

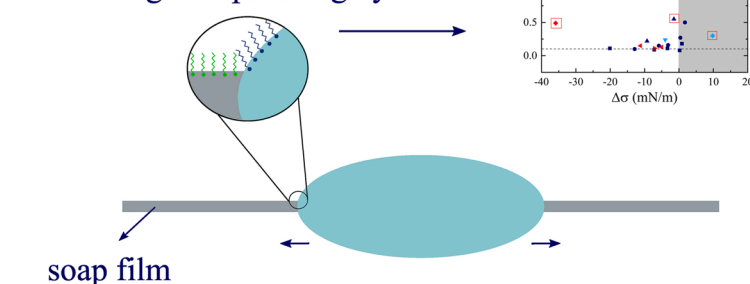
# Surfactant-surfactant interactions govern unusual Marangoni spreading on a soap film

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## GRAPHICAL ABSTRACT

Molecular structure of surfactants influencing the spreading dynamics



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## ABSTRACT

When a liquid spreads over another liquid, the presence of surfactants in one or both liquids can add to the complexity of the spreading dynamics. In this work, we investigate the influence of the surfactant-surfactant interaction on the Marangoni spreading. We systematically study the spreading behavior of various surfactant solutions with different molecular structures while keeping the macroscopic parameters of the solutions, such as surface tension and viscosity, equal. To simplify the system and to remove the influence of adsorption kinetics of the surfactants in the liquid phases and remove the effect of diffusion, we employ a unique configuration of “droplet on a soap film”. Our results show that when the surface tension gradient between the droplet and the soap film is not significantly large, the molecular structures and interactions between the surfactants in the droplet and the soap film dramatically influence the spreading scenario. Although, in general, the surface tension difference between the two solutions governs the spreading dynamics, for specific surfactants solutions, unusual spreading occurs that cannot be explained only by the surface tension differences.

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## 1. Introduction

When two liquids come into contact, the one with the lower surface tension spreads and covers the free surface to minimize the surface energy. The so-called Marangoni spreading is prevalent in nature and plays a crucial role in many industrial applications such as manufacturing detergents [1], pesticides [2], cosmetics, and food products [3]. The general approach to studying the dynamics of Marangoni spreading is to take the surface tension gradient as the driving force and scale it with the dissipative viscous term or inertial term, depending on the details of the system [4]. For pure liquids, the competition between the intermolecular cohesive and adhesive forces causes the tension exhibited by the interface, which for pure liquids such as water or alcohol is constant on large time scales. However, the presence of even a minute amount of surface-active agents, besides changing the initial value of the surface tension, imparts time dependency to the surface properties [5] and dramatically changes the spreading dynamics.

Surfactants are amphiphilic molecules with a polar hydrophilic head group and a hydrophobic tail. In an aqueous solution, they migrate to the interface to extend their hydrophobic tail out of the water continuum [6]. This leads to a decrease in surface tension even at very low concentrations of surfactants. An extensive body of research has been dedicated to studying the influence of surfactants and their adsorption kinetics on the surface characteristics [7–10], primarily due to the fact that many fluid systems in practice contain surface-active agents. For instance, many organic molecules have an amphiphilic nature, or in many applications, surfactants are used to alter the surface properties and foster foamability or liquid spreading. In a recent work, Petkova et al. [11] have shown that the adsorption kinetics and the physicochemical properties of the surfactants, in particular the ionic state of the surfactants, can have a dramatic influence on the foaming properties of the corresponding surfactant solutions.

In the past decades spreading and wetting in the presence of surfactants has attracted much attention [12–18]. Surfactants have diverse molecular structures, and their presence at the interface, besides weakening the surface tension, can change the surface chemistry, and a number of process that are not clearly related, for instance raising dynamics of a buoyant bubble [19] or fingering instabilities appearing at spreading front of a surfactant solution [20]. Among the extensive body of experimental and theoretical work on spreading and flow properties of surfactant solutions which have been carefully reviewed by Manikantan and Squires [19], a notable inconsistency can be found on whether the molecular structure of surface-active agents present at the spreading interfaces can influence the spreading dynamics. In several experimental studies considering the surface tension solely has failed to explain the spreading or wetting behavior of a surfactant solution [21–24]; therefore, the effect of the molecular structure and microscopic interaction of the surfactants had to be taken into account. In contrast, several other experimental and theoretical studies [14,25] indicate that the spreading dynamics of liquids on various surfaces are independent of the chemistry of the surfaces. The discrepancy lies in the diversity of the surface-active molecules and the complexity that they bring into the spreading process. Thus many aspects of the problem have remained unexplored, especially in the liquid-liquid spreading where surfactants are present on both liquid surfaces.

An intricate example is the spreading of surfactant solutions on suspended liquid films where both liquid phases contain surfactants. In our previous work [26], we have shown that when a droplet of surfactant solution is deposited on a soap film of a similar surfactant, it spreads and forms a new film in the center of the soap film. Depending on the initial surface tension difference between the two liquids, different spreading regimes were observed. When the droplet's surface tension was higher than the soap film ( $\Delta\sigma = \sigma_{\text{soap}} - \sigma_{\text{drop}} < 0$ ), spreading was driven by the Laplace pressure induced by the curvature at the rim of the droplet, resulting in slow-spreading dynamics that were explained by Tanner's model [27]. In contrast, when the surface tension of the soap

film was considerably higher than that of the droplet ( $\Delta\sigma > 0$ ), spreading took place in a much faster manner. We refer to the latter regime as the rapid spreading; in both regimes the radius of the spreading region evolved in time according to a power-law function ( $R \propto t^\alpha$ ) with the exponent  $\alpha$  differentiating the slow and rapid regimes. For the slow spreading, the exponent  $\alpha$  was close to 0.1, reciting Tanner's spreading law [27]. However, for the rapid spreading,  $\alpha$  started from 0.4 and increased with the increment of  $\Delta\sigma$ . The maximum  $\alpha$  for the system mentioned above was found to be 0.97. In that system, the surface tension gradient was considered as the driving force of the spreading, which was resisted by the inertial term; however, the effect of surfactant molecular structures and interactions was not investigated. The surfactants used in the droplet and the soap film were the same, or they had very similar and simple molecular structures with the same hydrophobic tail.

In this work, we systematically investigate the effect of surfactant-surfactant interactions and the surface charge on the Marangoni spreading on a soap film. We use the exact geometry of the previous study as it enables us to focus on the spreading dynamics in the absence of solid boundaries. Additionally, as we have shown in our previous work, in this configuration, after deposition on the soap film, the droplet forms a new film in the center of the soap and the contact area between the droplet and the soap film becomes limited to a circular rim around the droplet. In this configuration, because of the limited contact area and short time scales of the experiments, the effect of diffusion between the droplet and the soap film can be neglected.

We study a range of concentrations of various surfactants and deposit them on a soap film of SDS solution. We study the effect of molecular interaction and surface charge on the spreading dynamics besides the surface tension differences. Our results suggest that the interactions between the surfactants can shadow the effect of small surface tension gradients on the spreading. Therefore, our findings may help fine-tune the Marangoni flow dynamics to achieve desired spreading for applications that involve liquid-liquid spreading such as drug encapsulation and inkjet printing [28].

## 2. Experimental procedure and methods

To study the influence of surfactant charge on the Marangoni spreading we selected surfactants with various ionic states, including anionic, cationic and non-ionic surfactants. Solutions of three anionic surfactants: sodium dodecyl sulphate (SDS), ammonium lauryl sulphate (ALS) and dioctyl sulfosuccinate sodium salt (AOT), three cationic surfactants: Cetrimonium bromide (CTAB), trimethyloctylammonium bromide (OTAB), dodecyltrimethylammonium chloride (DTAC), and two non-ionic surfactants: Triton X100 and Silwet L77 were studied as working fluids. Aqueous solutions of the aforementioned surfactants were prepared at various concentrations by adding the required amount of powdered surfactant (or concentrated liquid in the case of ALS, Triton and Silwet) to Milli-Q water, and they were mixed overnight using a magnet stirrer. Concentrations were selected for each surfactant to keep the surface tension in a comparable range. The chemical composition and details of the hydrophobic parts of the surfactants are summarized in Table 1.

Since the time scale involved in the spreading process is short, the dynamic surface tension (DST) of the solutions should be addressed rather than the equilibrium surface tensions. The dynamic surface tension of the solutions was measured using a Kruss maximum bubble pressure tensiometer. The bubble pressure method has been widely used to measure DST of the fast decaying surface tension of low viscous solutions at short time scales. In this method, a small capillary is submerged into the desired solution to induce a bubble while the pressure inside the bubble is monitored using a pressure cage [29]. By increasing the volume of the bubble at a certain rate, its radius of curvature decreases while the inside pressure increases. When the radius of the bubble equals the radius of the capillary, the inside pressure reaches its

**Table 1**

Molecular structures and critical micellar concentrations of the surfactants with different ionic state.

	Surfactant	Molecular structure			CMC (mM)	Reference
		Hydrophilic tail	Polar head group	Released ion		
Anionic	SDS	CH <sub>3</sub> (CH) <sub>11</sub>	SO <sub>4</sub>	Na <sup>+</sup>	8	[30,31]
	ALS	CH <sub>3</sub> (CH) <sub>11</sub>	SO <sub>4</sub>	NH <sub>4</sub> <sup>+</sup>	7	[32]
	AOT	C <sub>19</sub> H <sub>37</sub> O <sub>2</sub>	(SO <sub>3</sub> )CO <sub>2</sub>	Na <sup>+</sup>	2.6	[33,34]
Cationic	OTAB	CH <sub>3</sub> (CH) <sub>7</sub>	N(CH <sub>3</sub> ) <sub>3</sub>	Br <sup>-</sup>	145	[35]
	CTAB	CH <sub>3</sub> (CH) <sub>15</sub>	N(CH <sub>3</sub> ) <sub>3</sub>	Br <sup>-</sup>	1	[30,31]
	DTAC	CH <sub>3</sub> (CH) <sub>11</sub>	N(CH <sub>3</sub> ) <sub>3</sub>	Cl <sup>-</sup>	22.6	[36,37]
Non-ionic	Triton X100	t-Oct-C <sub>6</sub> H <sub>4</sub> -(OCH <sub>2</sub> CH <sub>2</sub> ) <sub>x</sub> OH, x = 9–10			0.22	[38]
	Silwet	C <sub>24</sub> H <sub>39</sub> N <sub>3</sub> O <sub>3</sub> Si <sub>3</sub>			0.14	[39,40]

maximum. At the maximum pressure, the surface tension of the air-liquid interface can be calculated for a specific rate of volume change (surface age). With the help of this method, the dynamic surface tension can be measured for a range of timescales from 10 ms to several seconds.

The experimental set-up to study the spreading of surfactant solutions on the soap films is illustrated schematically in Fig. 1, left. In order to generate the soap film, a concentric cylinder (D = 40 mm) was dipped into a solution of 0.01 M SDS. Droplets of solutions of different surfactants were deposited on the soap film using a glass capillary. The following spreading was recorded using a Phantom V10 high-speed camera. The frames were image processed to track the radius of the spreading front in time. A typical spreading image is demonstrated in Fig. 1, right.

To study the effect of the molecular structures and ionic state of different surfactants on the spreading dynamics in macroscopic scales, we chose various surfactants from three categories, anionic, nonionic and cationic. In each class, several surfactants with different molecular structures were selected. In the next section, we explain the experimental results of each category separately, then we compare and discuss the spreading behavior of surfactants with the different ionic states.

### 3. Experimental results and discussion

#### 3.1. Anionic surfactant solutions

SDS, ALS and AOT were chosen as anionic surfactants, based on their molecular structures. SDS and ALS have an identical amphiphilic structure composed of a sulfate hydrophilic head group attached to a hydrophobic tail consisting of 12 carbons. Upon dissolving in water, SDS releases sodium ions while ALS releases ammonium ions. Comparing the spreading behavior of solutions of ALS and SDS with comparable surface tension can give us an insight into the influence of the released ion on the spreading.

AOT on the other hand has a very different molecular structure, in particular in the hydrophobic part. Two branched hydrophobic tails are attached to a polar sulphosuccinate head group in AOT. The polar head is comparable to that of SDS and ALS. However, the short and wide hydrophobic tail of AOT, makes it more surface-active and it can reduce

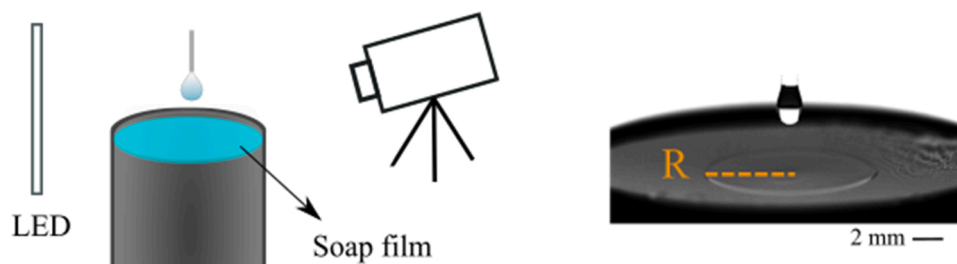
the surface tension more significantly in comparison to SDS and ALS at the same concentrations. The difference in the tails of AOT with respect to the other two surfactants also explains its lower CMC (2.6 mM) compared to SDS or ALS (8 and 7 mM respectively). In Fig. 2 (top row) dynamic surface tension of three surfactant solutions with various concentrations is demonstrated. As it is expected, by increasing the concentration of the surfactant, the surface tension decreased for all the solutions. However, the reduction of surface tension was more significant at higher concentrations of AOT. In all graphs, the surface tension of the soap film, composed of 0.01 M SDS, is illustrated by hollow circles as a reference.

To study the spreading dynamics, droplets of the surfactant solutions were deposited on a soap film and the radius of the spreading front (R) was tracked in time. In Fig. 2 (bottom row), R is shown as a function of time for various concentrations of each surfactant on a logarithmic scale. It should be noted that the origin of time for the spreading experiments was the instant that the droplet contacted the soap film. Therefore, for the first few milliseconds, although the droplet was in contact with the soap film, it was not fully detached from the capillary. This has caused the deviation from the general trends in the spreading data points for the initial 10–20 ms.

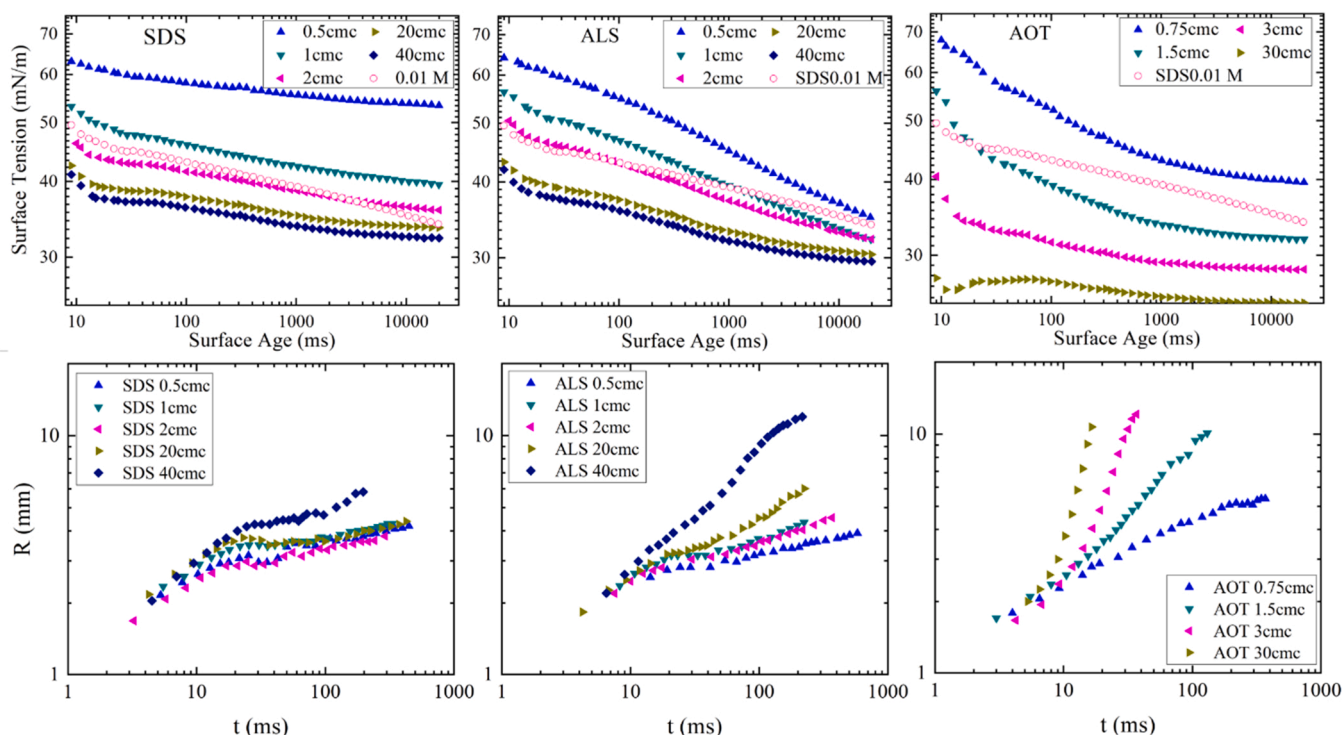
For all concentrations of SDS, the droplet formed a lens on the soap film and slowly spread in time. Power-law functions were fitted to the data series and exponent  $\alpha$  was approximately 0.1 for all the series indicating that the spreading was in the slow regime (Tanner's law). ALS solutions with concentrations of 0.5, 1 and 2 CMC followed the same trend as SDS solutions, however, for the concentrations of 20 and 40 CMC ALS, rapid spreading was observed with exponents of 0.27 and 0.5 respectively.

As it can be seen from the graphs, spreading dynamics were substantially faster for AOT solutions. Rapid spreading was observed for all the selected concentrations. Even the 0.75 CMC AOT solution despite its larger surface tension than that of the soap film showed a rapid spreading. The exponent  $\alpha$  increased from 0.5 for a concentration of 0.75 CMC to about 2 for 30 CMC.

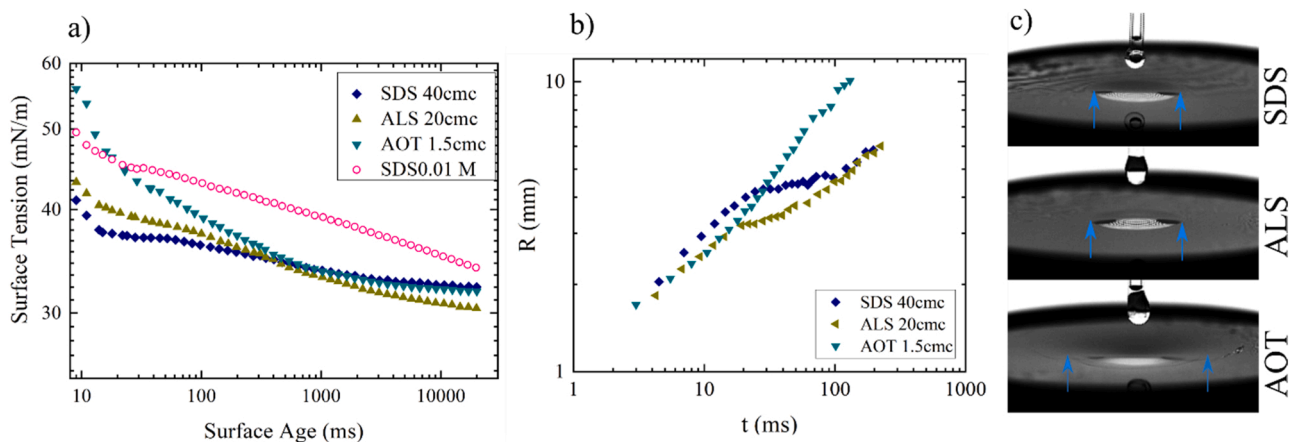
In Fig. 3 (left) the dynamic surface tensions of SDS 40 CMC, ALS 20 CMC and AOT 3CMC solutions are presented as a function of time. These three solutions showed similar DST, especially after 500 ms with ALS



**Fig. 1.** (Right) schematic view of the experimental set-up. A droplet of surfactant solution is gently deposited on the soap film while a high-speed camera records the following spreading. (Left) spreading of a droplet of Triton X100 ( $c = 20$  CMC) on a soap film of 0.01 M SDS. The radius of the spreading front (R) is indicated with a dashed line.



**Fig. 2.** (Top) Dynamic surface tension of various concentrations of SDS, ALS and AOT. (Bottom) Spreading radius of the same surfactant solutions on a soap film of SDS 0.01 M. The surface age presented on the axis of the surface tension graphs corresponds to the time after deposition of the droplet on the soap film which is shown on the horizontal axis of graphs on the bottom row (R versus t). Maximum error for dynamic surface tension data point is  $\pm 0.5$  mN/m.



**Fig. 3.** (a) Dynamic surface tension of SDS 40 CMC, ALS 20 CMC and AOT 2 CMC solutions. At selected concentrations, the three solutions showed the most similarity in the surface tension behavior. (b) Evolution of the radius of spreading front as a function of time for the above solutions on a soap film of 0.01 M SDS. Although the surface tension difference between AOT solution and the soap film is smaller than that of SDS and ALS before 500 ms, it spreads faster. Column of images on the right (c) shows the droplet of the three surfactant solutions, 100 ms after deposition on the soap film. The arrows indicating the spreading front. Maximum error for dynamic surface tension data point is  $\pm 0.5$  mN/m.

having slightly lower surface tension than the others, however, the difference didn't surpass 2 mN/m even at 20 s where it was maximum.

At short time scales, from 10 ms to 500 ms, (comparable to the time scale of a typical spreading), AOT showed a higher surface tension than the others, starting from 54 mN/m at 10 ms and steeply decreasing to almost 34 mN/m at 500 ms. In contrast, ALS and SDS started with lower surface tension at 10 ms but with slower dynamics, they reached the same surface tension of AOT at 500 ms. Therefore, the surface tension differences between these solutions and the soap film were negligible, suggesting similar spreading dynamics based on the previous studies [26]. Surprisingly, the spreading radius in these three samples grew with different exponents of 0.18 and 0.27 and 1.32 respectively. Although the

AOT solution had a smaller surface tension gradient than the soap film and even a negative surface tension difference for the time scales below 20 ms, it spread much faster than both SDS and ALS solutions. The exceptional spreading behavior of AOT has also been reported in previous studies of spreading on solid surfaces [41–43]. We know all these three surfactants have the same electric charge, however, AOT has two aliphatic tails and thus forms a thicker molecular chain. The unusual spreading of AOT can be related to the fact that the larger hydrophobic tails of AOT molecules are more difficult to pack on the surface compared to the SDS molecules in the soap film. These results indicate that surfactant's morphology and their interactions on the contact line can play a more important role than the surface tension differences in



the spreading dynamics, specifically when the surface tension differences are not significant.

### 3.2. Non-ionic surfactant solutions

For the non-ionic group of surfactants, we chose Silwet and Triton x100 which are widely used for industrial applications. Silwet is a commercial surfactant and known as a super spreader as it can readily spread on a variety of surfaces [44]. It also has broad applications in the agriculture and pesticide industry to assist the spreading of aqueous solutions on hydrophobic surfaces of leaves [18]. Silwet molecules consist of a trisiloxane head group attached to a short hydrophobic tail. For instance, the size of the hydrophobic tail of Silwet (9.7 Å) is much shorter than the hydrophobic tail of SDS ( $C_{12}H_{25}$  with a length of 15 Å) [45]. Triton on the other hand, is a common lab detergent and is often used for DNA extraction [46] and protein purification [47]. An aromatic ring connected to a polyethylene oxide chain plays the role of polar head group for Triton. Its hydrophobic tail has a branched structure consisting of 8 carbons.

The dynamic surface tension of these two surfactants at different concentrations is illustrated in Fig. 4 (left). As it can be seen, solutions containing Silwet have in general a lower surface tension compared to the solutions of Triton. The rate at which the surface tension decreases at the early times is also higher for Silwet solutions. By increasing the concentration to several CMC, the surface tension of the solutions converge to the same value at higher surface ages. At a time scale of 20 s, solutions of 70 and 700 CMC Silwet showed similar surface tensions about 20 mN/m, while surface tension of Triton solutions converged to 31 mN/m.

In Fig. 4 (right) radius of the spreading fronts of droplets containing Silwet and Triton at various concentrations are demonstrated when they are deposited on a soap film of 0.01 M SDS. For Triton at 2 CMC, the spreading dynamics were slow with a spreading exponent of 0.24, however, it was slightly faster than Tanner's regime. By increasing the concentration of Triton in the droplet, the surface tension difference between the droplet and the soap film increased and the spreading became faster. The spreading exponent for droplets of Triton 20 and 80 CMC was 1.1 and 1.2 respectively. Solutions of Silwet followed the same trend. For Silwet 70 CMC, the spreading exponent was 0.3 approximately matching the spreading of Triton 2 CMC. At a higher concentration of 700 CMC the surface tension difference was pronounced and the spreading exponent increased to 1.56. As it was mentioned for the anionic surfactants spreading, the first few milliseconds the droplet was still attached to the capillary, therefore, the initial data points were neglected during fitting power-law functions.

According to the spreading graph in Fig. 4, in the slow spreading regime, the evolution of the spreading front, for Silwet 70 CMC and Triton 2 CMC were closely similar. In the rapid spreading regime Silwet 700 CMC and Triton 80 CMC were nearly identical. However, these solutions had very different surface tensions. This clearly shows the influence of the size of the hydrophobic tail and the molecular interaction between hydrophobic parts of the two surfactants in the droplet and soap film could be dominant with respect to the effect of surface tension difference on the spreading dynamics on a soap film.

### 3.3. Cationic surfactant solutions

All cationic surfactants studied in this work consist of trimethylamine as their polar head group and a hydrocarbon chain as their hydrophobic tail. This allows us to solely study how the structure of the hydrophobic tail of surfactants influences the spreading of the droplet on the soap film. The length of the hydrocarbon chain varied for each surfactant. OTAB with only 8 carbon in its hydrophobic tail, had the shortest hydrocarbon chain. DTAC and CTAB with 12 and 16 carbon respectively had relatively larger hydrophobic parts. In Table 1, the chemical composition and details of the molecular structure of the mentioned surfactants are presented.

Fig. 5 (left), shows the dynamic surface tension of aqueous solutions of the three cationic surfactants. Solutions containing OTAB and DTAC showed approximately constant surface tension within the time scales of measurements, except for 1 CMC DTAC that its surface tension dropped from 47 mN/m at 2 s to 37 mN/m at 20 s. Solution of 0.1 CMC OTAB with a surface tension of 72 mN/m had the highest surface tension among cationic surfactant solutions. In contrast, 10 CMC DTAC solution has the lowest surface tension in the time window of 10–200 ms.

In the right panel of Fig. 5, the radius of spreading front of all four solutions is presented as a function of time. Although OTAB solution had a higher surface tension than the soap film it was the only solution that showed rapid spreading with a spreading exponent of 0.49. OTAB also had a considerably higher critical micellar concentration compared to the rest of the surfactants studied here, indicating the lower affinity of the OTAB molecules to each other and the higher potential energy that is needed for OTAB molecules to form micelles.

Spreading of the rest of the cationic solutions was in the slow regime and was governed by Laplace pressure, with the spreading exponent of approximately 0.1.

### 3.4. General discussion

A summary of the spreading exponent of all the surfactant studied in

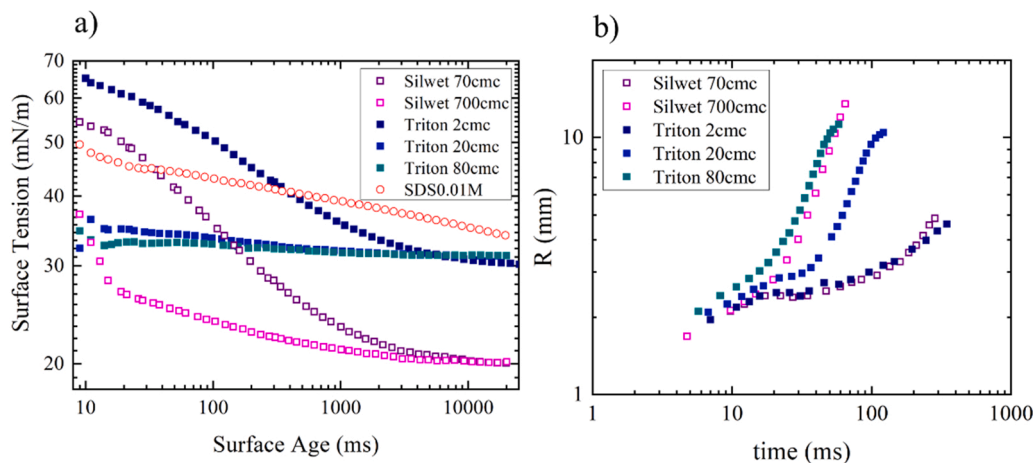
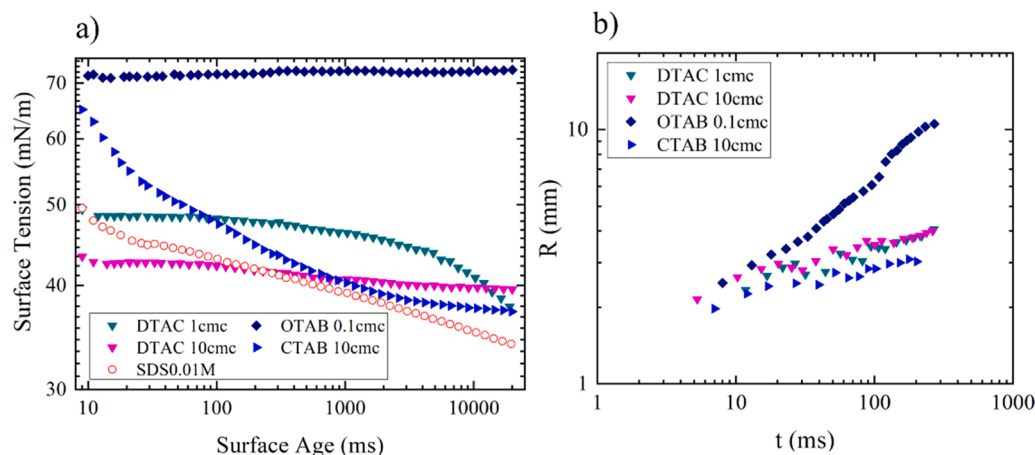


Fig. 4. (a) Dynamic surface tension of two nonionic surfactant, Triton X100 and Silwet at various concentrations. (b) Radius of the spreading front as a function of time for the non-ionic surfactant solutions on a soap film of 0.01 M SDS. Maximum error for dynamic surface tension data point is  $\pm 0.5$  mN/m.



**Fig. 5.** (a) Dynamic surface tension of cationic surfactants. (b) Evolution of the radius of the spreading front of cationic surfactant solutions as a function of time, when deposited on a soap film of 0.01 M SDS. Maximum error for dynamic surface tension data point is  $\pm 0.5$  mN/m.

this work is presented in Fig. 6 as a function of surface tension difference between the droplet and the soap film ( $\Delta\sigma$ ). The effective surface tension difference ( $\Delta\sigma$ ) between the droplets and the soap film was determined as follows: for the droplets, we considered a characteristic time scale given by  $\tau = L/u$ , where  $u$  is the average speed of the spreading film and  $L$ , the maximum radius of the spreading film for each experiment. For the SDS soap film, surface tension at 5 s was considered to calculate  $\Delta\sigma$  since in our experiments there was on average a 5 s gap between generating the soap film and deposition of the surfactants droplets.

As it can be seen in the graph for droplets with  $\Delta\sigma < 0$  spreading exponent was scattered around 0.1 with a few exceptions and with increasing  $\Delta\sigma$  to above zero the spreading dynamics were accelerated and  $\alpha$  increased sharply. The general trend observed here corroborates with the results reported in previous studies [26,48].

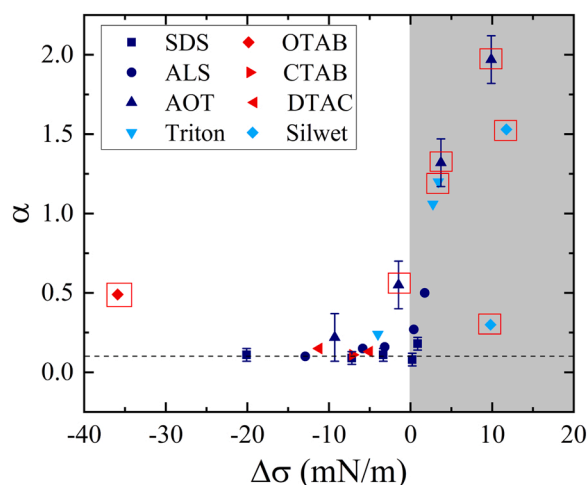
However, a few exceptions are exhibiting unusual spreading dynamics. These deviations which are highlighted by a square around the data point cannot be explained by solely considering the surface tension gradient. For instance, the spreading exponents for AOT solutions were in general much higher than what was expected. For AOT solutions with  $\Delta\sigma > 0$ ,  $\alpha$  was above 1, specifically for the highest concentration of AOT,

$\alpha$  was approximately 2 which was significantly higher than what has been reported in the previous studies. Even with  $\Delta\sigma < 0$  for AOT 1.5 CMC, rapid spreading was observed with an  $\alpha$  of 0.55, suggesting that the molecular interaction between AOT and SDS molecules were assisting Laplace pressure to accelerate the spreading and dominate the effect of negative surface tension difference. The case of OTAB was even more intriguing. Solution of 0.1 CMC OTAB, showed a fast spreading with an exponent of 0.49 despite its strongly negative surface tension difference with respect to the soap film. Triton also showed rapid spreading for all the concentrations studied here. Although for lowest concentrations of Triton  $\Delta\sigma$  was negative, the power-law exponent was higher than 0.1. Silwet solutions have surface tensions that are considerably lower than the soap film, therefore, they showed rapid spreading. Increasing the concentration of Silwet from 70 CMC to 700 CMC only led to a small change in  $\Delta\sigma$ . However, it caused a sharp increase in the spreading exponent from 0.3 to 1.53. This very rapid increase of the exponent for a very slight change in the surface tension difference cannot be explained based on the previous studies.

#### 4. Conclusion

The spreading behavior of various surfactant solutions was studied employing a unique geometry of “droplet on a soap film”. The influence of the ionic state of the surfactants on the spreading dynamics was investigated by studying the spreading of solutions of various cationic, anionic, and, non-ionic surfactants. The effect of surfactant-surfactant interaction on the spreading was probed by comparing the spreading dynamics of surfactant solutions with the similar macroscopic parameter (surface tension and viscosity) but with different molecular structure of the surfactant. An exceptionally rapid spreading behavior was observed for surfactants in each ionic category (AOT, Silwet and OTAB from anionic, non-ionic and cationic categories, respectively).

It can be concluded that although the surface tension difference between two surfactant solutions can outline the general trends of spreading (slow and rapid regimes), it cannot precisely predict the onset of rapid spreading. Our results show for an accurate prediction of spreading behaviors of surfactant solutions, a thorough understanding of molecular interactions between surfactants at both liquid phases is required. In particular, when the surface tension difference between the two fluids is not significant, the effect of molecular interactions is emphasized and is needed to be considered. This study raises new questions and opens a new avenue for studying the liquid-liquid spreading in the presence of surfactants. These results might be useful for tuning the Marangoni flow dynamics to achieve desired spreading for applications in drug encapsulation and inkjet printing.



**Fig. 6.** The power-law exponent ( $\alpha$ ) for the spreading of droplets of various surfactant solutions deposited on a soap film of 0.01 M SDS. In the grey region, surface tension difference is promoting the spreading. The horizontal dashed line represents the Tanner's regime with an exponent of 0.1. The unusual spreading exponents are highlighted by a red square around them. Typical error bars for two sets of data (SDS with small uncertainty and AOT with the largest error bar) are shown on the graph.

## CRediT authorship contribution statement

**Melika Motaghian:** Experiments, data analysis, modelling and writing. **Erik van der Linden:** Scientific discussion, modelling, editing and commenting. **Mehdi Habibi:** Supervision, scientific discussion, modelling, editing and commenting.

## Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: The project is funded by Netherlands Organization for Scientific Research through NWO-VIDI grant No. 680-47-548/983.

## Data Availability

Data will be made available on request.

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