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Superspreading: Aqueous Surfactant Drops Spreading on Hydrophobic Surfaces

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Drops spreading over solid surfaces represent a basic phenomenon important to a wide variety of coating and deposition processes.[1−5] Efficient deposition is critical to most painting, coating, and solution delivery applications. The obvious solution to improve deposition is to add surface-active agents to the droplets to improve the spreading ability of the solutions.[6] However, a full quantitative understanding of the influence of surfactant addition on the spreading dynamics is still lacking.

In this note, we study the effect of surfactant addition on the spreading rate of aqueous droplets on hydrophobic surfaces. We show that with comparable equilibrium surface tensions, certain surfactants accelerate the spreading, whereas others slow it down. We demonstrate that the mechanism of the accelerated "superspreading"[7] is fundamentally different from that of classical surface-active agents and suggest an interpretation of our findings that clarifies this mechanism.

We study aqueous drops spreading over smooth, solid hydrophobic surfaces. The model surface we discuss here is transparency film for overhead projection (Stabilo, Ref 7250),[8] a poly(ethylene terephthalate) (PET) surface without surface coating. When deposited as is done in the experiments, pure water has a 70° contact angle on this substrate. A Zisman plot using different liquids shows that its critical surface tension (the surface tension of the liquid that will just spread over this surface) is $\gamma_c = 24 \pm 2$ mN m^{-1}. For water, the advancing and receding contact angles are 77° and very close to zero, respectively. Scanning electron microscopy shows that the surface is very smooth; a small amplitude roughness develops at length scales smaller than 100 nm. As a "normal" surfactant, we use the anionic surfactant AOT (dioctyl sulfosuccinate sodium salt, from Sigma),[9] with a molar

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(8) Again, similar results were obtained for the different surfactants using different substrates: Plexiglas and Terphene.
(9) These results are representative also for other surfactants that we tested: the cationic surfactant C$_{16}$TAB and the nonionic surfactant C$_{12}$E$_5$.
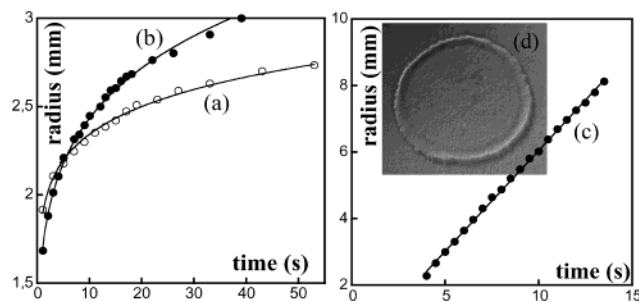

Figure 1. (a) Dynamics of an aqueous AOT drop spreading over a hydrophobic surface. The line is a fit to a power-law evolution $R = Ct^{1/10}$ yielding the prefactor C. (b,c) Dynamics of aqueous trisiloxane drops. The lines are fits to a power-law evolution $R = Ct^{\alpha}$ yielding a power of (b) 0.16 and (c) 1. (d) Photograph of the spreading trisiloxane solution droplet at the highest surfactant concentration used here. The radius of the droplet is 3 mm.

mass of 444.6 g/mol and a critical micelle concentration (cmc) of 4×10^{-3} mol L^{-1}. Above the cmc, the surface tension is 24 ± 1 mN m^{-1}. This is similar to the critical surface tension of the surface. However, we do see a clear transition from nonspreading to spreading upon increasing the AOT concentration; the data presented here are only for those concentrations that spread. As the superspreading[7] surfactant, we used the trisiloxane[10] (M(D′E$_8$OH)M (M = Me$_3$SiO$_{1/2}$, D′ = −MeSiO, E$_8$ = −CH$_2$CH$_2$CH$_2$(OCH$_2$-CH$_2$)$_8$, and Me = CH$_3$), from Dow Corning) of molar mass 632 g/mol and critical micellar concentration 4×10^{-4} mol L^{-1}, as determined from surface tension measurements. These measurements give $\gamma = 22 \pm 2$ mN m^{-1} above the cmc. Using a microsyringe, we produce small drops of a few microliters, which are gently deposited on the substrate, and the radius of the droplets in time is monitored by a CCD camera.

The starting point for the experiments is a reference system without surfactants on the same substrate. To have similar liquid−vapor interfacial tensions as the surfactant solutions, we use silicon oils. These have a low liquid−vapor surface tension ($\gamma = 21$ mN m^{-1}), so that their initial spreading coefficient is positive: they spread spontaneously even in absence of surfactants. Different oils allow varying the viscosity over several orders of magnitude. We find that the spreading rate of the droplets is well described by the classical Tanner's law:[11] $R(t) = \Omega^{3/10}(\gamma t/\eta)^{1/10}$, with Ω the droplet volume, γ the surface tension of the liquid−vapor interface, and η the viscosity of the spreading fluid. This equation shows that capillarity is the driving force for the spreading, whereas viscosity slows it down. It follows that the droplet radius increases slowly in time: $R \propto t^{1/10}$.

The spreading of the AOT solutions turns out to be similar to that of the oils, at least for high surfactant concentration. At low surfactant concentration, around the cmc, the drops hardly spread, and it is difficult to

(10) Other trisiloxane surfactants that we used (L7604 and L7200 from Rhodia) show the same generic behavior.
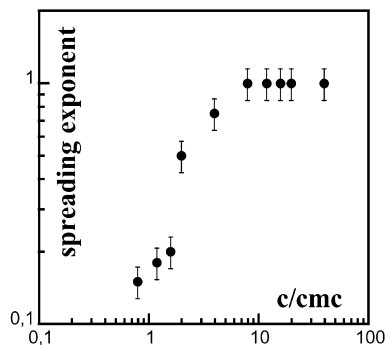(11) Tanner, L. H. *J. Phys. D*: *Appl. Phys.* **1979**, *12*, 1473.

Figure 2. Power α from the evolution of the radius $R = Ct^\alpha$ for the superspreading of the trisiloxane solutions.

distinguish between spreading with a small power of t and no spreading at all. At higher concentrations, the droplet clearly spreads after the initial deposition stage. Figure 1a shows data for an AOT solution at 7.5 times the cmc. The evolution of the radius can be fitted to a power law $R(t) = Ct^{1/10}$; however, the prefactor C turns out to depend slightly on concentration. The prefactor is about 0.75 mm s$^{-0.1}$ for low concentrations and increases toward the value of 1 mm s$^{-0.1}$ for higher concentrations. The latter is in fact the prefactor deduced for the silicon oil reference system with the same viscosity; for the AOT system, viscosity measurements show that increase due to the addition of surfactant is negligible. Also, as all of the measurements are above the cmc, where the equilibrium tension depends only very weakly on the bulk surfactant concentration, the observed variations cannot be attributed to a variation in the equilibrium surface tension. This implies that *the surfactant slows down the spreading* in comparison with the reference system. That the prefactor for the AOT solutions is different from Tanner's law then suggests that the dynamic surface tension needs to be taken into account.[12] As the creation of new area is faster than the arrival of surfactant molecules to the interface, this can decrease the dynamic spreading coefficient and slow the droplet dynamics.

The behavior of the trisiloxane surfactants is completely different. We observe that for all concentrations investigated (both above and slightly below the cmc), the spreading is faster than that of the corresponding silicone oil with the same equilibrium surface tension and viscosity: for a given time after deposition, always a larger radius is observed for the trisiloxane solutions. Figure 1b,c shows the effect of increasing the surfactant concentration: the spreading becomes much faster than $R \propto t^{0.1}$, the power of t obtained from fitting a power-law behavior to $R(t)$ increasing with increasing surfactant concentration. For the highest bulk concentrations, a linear relation $R \propto t$ is obtained (Figure 1c), a power 1 order of magnitude larger than that predicted by Tanner's law. The results for the fits to a power-law behavior are summarized in Figure 2. It should be emphasized that we are likely to be in a crossover regime between capillarity-dominated spreading and a superspreading regime for which the motor driving the spreading is clearly different. Therefore, the power-law fits, which provide a good way to describe our data, should be considered as effective power laws, only valid over a limited range. Therefore, whereas the AOT appeared to slow the spreading, *the trisiloxane system accelerates the spreading relative to the reference system.*

Again, viscosity measurements show that the viscosity change is at most a few percent.[13]

Explanation of this effect poses a challenge as both dynamic surface tension effects and inertial forces can only slow the dynamics. Although gravitational forces can lead to an acceleration ($R \propto t^{1/8}$ [14]), this is still too slow to account for the observed deviations from Tanner's law. We have also verified that the humidity of the air does not change the spreading dynamics significantly. Changing the relative humidity between 30 and 80%, we find a slight (maximum 10−15%) increase in the prefactor, but the power laws remain the same. Therefore, there must be a different driving force for the spreading, leading to the fast dynamics. This is emphasized by a visual inspection of the droplets: hardly visible for lower concentrations, at the highest concentrations (for which the linear behavior $R \propto t$ is obtained) the droplet spreads very fast, and the fluid collects mostly in a rim forming the perimeter of the droplet (Figure 1d). The peculiar form of the droplet shows that the capillary forces are largely dominated by the driving force for the spreading. The most natural candidate for this, which can also influence the spreading rates of normal surfactants under certain circumstances, is a Marangoni effect.[6,12,15]

Such a Marangoni effect should then find its origin in gradients in surfactant concentration. As the spreading is very rapid for the trisiloxane surfactants, it seems reasonable to neglect the contribution due to capillarity and discuss spreading due to Marangoni effects only. Then, the Marangoni stresses lead to a pressure gradient $\nabla P \approx (1/h)\nabla\gamma$ (γ being the surface tension) that drives the spreading, and the balance between the Marangoni stresses and the viscous stresses that slow the spreading reads[5]

$$\frac{\partial R}{\partial t} \approx \frac{h^2}{\eta}\nabla P \qquad (1)$$

with η the viscosity and h the droplet height; in addition, from mass conservation we have $h \propto 1/R^2$, with R the droplet radius. The only remaining question is then over what distance the surface tension gradient acts. As we have no a priori knowledge of this, we will simply consider three different options.

First, the surface tension gradient may be radial: $\nabla\gamma \approx (\gamma - \gamma_e)/R$. In this case, simple dimensional analysis of eq 1 immediately yields $R \propto t^{1/4}$, a result also obtained by Nikolov et al.[15] using similar arguments. Second, we may choose that the surface tension gradient be established over a fixed length l. If this were the case, we find $R \propto t^{1/3}$ from eq 1. Finally, one may guess $\nabla\gamma \approx (\gamma - \gamma_e)/h$, so that the surface tension gradient is established over the height of the droplet. In this case, dimensional analysis gives $R \propto t$; the droplet radius increases linearly in time, as is observed in the experiment for the highest surfactant concentrations. For this last result, we do not need the relation $h \propto 1/R^2$, which is surely violated for drops such as that shown in Figure 1d.

Although the direction of the surface tension gradient remains an important open question, these simple considerations show that the Marangoni stresses can provide

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(13) However, a marked increase in the viscosity can be observed for $c > 100$ cmc, which could consequently be at the origin of reported maxima in the spreading rate versus surfactant concentration in ref 7.

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a motor for the spreading that leads to powers that are much larger than the 1/10th power of Tanner's law. In addition, the different choices for the surface tension gradient suggest the following interpretation of our data. Once more, it is likely that at low surfactant concentration, arrival of molecules from the bulk is slow; this implies that the gradient in surfactant concentration is probably established both in the radial and in the height direction. From the above arguments, this leads to an effective spreading power that is between 1/4 and 1. The experiment also reveals that when the bulk surfactant concentration is increased, the power increases also, to settle at a plateau value of 1 for the highest concentrations. This suggests that when the surfactant concentration is high, the radial direction is saturated rapidly, and the surface tension gradient is established mainly over the height of the droplet.

The superspreading may therefore be due simply to a large affinity of the surfactant molecules for the solid substrate. Namely, if the surfactant molecules are transported rapidly and efficiently over the (small) height of the droplet in order to saturate the solid surface, this entails a large surface tension gradient over a small distance, and consequently a large Marangoni force. This, in turn, leads to the linear time evolution of the radius, as is observed in the experiment. The difference with the "classical" surfactants observed here is then either a difference in affinity for the solid substrate or a difference in the transport efficiency to that same substrate, a question that remains to be answered.