2 R / \sigma \ll 1$ , where  $\rho$  is the liquid density and  $u$  is the liquid velocity). In this case the kinetics of thinning is independent of the flow rate.<sup>32</sup> 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 frames/s.

The surface tension at the time 30 s,  $\sigma_{30}$ , was determined to compare this value with the value obtained later from the kinetics of pinching,  $\sigma_{cf}$ . The essential point here is that the process of drop detachment is very quick in comparison with the equilibration time of 30 s. Therefore,  $\sigma_{30}$  can be considered as the surface tension at the instability onset, i.e., immediately before the thinning and pinch-off took place. If there is any depletion, i.e., decrease in the surface concentration, which is not compensated by the surfactant adsorption, then the surface tension found from the pinching kinetics should be higher than that found experimentally immediately before the drop destabilization,  $\sigma_{30}$ .

It should be stressed that in most industrial processes, the drop formation occurs continuously, often with high flow rates and formation rates. In the continuous process it is impossible to measure the dynamic surface tension immediately before the drop destabilization as the drop is deformed due to flow. The proposed experimental protocol allowed this continuous process to be divided into two stages—equilibration and destabilization—and to make direct measurement of the surface tension immediately before destabilization.

The surface tension  $\sigma_{30}$  was also compared with the dynamic surface tension at  $t = 30$  s found from the measurements by maximum bubble pressure tensiometer BPA-1S, Sinterface, to see the effect of difference in the experimental protocols, such as much smaller volume of surfactant solution in the drop configuration and the thermal convection inside the drop or the measuring cell. The equilibrium surface tension was measured using the tensiometers DSA100 (drop shape analysis) and K100 (Wilhelmy plate), Krüss.

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. The presented results are the average from at least three independent measurements.

## RESULTS AND DISCUSSION

The ionic surfactants have been chosen for this study because their cmc and activity can be easily controlled by adding a salt to the solution. SLES is a technical grade surfactant broadly used in industry. Triton X-100 is a commonly used nonionic industrial surfactant with relatively high molecular mass  $M = 625 \text{ g mol}^{-1}$  and therefore smaller diffusion coefficient when compared with other surfactants used in this study. SLES and Triton X-100 have been chosen to check the generality of the

obtained results. All used surfactants form micelles at concentrations above the cmc. The surfactants cover a broad range of the cmc values presented in Table 1, which reflects the broad range of their surface activities. It is seen from Table 1 that the cmc values for C<sub>16</sub>TAB + NaBr and SLES + NaCl at the chosen salt concentrations are close to each other.

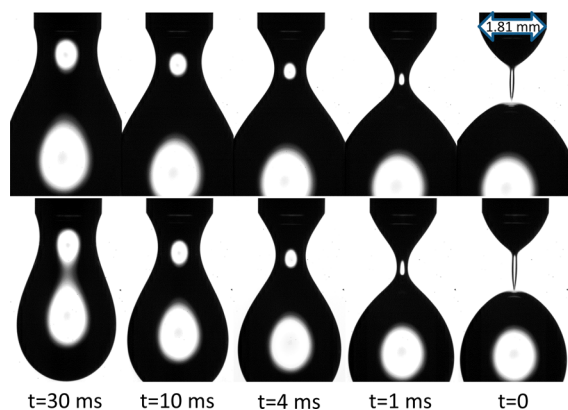
The values in Table 1 have been obtained from the surface tension isotherms at concentrations close to the cmc. They are in good agreement with the literature data given in refs 33 and 34. The value,  $c$ , of cmc for C<sub>16</sub>TAB in 10 mM solution of NaBr was estimated using the literature value for aqueous solution of C<sub>16</sub>TAB from the equation<sup>34</sup>

$$c^* = f((c + c_{\text{NaBr}})c)^{0.5} \quad (1)$$

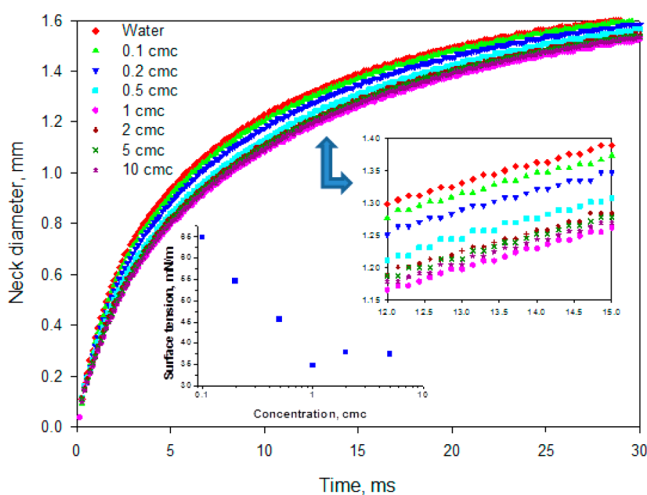
where  $c^*$  is the mean ionic product,  $c_{\text{NaBr}}$  is the concentration of NaBr, and  $f$  is the average activity coefficient of the ions in the bulk. For a 1:1 electrolyte  $\log(f) = -0.5115\sqrt{I}/(1 + 1.316\sqrt{I}) + 0.055I$ , where  $I = 0.5\sum c_i z_i^2$  is the ionic strength of the solution,  $c_i$  are the molar concentrations of ions ( $\text{mol L}^{-1}$ ), and  $z_i$  are the charge numbers of ions ( $z_i = 1$  in the considered case). The value,  $c$ , of cmc at a certain  $c_{\text{NaBr}}$  can be found from eq 1 under the assumption that the value of the mean ionic product at the cmc does not depend on the electrolyte concentration. The accuracy of this assumption is confirmed for example by Figure 3.51 in ref 34. It was impossible to find the cmc value for SLES + 0.1 M NaCl using eq 1 because the purchased compound already contained some electrolytes. Therefore, for this composition the only experimental value found from the isotherm in this study is available.

The results below are presented versus the concentrations normalized by the cmc values. Such presentation was chosen because the values of the equilibrium surface tension at the same concentration in cmc units are close to each other for the different surfactants of the same structure. That is, the difference in the thinning kinetics at the same normalized concentrations of different C<sub>n</sub>TABs can be only caused by the difference in dynamic surface tension, i.e., in adsorption kinetics.

Images showing the thinning of liquid bridges during the detachment of drops of C<sub>10</sub>TAB aqueous solutions of two different concentrations are presented in Figure 1. The time at  $t = 0$  corresponds to the moment of pinch-off, and the positive values correspond to the time remaining to the pinch-off. Figure 1 shows clearly that the process of thinning slows down with an increase of the surfactant concentration, as the changes in the diameter of the neck (the thinnest part of the bridge) inside 30 ms are smaller at the concentration 10 cmc. For example, inside the last millisecond the neck diameter decreases to zero from the value of 0.339 mm at the concentration 0.1 cmc, whereas the decrease is only 0.274 mm for 10 cmc. Inside the last 10 ms the change in the neck diameter is 1.208 mm for 0.1 cmc and only 1.097 mm for 10 cmc. If we start with a neck diameter of 1.6 mm, then the time to pinch-off is 29.3 ms for the concentration 0.1 cmc but is 37.4 ms for 10 cmc. The kinetics of thinning for all studied concentrations of C<sub>10</sub>TAB are presented in Figure 2. The insets to Figure 2 show the changes in equilibrium surface tension with concentration and focus on the kinetics for times between 12 and 15 ms.



**Figure 1.** Kinetics of thinning of liquid bridges during the detachment of surfactant ( $C_{10}$ TAB)-laden aqueous drops from the tip of a capillary ( $d = 1.81$  mm) under gravity. Surfactant concentrations  $c = 0.1$  cmc (upper row) and  $c = 10$  cmc (bottom row).



**Figure 2.** Dependence of the neck diameter on time remaining to the detachment by thinning  $C_{10}$ TAB-laden bridges. The inset on the left shows the surface tension isotherm for aqueous solutions of  $C_{10}$ TAB near the cmc, and that on the right zooms the curves sequence for the time between 12 and 15 ms.

Figure 2 shows that the kinetics follows precisely the changes in surface tension: the kinetics of 0.1 cmc solution are only slightly slower than that of pure water; the kinetics of solutions at concentrations above the cmc are very similar. The slowest kinetics were observed at concentration of 1 cmc, at which the surface tension demonstrates a small minimum, most probably due to the presence of a small amount of more surface active impurities.

As the neck radius decreases (Figure 1), the capillary pressure, being the driving force of thinning, increases. That is why the fastest thinning occurs close to the moment of pinch-off. The kinetics near the pinch-off are determined by the forces opposing the capillary thinning. If viscous dissipation dominates, then the neck diameter decreases linearly with time.<sup>3,4</sup> In this study, inertial kinetics<sup>2</sup> in the vicinity of pinch-off was observed for all solutions in the whole range of concentrations with the neck diameter  $D$  decreasing according to the equation

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

or

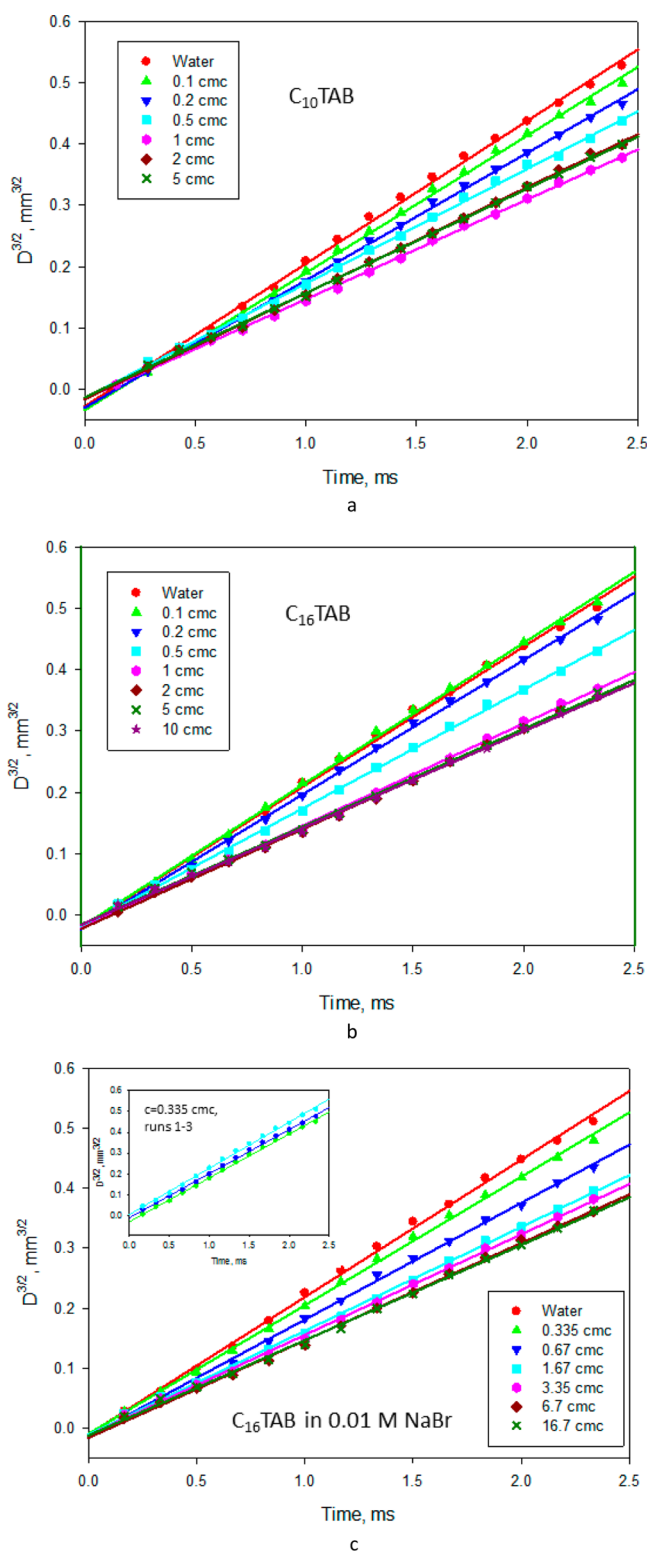
$$D^{3/2} \sim \left( \frac{\sigma}{\rho} \right)^{1/2} (t - t_0) \quad (2a)$$

where  $t$  is the time and  $t_0$  is the time corresponding to the pinch-off moment. Examples of the kinetics at  $t - t_0$  close to zero time showing the linear dependence of  $D^{3/2}$  vs  $(t - t_0)$  are given in Figure 3. It is seen from Figure 3 that for all studied solutions a linear dependence of  $D^{3/2}$  on time is observed. That means that there are no essential changes in the surface tension near the pinch-off at the time scale of 0.1–2.5 ms. However, as is seen from comparison of Figures 2 and 3, the linear region covers only the last several milliseconds before pinch-off, whereas the whole thinning process takes tens of milliseconds. To prove that there were no changes in surface tension during the whole thinning process, the comparison of the values of surface tension at the beginning, which is close to  $\sigma_{30}$ , and the end of the thinning process is necessary.

According to eq 2a, the slope of lines in Figure 3 should be proportional to  $(\sigma/\rho)^{1/2}$ . Therefore, comparing the slope of the curves at various concentrations with that of pure water (surface tension  $\sigma = 72.5$  mN  $m^{-1}$  at 22 °C), it is possible to calculate the effective surface tension at the neck and to compare it with the equilibrium surface tension,  $\sigma_{eq}$  and with the dynamic surface tension at the onset of the instability,  $\sigma_{30}$ . To estimate the error of such calculations, the kinetics of the neck thinning for a dodecane drop ( $\rho = 0.75$  g  $cm^{-3}$ ,  $\sigma = 24.9$  mN  $m^{-1}$ <sup>35</sup>) was compared with that of pure water. Dodecane demonstrated inertial kinetics similar to water, and the effective surface tension found from the slope of the line  $D^{3/2}$  vs  $(t - t_0)$  was  $\sigma_{ef} = 21.8$  mN/m. Therefore, it can be concluded that the calculations performed in this way give quite realistic, but slightly underestimated, values of surface tension. The values of  $\sigma_{eq}$ ,  $\sigma_{30}$ , and  $\sigma_{ef}$  for some of the studied surfactants are presented in Tables 2–5.

It should be noted that the time at  $t = 0$  is ascribed to the first frame displaying that there is already no connection between the neck and the main drop (see Figure 1). Obviously, the real detachment occurs during the time between this frame and the previous one, when the drop was still attached to the neck. That means that  $t = 0$  in reality is  $t < 0$ , and the maximum shift is equal to the time span between frames, i.e., 1/7 ms. That is why all fitting lines in Figure 3 demonstrate small apparent negative values of the neck diameter at  $t = 0$ . The experimental values at different measurements of the same solutions are therefore shifted relative to each other as shown at the inset in Figure 3c. At the same time, it is seen from the inset in Figure 3c that the slopes of the lines are very close to each other. The variation in slopes between measurements, but not the variation in the neck diameters, is important in these measurements because it determines the variation in the calculated values of  $\sigma_{ef}$ . The corresponding experimental errors are given in Table 4.

The maximum experimental error in the slope and therefore in  $\sigma_{ef}$  is observed for  $C_{16}$ TAB in 0.01 M NaBr for concentrations below the cmc because for these solutions the surface tension changes noticeably with time around  $t = 30$  s, as is seen from the data on dynamic surface tension presented in Figure 4a. For the same reason the error in  $\sigma_{30}$  is also the highest for these solutions. Note that the data on dynamic



**Figure 3.** Short-time kinetics of the neck thinning depending on the surfactant concentration: (a)  $C_{10}\text{TAB}$ , (b)  $C_{16}\text{TAB}$ , and (c)  $C_{16}\text{TAB}$  in 0.01 M NaBr; inset shows the results of three measurements at concentration 0.335 cmc.

surface tension for  $C_{16}\text{TAB}$  in 0.01 M NaBr (Figure 4a) are in good qualitative agreement with the kinetics presented in Figure 3c for the same surfactant. According to Figure 4a at time  $t = 30$  s the surfactant solutions with concentrations 6.7 cmc and 16.7 cmc have already reached equilibrium surface

tension, i.e., have the same surface tension and the lines in Figure 3c for these solutions coincide. The solution at concentration 3.35 cmc, which has the same equilibrium surface tension, has not yet reached equilibrium at  $t = 30$  s, having higher surface tension and the slope of the corresponding line in Figure 3c is higher.

Figure 3a presents the results for the most soluble of the studied surfactants,  $C_{10}\text{TAB}$ , with  $\text{cmc} = 60$  mM. For this surfactant the essential difference in the kinetics when compared to pure water is observed already at the concentration 0.1 cmc (cf. Figure 2). The minimum slope is observed at  $c = 1$  cmc corresponding to the minimum surface tension (see inset in Figure 2).

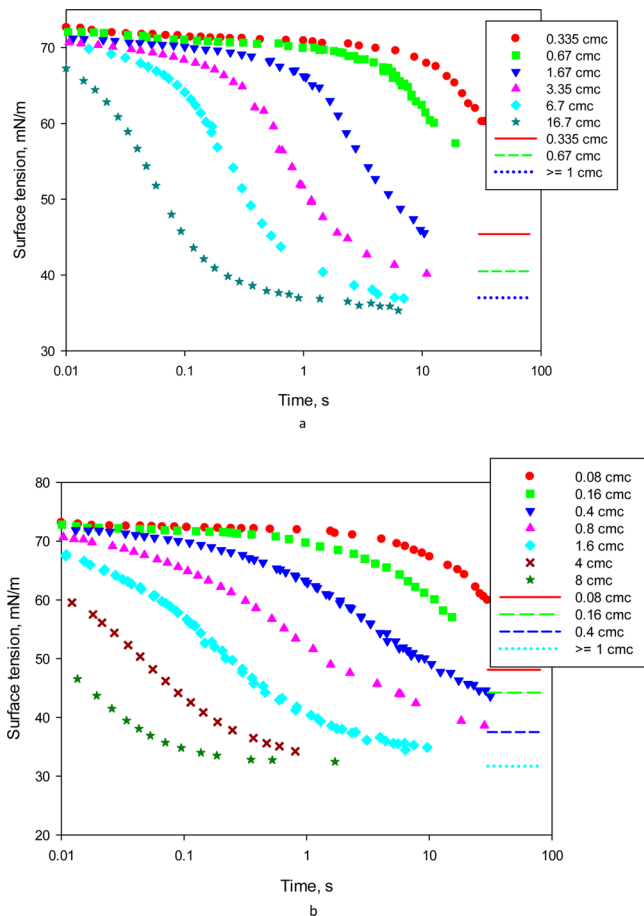
For all studied solutions of  $C_{10}\text{TAB}$  the dynamic surface tension at the instability onset,  $\sigma_{30}$ , was close to the equilibrium surface tension. Calculated values  $\sigma_{\text{ef}}$  were also very close to the equilibrium values as it is shown in Table 2. The maximum difference between  $\sigma_{30}$  and  $\sigma_{\text{ef}}$  was 1 mN/m. Therefore, it can be concluded that solutions of  $C_{10}\text{TAB}$  in the studied range of concentrations behave like pure liquids with surface tension equal to the equilibrium value at corresponding concentration. Such behavior can be explained by very high cmc value of this surfactant, that is, the high molar concentration even at 0.1 cmc, resulting in a quick equilibration. A decrease of equilibration time with an increase of concentration is illustrated by the data presented in Figure 4 where equilibrium surface tension is achieved later for smaller concentrations of the same surfactant. Solutions of  $C_{12}\text{TAB}$ ,  $\text{cmc} = 15$  mM (data are not shown), behave rather similar to  $C_{10}\text{TAB}$ ; i.e., they also can be considered as pure liquids with corresponding surface tensions.

For a further decrease of cmc the behavior begins to change. The solution of  $C_{16}\text{TAB}$  at  $c = 0.1$  cmc behaves like pure water (Figure 3b and Table 3). For larger concentrations the slope decreases with concentration, but both  $\sigma_{30}$  and  $\sigma_{\text{ef}}$  are larger than the equilibrium surface tensions for  $c = 0.2$  cmc and  $c = 0.5$  cmc (see Table 3). It should be stressed that the difference between  $\sigma_{30}$  and  $\sigma_{\text{ef}}$  is in the range of the experimental/calculation error for these concentrations. Therefore, it can be concluded that the solutions of less soluble surfactants, such as  $C_{16}\text{TAB}$ , cannot be treated as pure liquids; for them the dynamic mass-exchange processes during the drop formation and detachment are of importance. It follows from the experimental results that the dynamics of adsorption of  $C_{16}\text{TAB}$  from the bulk during the drop formation is more important than the depletion of surfactant from the neck.

A further deviation from the behavior of pure liquids is observed for even less soluble compositions  $C_{16}\text{TAB}$  in 0.01 M NaBr (Figure 3c and Table 4) and SLES in 0.1 M NaCl (results not shown). In this case the slope of the line  $D^{3/2}$  vs  $(t - t_0)$  becomes independent of concentration only at concentrations  $c > 6$  cmc. At concentrations below 1 cmc and even at  $c = 1.67$  cmc the dynamic surface tension of  $C_{16}\text{TAB}$  in 0.01 M NaBr is higher than the equilibrium surface tension (Table 4). As a result, the neck thinning occurs faster than it can be expected from the value of the equilibrium surface tension. It is interesting to note that for these concentrations  $\sigma_{\text{ef}}$  is on average a slightly higher than  $\sigma_{30}$ . Therefore, it can be assumed that for such low concentrations both the dynamic surface tension ( $\sigma_{30}$ ) and the depletion of surfactant during the neck thinning (evidenced by a larger value of  $\sigma_{\text{ef}}$  as compared to  $\sigma_{30}$ ) influence the bridge kinetics. Nevertheless, even in this case the effect of dynamic surface tension is stronger.

Table 2. Equilibrium and Effective Surface Tension at Formation and Detachment of Drops of Aqueous Solutions  $C_{10}$ TAB

	$c$ , cmc							
	0	0.1	0.2	0.5	1	2	5	10
$\sigma_{\text{eq}}$ mN/m	72.5	66.8	56.6	47.6	36.7	39.8	39.4	38.7
$\sigma_{\text{ef}}$ mN/m		66.8	57.8	46.3	35.6	39.7	38.9	36.7



**Figure 4.** Dynamic surface tension of solutions of (a)  $C_{16}$ TAB in 0.01 M NaBr and (b) Triton X-100. The lines show the values of equilibrium surface tension for the corresponding concentrations; the beginning of each line corresponds to  $t = 30$  s.

The shape of surface tension isotherm of Triton X-100 is very different from that of other surfactants used in this study.<sup>33</sup> Nevertheless, the behavior of solutions of this surfactant is in line with that discussed above. The value of cmc for Triton X-100 is 0.25 mM, i.e., larger than that of  $C_{16}$ TAB in 0.01 M NaBr (0.1 mM) but smaller than that of  $C_{16}$ TAB (0.9 mM). Dynamic surface tension of Triton X-100 is shown in Figure 4b, which displays that equilibrium value of surface tension is attained at 30 s for solutions with concentration between 1.6 and 4 cmc, which is in agreement with the results of Table 5. This

concentration is between corresponding values for  $C_{16}$ TAB and  $C_{16}$ TAB in 0.01 M NaBr.

Note that after the instability onset there are two competing processes: (i) a decrease in the surface concentration in the neck region due to possible local increase in the surface area and due to surface convective mass transfer (surface convection is directed from the neck up and down as liquid is expelled by the capillary pressure) and (ii) surfactant transfer to the interface and adsorption. The last process is driven by the difference in the chemical potential of molecules in the bulk and at the surface. There are two contributions to this difference: the decrease in the surface concentration due to bridge thinning and difference between dynamic and equilibrium adsorption attained at  $t = 30$  s. Therefore, in the case when dynamic surface tension at the instability onset is higher than the equilibrium surface tension the flux to the surface is higher when compared with solution of the same bulk concentration, but previously equilibrated with the surface. Maybe this is the reason that  $\sigma_{\text{ef}} \leq \sigma_{30}$  in the most of studied cases.

The direct measurement of surface tension at  $t = 30$  s instead of using the data from the time dependence of surface tension measured by maximum bubble pressure method (the only method giving the reliable data on the time scale of tens of seconds) was chosen in this study to avoid experimental errors related to the difference in experimental conditions. However, the comparison of the results in Figure 4 with those in Tables 4 and 5 shows a good agreement proving that the dynamic surface tension measured by the maximum bubble pressure method can be used for estimation of surface tension in the drop formation experiments.

It is instructive to compare the thinning kinetics for the solutions of different surfactants at the same concentration (Figure 5) keeping in mind that the surface activity of surfactants increases with a decrease in cmc. At the chosen concentration of 3 mM solution  $C_{10}$ TAB (the data are not shown) behaves similarly to pure water because at this concentration its equilibrium surface tension is close to that of pure water. The surface activity of  $C_{12}$ TAB is higher than that of  $C_{10}$ TAB; that is why at the same concentration it has lower surface tension and slower bridge kinetics. For  $C_{16}$ TAB the concentration of 3 mM exceeds the cmc value; that is why the kinetics for this solution are the slowest. It should be stressed that all three discussed solutions at this concentration behave as pure liquids with the surface tension equal to the equilibrium value, but the bridge thinning kinetics are different

**Table 3.** Equilibrium, Dynamic, and Effective Surface Tension at Formation and Detachment of Drops of Aqueous Solutions  $C_{16}$ TAB

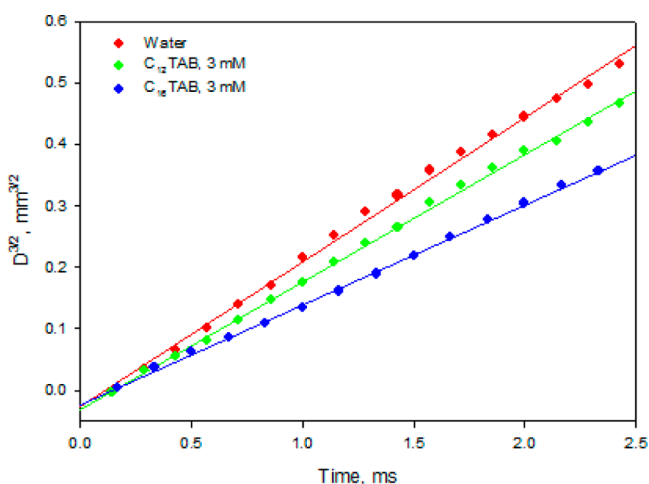
	$c$ , cmc							
	0	0.1	0.2	0.5	1	2	5	10
$\sigma_{\text{eq}}$ mN/m	72.5	67.3	60.4	47.9	37.5	37.5	37.5	37.5
$\sigma_{30}$ mN/m		70.9	64.0	51.6	39.4	38.3	37.3	37.2
$\sigma_{\text{ef}}$ mN/m		71.9	63.5	49.8	36.9	35.2	34.3	33.5

**Table 4. Equilibrium, Dynamic, and Effective Surface Tension at Formation and Detachment of Drops of Aqueous Solutions  $C_{16}TAB + 0.01 M NaBr$** 

	$c, \text{ cmc}$						
	0.335	0.67	1.67	3.35	6.7	16.7	33.5
$\sigma_{eq}$ mN/m	$45.4 \pm 0.2$	$40.5 \pm 0.2$	$37.2 \pm 0.2$	$37.2 \pm 0.2$	$37.2 \pm 0.2$	$37.2 \pm 0.2$	$37.2 \pm 0.2$
$\sigma_{30}$ mN/m	$61.8 \pm 2$	$47.9 \pm 0.8$	$37.8 \pm 0.5$	$36.7 \pm 0.2$	$36.5 \pm 0.2$	$36.5 \pm 0.2$	$36.3 \pm 0.2$
$\sigma_{ef}$ mN/m	$60.6 \pm 1.8$	$51.4 \pm 0.8$	$39.2 \pm 0.3$	$36.9 \pm 0.2$	$34.7 \pm 0.2$	$33.1 \pm 0.2$	$31.8 \pm 0.2$

**Table 5. Equilibrium, Dynamic, and Effective Surface Tension at Formation and Detachment of Drops of Aqueous Solutions Triton X-100**

	$c, \text{ cmc}$							
	0	0.08	0.16	0.4	0.8	1.6	4	8
$\sigma_{eq}$ mN/m	72.5	42.8	38.4	31.0	30.2	30.0	30.2	30.1
$\sigma_{30}$ mN/m		55.4	49.2	41.5	35.8	33.9	33.7	31.1
$\sigma_{ef}$ mN/m		53.9	49.7	41.4	33.8	29.3	28.5	28.5

**Figure 5.** Short-time kinetics of the neck thinning for the similar molar concentration, 3 mM, of surfactants in solution.

because of different surfactant activities, resulting in different equilibrium surface tensions. At lower molecular concentrations the behavior of all studied solutions should deviate from that of pure liquids, but for  $C_{10}TAB$  and  $C_{12}TAB$  these concentrations fall in the range where the difference between the surface tension of the surfactant solutions and the surface tension of water is negligible.

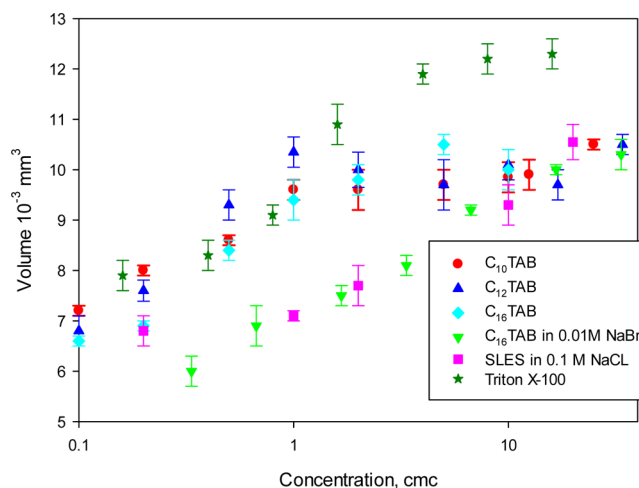
The analysis above reveals the possibilities for the prediction and control of the kinetics of surfactant-laden bridges. Under the conditions used in this study the depletion of a surfactant from the neck is much less important than the dynamic surface tension at the surfactant cmc above 0.1 mM. Therefore, for such surfactants the dynamic surface tension at the time scale of the drop formation can be used as an effective value of the surface tension. Obviously, the faster is the drop formation, the higher is the effective surface tension for the same surfactant solution. For surfactants of small cmc (0.1 mM and less), especially at concentrations below cmc depletion of the surfactant from the neck region can be noticeable and the thinning can occur faster than expected from the values of dynamic surface tension.

It should be stressed that the mutual importance of two processes, adsorption of surfactant on the growing drop surface and its depletion from the thinning neck, depends on the ratio of the full time of the drop formation and the time from the

instability onset to the moment of pinch-off. The last can be estimated from the characteristic time scale of the bridge thinning, which is proposed to be  $\tau_c = (\rho R^3/\sigma)^{1/2}$  for the inertial kinetics considered here.<sup>36</sup> For the bridges considered in this study  $\tau_c \sim 10$  ms. The time of the drop formation in this study was about  $\tau_d \sim 30$  s; therefore  $\tau_d/\tau_c \sim 3000$ . At a faster drop formation (smaller  $\tau_d/\tau_c$ ) the dynamic surface tension should become even more important, whereas at a slower one the depletion processes can come forward. It should be stressed that the above conclusion are made under condition  $We \ll 1$ .

The presence of a surfactant influences not only kinetics but also the limiting length of the bridge. The numerical simulations performed in ref 19 have shown that the limiting length of the surfactant-laden bridge should be larger than that of the surfactant-free bridge if an essential amount of surfactant remains on the neck surface in the vicinity of the pinch-off point. In all compositions studied here the limiting length of the surfactant-laden bridges increased with concentration and at concentrations above cmc was up to 8% higher than that of the surfactant free bridge, confirming that surfactant remains on the bridge surface.

The above results on the surfactant presence in the neck near the moment of pinch-off are confirmed by the results on the size of satellite droplets (Figure 6). The size of the satellite

**Figure 6.** Dependence of size of the satellite droplets on concentration.



droplets increases with the increase of surfactant concentration for all studied surfactants. For  $C_{10}$ TAB and  $C_{12}$ TAB the satellite size levels off at concentrations about cmc, at which, according to Figure 3, the effective surface tension in the neck region also levels off.

With a decrease in the cmc value, the concentration (in terms of cmc) at which the maximum size of the satellite drops is achieved increases. That means that even in the case when there is a large additional source of surfactant in the bulk (micelles), the surfactant solution does not always behave like a pure liquid. In the case of a small cmc, i.e., relatively small total amount of surfactant in the system, the processes of mass transfer and mass exchange have a considerable effect on the system dynamics even at concentrations far above cmc. It should be noted that the size of the satellite droplets is more sensitive to the depletion of surfactant from the neck immediately before the pinch-off than the kinetic data on the bridge thinning. The kinetic data are limited by the time and space resolution of the camera used, whereas the size of the satellite droplets reflects the whole kinetics up to the secondary pinch-off (near the capillary). This may explain why for  $C_{16}$ TAB in 0.01 M NaBr the size of the satellite droplets increases up to the concentration 33.5 cmc, whereas the observed kinetics of the bridges thinning does not change at concentrations above 6.7 cmc.

For Triton X-100  $\sigma_{ef}$  is the same for concentrations of 4 and 8 cmc, whereas the satellite size still increases by the increase of concentration. This can be a manifestation of the further depletion of the surfactant from the neck at the time scale below the time resolution of this study. It is noteworthy that the size of satellite droplets formed from SLES + 0.1 M NaCl solutions changes very similarly to that of  $C_{16}$ TAB + 0.01 M NaBr solutions, confirming that the dynamic processes near the pinch-off do not depend noticeably on the nature of surfactant. The maximum size of satellite droplets formed by Triton X-100 solutions is larger than that for ionic surfactants. This can be related to the lower surface tension at cmc for this surfactant (32 mN/m vs 37 mN/m for  $C_n$ TABs). On the other hand, the maximum size of satellites for  $C_{16}$ TAB in 0.01 M NaBr and SLES + 0.1 M NaCl is beyond the range of concentrations studied, and therefore the large size of satellites can be related to small cmc values of these surfactants. Appearance of large satellite droplets for such surfactants at concentrations far above cmc was predicted in a numerical study.<sup>24</sup>

The obtained here results are in good agreement with those available in the literature. In ref 26 the deformation and breakup of liquid bridges was studied for solutions of three different surfactants: sodium dodecyl sulfate, Silwet, and Heliosol at concentrations of 0.5 mass %, which was above cmc for all surfactants. It was shown that the kinetics near the pinch-off was slower than that of pure water for all three surfactants, confirming that surfactant was present in the neck. In ref 27 drop formation was studied for aqueous solutions of Triton X-100 surfactant at concentrations 0.01 and 0.05 mass % under different flow rates. It was shown that at small flow rates (corresponding to the considered here case) the behavior of the surfactant solutions is different from that of pure water, in particular the length of the bridges increases with the increase of surfactant concentration as does the size of the satellite droplets.

In summary, the dynamics near the pinch-off and the size of satellite droplets are determined by the equilibrium properties for the less active surfactants  $C_{10}$ TAB and  $C_{12}$ TAB (large cmc);

it is determined by the dynamic surface tension at the characteristic time scale of the drop formation for the surfactants of intermediate activity  $C_{16}$ TAB and Triton X-100, whereas for highly active surfactants  $C_{16}$ TAB in 0.01 M NaBr and SLES in 0.1 M NaCl the depletion of surfactant from the pinch-off region can be not negligible.

## CONCLUSIONS

The kinetics of thinning of liquid bridges during the formation of surfactant-laden aqueous drops was studied for solutions of five surfactants: cationic, anionic, and nonionic, with values of cmc in the range 0.1–60 mM. The investigated concentrations of the surfactants varied over 2 orders of magnitude including those below and above cmc. It was found that all studied solutions obey the inertial kinetics of bridge thinning near the pinch-off.

The proposed experimental protocol enabled comparison of the equilibrium surface tension, the surface tension before the instability onset, and the effective surface tension at the neck near the pinch-off point. It was found that in the limit of small flow rates ( $We \ll 1$ ) the less active surfactants with a high cmc values (15 mM and higher) behave like pure liquids with the surface tension equal to the equilibrium value even at the concentrations as small as 0.1 cmc. When cmc decreases (activity of surfactant increases), the effect of the dynamic surface tension becomes more important. The depletion of the surfactant from the neck region exceeded the experimental error only for the surfactant of the highest activity and lowest studied cmc, 0.1 mM. It was proposed that at the ratios of the time scale for the drop formation and that of bridge thinning similar to those used in this study ( $\sim 3000$ ) or smaller the dynamic surface tension on the time scale of the drop formation can be used as the effective value describing the bridge thinning.

For all studied surfactants the size of the satellite droplets increased with the increase of concentration and leveled off at the concentrations above cmc. The concentration (in terms of cmc), at which the maximum size of the satellite droplets was observed, increased with the decrease of the surfactant cmc. The results on the satellite droplets are in agreement with the kinetics data and the obtained values of the effective surface tension at the neck. However, for the surfactants with small value of cmc the satellite size continues to increase considerably even at concentrations far above cmc, when effective surface tension becomes nearly constant. This can be a manifestation of the further depletion of the surfactant from the neck at the time scale below the time resolution of this study.

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### Notes

The authors declare no competing financial interest.

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