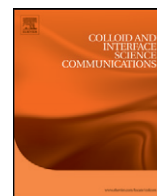




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Rapid Communication

Surfactant Enhanced Spreading: Catanionic Mixture

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ABSTRACT

The spreading behaviour of aqueous solutions of mixture of two surfactants sodium 1-decane sulfonate and dodecyltrimethylammonium bromide is investigated on two hydrophobic substrates. The solutions demonstrate rapid complete wetting on polyethylene film and only partial wetting on silanized glass. It is shown that the spreading behaviour depends crucially on the age of the mixture and is determined by the crystal growth affecting the surface tension of solution. An increase of surface tension with time results in an interesting phenomenon – a transition from complete to partial wetting, that is, a droplet of freshly prepared mixture first spreads completely but after some time the solution assembles into the droplet again.

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1. Introduction

Trisiloxane surfactants referred to as superspreaders till now are the best agents to enhance spreading of aqueous solutions over hydrophobic surfaces [1,2]. The solutions of these surfactants can wet such hydrophobic surfaces as polyethylene, and polypropylene, demonstrating a very rapid spreading over large area: the typical spreading time ~1 min and the spreading factor, which is the ratio of the area covered by the surfactant solution to the area of the base of pure water droplet of the same volume, is about 100 [2]. After a short inertial stage of spreading the area increases linearly with time with spreading rate reaching 100 mm²/s [1], which is much faster than predicted by Tanner for pure liquids $S \sim t^{0.2}$ [3] in the case of complete wetting. The unusual spreading properties of trisiloxane solutions have been ascribed to the hammer-shaped molecular geometry of trisiloxane, its high affinity to substrates, formation of bilayers and vesicles instead of micelles in the bulk phase, fast adsorption kinetics, and very low surface tension [1,2,4,5].

First of all the conditions for complete wetting are to be satisfied to make superspreading possible. This means that the spreading coefficient S has to be positive [6]:

$$S = \gamma_{sv} - (\gamma_{sl} + \gamma_{lv}) > 0, \quad (1)$$

where γ_{sv} , γ_{sl} and γ_{lv} are the solid/vapour, solid/liquid and liquid/vapour surface tensions respectively. It should be emphasised that a positive value of the spreading coefficient is necessary, but not a sufficient

condition for superspreading. Very fast spreading kinetics of trisiloxanes (“superspreading”) is to be explained. It has been shown that the Marangoni effect (flow generated by the surface tension gradient) is an essential part of superspreading mechanism giving $S \sim t^{0.5}$ [7,8]. Surfactant adsorption kinetics is of importance for establishing Marangoni flow as it is responsible for formation of surface concentration gradients [9]. However there should be other important parameters involved in the explanation, for example even faster spreading rates than $S \sim t^{0.5}$ or a maximum in the spreading rate observed for moderately hydrophobic substrates [1]. The recently published theoretical results [10] give a good promise that the complete mechanism will be explained in the near future.

According to Eq. (1) an increase in γ_{sv} should result in an increase of the spreading coefficient and it could therefore be expected that broader range of surfactant solutions will demonstrate complete wetting behaviour on less hydrophobic substrates. Indeed, it was found that solutions of ethoxilated alcohols [11,12], glucoside surfactants [12] and even some ionic surfactants, didodecylidimethyl ammonium bromide (DDAB) and sodium bis(2-ethylhexyl) sulfosuccinate (AOT) [13] demonstrate very similar spreading properties to trisiloxanes, but on solid surfaces of higher energy, i.e. less hydrophobic than polypropylene and polyethylene. The term “surfactant enhanced spreading” was introduced in Refs [11–13] to emphasise that the ability of spreading fast is not the property of trisiloxane surfactants only.

Adsorption of surfactants can decrease both γ_{sl} and γ_{lv} and in this way promotes spreading [14]. The surface tension of aqueous trisiloxane solutions falls down to ~20 mN/m [15] which is much lower than the minimum of surface tension demonstrated by common hydrocarbon surfactants (>30 mN/m [1]). That is why trisiloxanes are

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expected to spread on more hydrophobic substrates than common hydrocarbon surfactants. It is known, however, that fluorosurfactants, despite the extremely low surface tension of aqueous solutions, equal or even lower than that of trisiloxanes, do not spread on polypropylene and polyethylene, having much higher contact angles on these substrates than can be expected [4,6]. It has been assumed that the low adsorption on solid/liquid or possible adsorption on solid/vapour interfaces is responsible for this poor wetting performance [16].

The importance of adsorption on solid/liquid interfaces was proven in [17] where the wetting properties of a broad range of cationic surfactants were studied. Catanionic surfactants, which are a mixture of cationic and anionic surfactants, demonstrate considerable synergism in adsorption behaviour. It was shown in [17] that the spreading factor (ratio of area wetted by surfactant solution to that of pure water) for some cationic mixtures is comparable to trisiloxane solutions and even exceeds it when being spread on polyethylene. However, individual surfactants from the mixture do not wet polyethylene. Investigation of adsorption on polyethylene in the range of low concentrations showed a considerable increase in adsorption for the mixture as compared with individual surfactants. Therefore, it was concluded that the adsorption on solid/liquid interface is crucial for spreading performance. Adsorption at higher concentrations, when enhanced spreading was observed, was not investigated because the solubility in water is much lower for the mixture than for the individual surfactants. To the best of our knowledge, [17] was the only publication on surfactant enhanced spreading for cationic mixtures. Because of precipitation (crystallisation) the spreading in [17] was studied not for premixed solutions, but in a two-step procedure, applying a droplet of one surfactant on top of another.

Below we consider spreading of binary mixture of cationic surfactants to answer the following questions: i) Is it possible to observe an enhanced spreading for premixed solutions or is the two-step procedure crucial for it? ii) Is the enhanced spreading related to the surface tension? iii) What is the spreading kinetics for cationic surfactant solutions? and vi) How does precipitation/crystallisation affect the spreading performance?

2. Experimental

Dodecyltrimethylammonium bromide, DoTAB, (Fluka, >99%), sodium 1-decane sulfonate, SDeS, (Fluka, >99%), BREAK-THRU S 278, BT-278, (Evonik), trimethoxy(octadecyl)silane (Sigma-Aldrich, >90%), heptane (HCROMASOLV®, Sigma-Aldrich, >99%), octanol (HCROMASOLV®, Sigma-Aldrich, >99%), iso-propanol (Fisher Scientific, analytical reagent grade), and ammonia hydroxide solution (Sigma-Aldrich, 28–30%) have been used as purchased. Solutions of individual surfactants have been prepared in ultra-pure water produced by Millipore Q (15 MΩ cm). Solutions have been mixed immediately before each spreading experiment. We used 1:1 mixtures by weight (molar ratio SDeS:DoTAB ~ 1.26) demonstrating the best spreading characteristics according to [17]. We also used the two-step procedure in which the results do not depend on order of deposition of droplets: a droplet of SDeS on the top of a DoTAB droplet or the opposite [17].

Substrates used were polyethylene film (PE) and hydrophobised glass slides (HG). Low density (LDPE) polyethylene film, thickness 0.05 mm (GoodFellow) has been cut into pieces 4 × 4 cm, washed for 15 min with iso-propanol in ultrasonic bath, rinsed with plenty of water and dried in an oven at 50 °C. Microscope glass slides (Fisher Scientific) have been soaked for 1 h in concentrated ammonia hydroxide solution, thoroughly washed with water in ultrasonic bath, dried in an oven at 140 °C for 1 h, silanized by immersion in a 5 mM trimethoxy(octadecyl)silane solution in heptane for 24 h, washed 3 times with heptane and dried in an oven at 70 °C for 1 h [18]. Hydrophobicity of substrates was estimated by measuring the contact angle of pure water and octanol.

Contact angle of pure water on both substrates was nearly identical $102 \pm 3^\circ$. This observation was not expected because PE surface is composed mainly of CH₂ groups, whereas HG surface is mostly composed of CH₃ groups, that is, HG surface is supposed to have lower surface energy. That is why octanol, having much lower surface energy (~27 mN/m at room temperature) than water (~72 mN/m at room temperature) was used for an additional test. This test has shown that octanol spreads completely on PE substrate, whereas a partial wetting with contact angle $30 \pm 2^\circ$ was observed on HG substrate.

This difference can be explained if we take into account that HG is a smooth substrate (surface roughness $R_{\text{rms}} = 1.9 \pm 0.2$ nm, as measured by AFM, scanned area $80 \times 80 \mu\text{m}$) whereas PE film possesses an essential roughness, $R_{\text{rms}} = 34.5 \pm 1.2$ nm. The apparent contact angle of a non-wetting liquid (with contact angle larger than 90°) increases with an increase in roughness according to both Cassie–Baxter and Wenzel's models, whereas the contact angle of a wetting liquid (with contact angle smaller than 90°) according to Wenzel's model decreases with an increase in roughness [19]. Therefore PE film due to its roughness demonstrates overestimated contact angle for water and underestimated one for octanol and it can be concluded that it is less hydrophobic than HG surface.

Liquid–air interfacial tension has been measured using DSA100 (Kruss) using drop shape analysis method on buoyant bubble for both freshly prepared mixtures and after ageing for 48 h, to get a solution in equilibrium with crystals (precipitate)/micelles. After the solution was left in a sealed container for 48 h most crystals precipitated. Then the sample of saturated solution was taken carefully from the upper part of the container and surface tension was measured on this sample. There still have been some crystals that remained in the solution, but not too much and they do not disturb the surface tension measurement. The difference in the surface tension of samples of different concentrations after ageing did not exceed 1.2 mN/m, which is within the experimental error for the surface tension measurements (maximum standard deviation ± 0.8 mN/m).

Contact angles were measured using the same DSA100 (Kruss). The kinetics of spreading was investigated using a home-made device capturing images of spreading area from above with video camera at the rate of 30 fps. The spread area on selected images was determined using ImageJ free software.

Most of the experiments were performed at room conditions (temperature 23 ± 1 °C, relative humidity $53 \pm 2\%$), but some of them in a closed chamber with 100% humidity.

3. Results and Discussion

Mixtures of cationic and anionic surfactants demonstrate two types of aggregation processes: crystallisation/precipitation and micellization in the broad sense, because not only micelles, but vesicles and/or bilayers can be formed as well [20]. We observed formation of plate-like crystals at all concentrations studied (≥ 0.1 g/l). Curve 2 in Fig. 1 demonstrates clearly that the surface tension of the cationic solutions at equilibrium remains constant at concentrations ≥ 0.1 g/l and its value is rather high, ~46 mN/m. That is why aged mixed solutions do not spread on any of the substrates studied and show high contact angles $84 \pm 4^\circ$ on PE.

However, immediately after mixing the clear solutions without any crystals/precipitate visible were obtained with much lower surface tensions, close to that of trisiloxanes (curve 1 in Fig. 1) because crystallisation process takes a certain time to complete. Note, that the surface tension of micellar solutions of individual ionic surfactants used is much higher, about 37 mN/m [21]. Fig. 1 shows that surface tension of freshly mixed solutions (curve 1) levels off at the concentration around 0.2 g/l, which can be considered as critical micelles concentration (CMC).

Very good wetting properties of freshly mixed solutions, similar to those of trisiloxane solutions, can be expected based on surface tension data presented by curve 1 in Fig. 1. Indeed, the complete wetting was

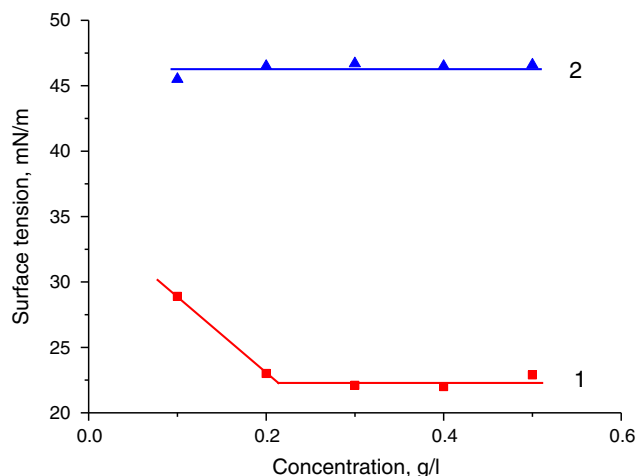


Fig. 1. Surface tension vs concentration for SDeS/DoTAB aqueous solutions: 1 – immediately after mixing, 2 – solutions at equilibrium with crystals.

observed on PE at concentrations above 0.2 g/l. Noteworthy, that in this case critical wetting concentration, CWC, (concentration above which complete wetting occurs) coincides or at least is very close to CMC. For comparison, please remind that for trisiloxanes the CWC is several times higher than the CMC [22].

Only partial wetting with contact angle $26 \pm 3^\circ$ occurs on HG in the case of binary mixture of surfactants. Therefore it can be concluded that the spreading behaviour of cationic aqueous solution of SDeS/DoTAB is very similar to that of octanol with the close contact angle on HG and complete wetting on PE.

The trisiloxane surfactant BT-278 is a better spreading agent than the cationic mixture under consideration because it spreads completely over both PE and HG. This may be because of its slightly lower surface tension, ~ 20 mN/m, vs ~ 22.5 mN/m for the cationic mixture and possibly better adsorption on liquid/solid interface. Note, $\gamma_{lv}\cos(\theta)$ for cationic solution on HG ~ 20 mN/m, which is close to BT-278 surface tension.

The final spreading area for the cationic solution increases with the concentration (Fig. 2), as the rate of spreading does, which is the slope of curves in Fig. 3. It seems that the spreading area on HG decreases slightly at large concentrations. However this decrease is of order of the experimental error. Therefore we do not discuss here the possible reasons for such behaviour before proving it by using other substrates or other surfactant mixtures. The data

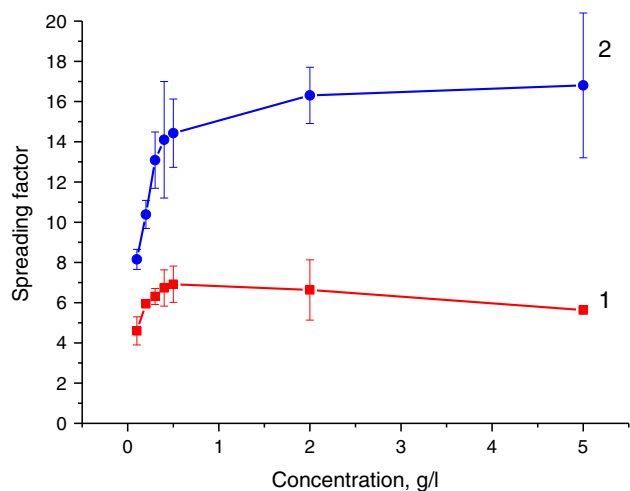


Fig. 2. Spreading factor vs concentration for aqueous SDeS/DoTAB solutions: 1 – on HG, 2 – on PE.

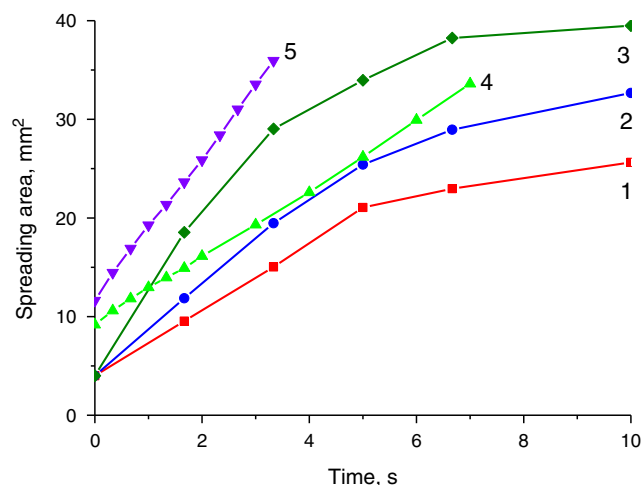


Fig. 3. Kinetics of spreading on PE substrate: SDeS/DoTAB, 1 – 0.3 g/l, 2 – 0.4 g/l, 3 – 2 g/l; BT-278, 4 – 0.3 g/l, 5 – 0.5 g/l.

presented in Figs. 2 and 3 are the average of at least 5 measurements performed by a two-step procedure. The maximum spreading factor on PE substrate is around 18, which is several times lower than the reported spreading factors for trisiloxanes [1,2] and 20 times lower than it was reported in [17] for the same cationic mixture on food-bag polyethylene. Such a large difference with [17] can be due to the difference in substrate roughness and chemistry (supermarket bags have been used in [17]). Another reason can be the difference in the experimental procedure. The maximum spreading factor for BT-278 on our PE substrate was more than 3 times larger than for cationic mixture, and the thickness of the spread layer estimated from the known droplet volume and area of spreading was 3 times smaller, $17 \mu\text{m}$ for BT-278 vs $48 \mu\text{m}$ for SDeS/DoTAB.

In Fig. 3 the kinetics of spreading of the cationic mixture is compared with that of trisiloxane superspreader BT-278. Initially for both surfactants the area increases linearly with time and spreading rate (the slope of dependences in Fig. 3) is rather similar for both surfactants. However, for SDeS/DoTAB solutions spreading rate slows down after 3–5 s whereas BT-278 solutions keep a high spreading rate much longer. Most probably this is because of crystal formation in the mixed solutions. The crystals cause depletion of bulk concentration, but more importantly they can co-adsorb onto the liquid/air interface retarding it and in this way increasing the resistance to spreading. The supply of crystals to the interface is due to the thermal convection, which is unavoidable even in a covered cuvette. Slow convective motion of crystals was observed during the surface tension measurement. The evidence of crystal adsorption and surface retardation is given in Fig. 4. The snapshots have been taken during a surface tension measurement. Initially despite the presence of crystals the bubble keeps the shape obeying the Young–Laplace equation (Fig. 4a), but after a certain time the bubble surface becomes rather rigid, the bubble cannot keep the Laplacian shape anymore, preventing surface tension measurement (Fig. 4b). If a new bubble is formed in the same solution it again goes through the stages presented in Fig. 4a and b.

Typical characteristic times of micellization are sufficiently short, from milliseconds to tens of seconds [23], whereas nucleation and crystal growth proceed more slowly. When the crystals grow in a micellar solution, a decrease in the concentration of monomers due to crystallisation is compensated by the micelles' destruction and, as a result, surface tension remains constant until there are still micelles remaining in the solution. It is confirmed by our observations: there was no increase in surface tension during several minutes of the measurement despite the visible crystal growth. The difference in the timescales of micellization and crystal growth results in an interesting phenomenon: a transition from complete to partial

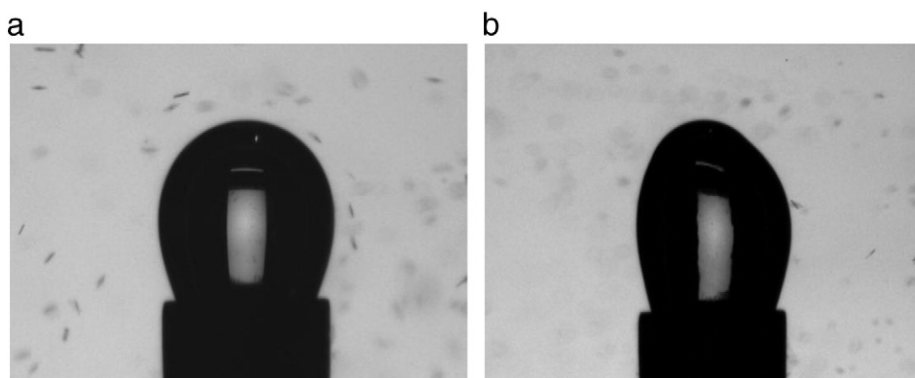


Fig. 4. An air bubble in SDeS/DoTAB 0.2 g/l solution: a – the Laplacian shape immediately after the bubble formation, b – the non-Laplacian shape caused by crystal adsorption.

wetting in the course of spreading presented in Fig. 5. A droplet of SDeS/DoTAB freshly mixed solution spreads very quickly over PE substrate. However, after some time due to the crystal growth the concentration decreases below CMC and the conditions for complete wetting are not fulfilled any more: spreading is followed by dewetting, when the solution assembles into the droplet again as shown in Fig. 5. The mechanism of this phenomenon is related to crystallisation, because the time lag between the complete spreading of the droplet and the beginning of dewetting decreases if the mixed solution is kept several minutes before the drop is deposited on substrate. If the solution is kept for a longer time (depending on the concentration) the droplets do not spread at all. This experiment was repeated under 100% humidity (to prevent evaporation) and no substantial difference was found.

4. Conclusions

The performed study has shown that mixtures of anionic (SDeS) and cationic (DoTAB) surfactants demonstrate a partial wetting on silanized glass, but wet completely polyethylene film with initial spreading rates comparable to that of trisiloxane superspreaders. Such behaviour was observed at concentrations above CMC, i.e. for these mixed solutions CWC practically coincides with CMC, which is different from trisiloxane surfactants where CWC is several times larger than CMC.

The complete wetting of mixtures on hydrophobic substrate and high initial spreading rate is due to strong synergetic effect resulting in a much higher surface activity of mixture in comparison to single components on both liquid/air and liquid/solid interfaces. In particular, the surface tension of mixture above CMC (22.5 mN/m) is much lower than the surface tensions of micellar solutions of common ionic and non-ionic surfactants (>30 mN/m) and is comparable to that of trisiloxanes (20 mN/m).

The maximum spreading factor of surfactant mixtures studied on PE substrate is more than 3 times lower in comparison to superspreader BT-278, because the spreading rate of mixture slows down much earlier than that of the superspreader. The possible reason of that is the crystallisation in mixed solutions and the surface retardation due to the crystals' adsorption.

The critical crystallisation concentration is lower than CMC. That is why crystallisation occurs at all concentrations when complete wetting was detected. Solution retains a low surface tension for a certain period of time after mixing despite the crystal growth because the micelles supply material necessary for crystal growth. However, the surface tension begins to increase after all micelles disintegrate. This results in an interesting phenomenon: a transition from complete to partial wetting, that is, a droplet of freshly prepared mixture first spreads completely but after some time the solution assembles into the droplet again.

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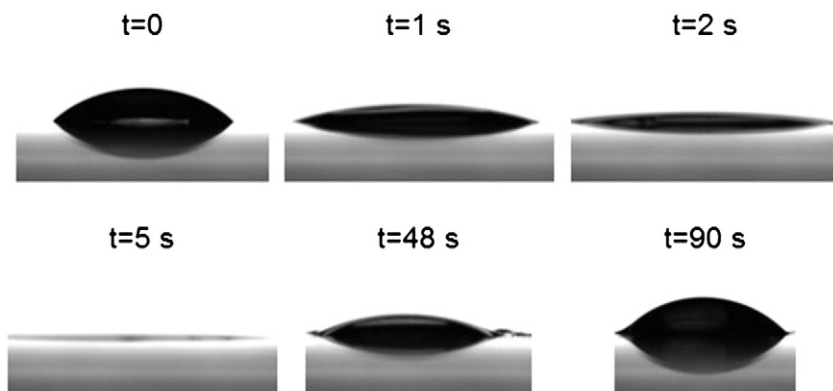


Fig. 5. Transition from complete to partial wetting due to crystallisation of SDeS/DoTAB 0.5 g/l solution.

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