



## Insights into surfactant-assisted superspreading



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### ABSTRACT

Recent developments in “superspreading” are highlighted showing this phenomenon to be due to the combined effect of diffusion processes, Marangoni stresses, surfactant, solvent and substrate chemistry, and ambient conditions. The ultimate resolution of the driving mechanisms will involve the application of molecular dynamics simulations together with continuum-scale modeling and multi-scale experimentation.

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### 1. Introduction and background information

Recently, the study of wetting and spreading of water or aqueous solutions on solid substrates or liquid supports has gained new momentum in view of interesting applications that require the delicate control of wetting process [1]. The degree of wettability for an aqueous droplet on a hydrophobic substrate is characterized by the contact angle  $\theta$ , subtended between the liquid–vapor (LV) surface and the solid–liquid (SL) interface at the contact line with the solid–vapor (SV) surface (cf. Figs. 1, 3). When the contact angle is higher than  $90^\circ$ , the substrate is hydrophobic, whereas contact angles smaller than  $90^\circ$  characterize a hydrophilic substrate. The statics and dynamics of wetting/dewetting and other factors (e.g., the substrate geometry) that may influence wetting on solid or liquid supports have been extensively discussed previously [1–7]. Some of this work has put particular focus on the transitions between partial and complete wetting/dewetting states based on thermodynamic arguments [5], while the understanding of the droplet dynamics at the contact line still remains a challenging problem [6,7].

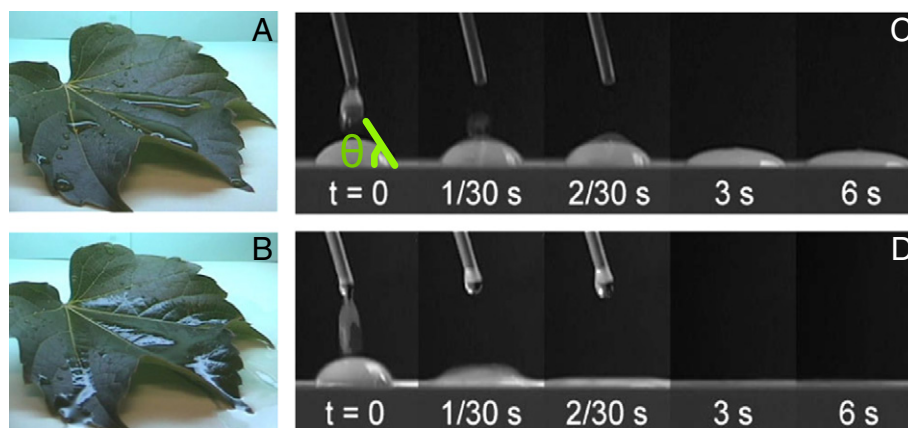
Although, for most common applications, the wetting of liquids (droplets) on hydrophobic substrates suffices [1], there are applications that require the enhanced or complete wetting of hydrophobic

substrates by aqueous droplets. For instance, the increase in the efficiency of herbicides through enhanced spreading on hydrophobic leaves of plants (cf. Fig. 1), the spreading of active pharmaceutical ingredients in the airways to aid in the cure of respiratory distress syndrome that causes the collapse of small airways during exhalation due to high interfacial tensions at the walls of the respiratory tubes, and the development of efficient coating technologies on substrates of varying degrees of hydrophobicity, are only a few examples where enhanced spreading on hydrophobic substrates has immediate implications [1]. In physical terms superspreading translates to the reduction of the SL interfacial tension and the LV surface tension and/or the increase of the SV surface tension. This can be expressed mathematically by the so-called spreading factor  $S = \sigma_{SV} - (\sigma_{LV} + \sigma_{SL})$ , where  $\sigma_{SV}$ ,  $\sigma_{LV}$  and  $\sigma_{SL}$  refer to the SV and LV surface tensions, and the SL interfacial tension, respectively. Positive values of the spreading factor indicate that spreading is energetically favored [8]. A strategy to achieve enhanced or complete spreading on hydrophobic solid substrates is by dissolving substances that are known as surface-active agents, or “surfactants”. These molecules adsorb at interfaces altering their free energy. A key element for this ability is that one structural part of the molecule is hydrophilic, while the other part has very little attraction for the aqueous solvent [9–14].

Here, we focus on low molecular weight surfactants that have the ability to promote rapid and complete wetting of aqueous droplets on hydrophobic substrates (e.g., Parafilm or polyethylene), where the final macroscopic contact angle attains values close to zero. Such

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**Fig. 1.** Spreading of a water droplet on leaf's surface (A), and of an aqueous solution of a commercial superspreader (Silwet L-77) (B). (C), an alkyl polyethoxylate/alcohol solution on a moderate hydrophobic polycarbonate substrate, and (D) a trisiloxane solution sessile aqueous droplet.  $\theta$  is the macroscopic contact angle. Figure adapted from Refs. [20\*,47\*].

surfactants are widely known as “superspreaders” or “superwetters”, and the phenomenon is called “superspreading” or “superwetting”. Superspreading is characterized by a power law dependence of the droplet radius on time ( $R \sim t^\alpha$ ) with  $\alpha$  being an exponent in the higher values of the range 0.16–1 [15]. In this case, apart from a prefactor that depends on surfactant concentration,  $\alpha$  increases significantly with surfactant concentration while viscosity changes  $\alpha$  by only a few percent [15]. Slow spreading dynamics at low concentrations also indicate that diffusion of surfactant molecules from the bulk to the interfaces plays an important role in the spreading process.

The most common superspreaders are trisiloxane surfactants, which consist of a non-polar trisiloxane head-group and an organic polar group, e.g., polyoxyethylene (pEO) or polyoxypropylene (pPO) [8]. A widely used notation for trisiloxane surfactants is  $M(D'E_n)M$ , where M refers to the  $(CH_3)_3SiO-$  group, D' corresponds to the  $CH_3Si(CH_2)_3-$  group of atoms (a methyl group may be often substituted with another unit), and  $E_n$  is an ethoxylated chain  $-(OCH_2CH_2)_nOR$  with R being typically  $-H$ ,  $-CH_3$  or  $-CH_2CO_2H$  groups. Trisiloxane surfactants can achieve 25 times greater spreading area than pure water with common surfactants, such as polyethoxylated alcohols [8]. There is still scope for significantly improving the performance of existing superspreaders. Recently, it was shown that glucosamide-based trisiloxane surfactants exhibit comparable spreading properties to common trisiloxane surfactants, e.g., Silwet L-77 [16]. On the contrary, recently synthesized double-tailed trisiloxane surfactants did not show the same efficiency (rate and area of spreading) in spreading in comparison with common trisiloxane surfactants [17].

The superspreading phenomenon has been studied over the last two decades with the focus placed on trisiloxane surfactants [8,18–24\*]. Much of the ability of trisiloxanes as superspreaders has been attributed to their peculiar T-shaped geometry [8,21]. Due to this geometry, some trisiloxane surfactants are able to form bilayers above a Critical Aggregation Concentration (CAC), a concentration several times lower than Critical Wetting Concentration (CWC) that is required to initiate superspreading [20\*,24\*,25\*]. Bilayer-forming surfactants are known to spread faster than micelle-forming ones, suggesting that the spreading process depends on surfactant microstructure [26,8,21,18]. It is also believed that the adsorption of these bilayers on the substrate facilitates superspreading, and it is favored by the presence of methyl groups in trisiloxane, in contrast to common hydrocarbon surfactants that are dominated by methylene groups. This enables trisiloxanes to spread over lower-energy substrates, i.e., hydrophobic substrates [8,21]. On the contrary, on less hydrophobic substrates the droplet forms an unstructured wedge-shaped film at the spreading edge, showing that trisiloxane surfactants orient differently depending on the substrate

hydrophobicity [8,21]. Moreover, bilayer mesophases are also believed to enhance spreading by means of an ‘unzipping’ mechanism, where water flows through channels of bilayers [21]. Although aggregates and vesicles favor the spreading process, it is known that they do not initiate it [19], which means that the presence of aggregates is not a requirement for superspreading as was suggested in Ref. [11].

In contrast to pure liquids where the spreading process is dominated by hydrodynamic effects, in surfactant-assisted spreading the transport of surfactants at the interfaces is a factor that plays a major role indicating that diffusion processes may be an important part of the superspreading mechanism [18]. The superspreading process is presumably characterized by two- or three-stage spreading dynamics [23\*], or in some cases even by four stages [24\*]. In the two-stage spreading dynamics scenario, an initial, fast spreading process takes place, which depends on inertia, capillarity, and relaxation of interfacial tensions, where the Marangoni effect (explained below) also contributes to the spreading dynamics. During the second stage, where the area increases linearly with time, the spreading process relaxes towards the final contact angle. The latter stage is a diffusion-mediated process and depends on the rate of adsorption of surfactants at the interfaces [8,20\*,21,23\*]. The duration of the linear period and the limiting area are proportional to surfactant concentration, whereas the final contact angle decreases with higher surfactant concentration [21]. A main challenge in interpreting the dynamics of the superspreading mechanism is to explain the maxima that appear in the spreading rate vs. the surfactant concentration and the substrate surface energy, which is a sign of the presence of competitive processes [8,20\*].

The Marangoni effect is another contributing factor to superspreading [19]. Differences in surfactant concentration between the droplet's apex and the three-phase contact line induce surface tension gradients that cause Marangoni flow, as a result of which the diffusion and the adsorption of surfactant molecules at the interfaces are also affected. The initiation of a surface tension gradient is a complex phenomenon and depends on many factors, e.g., the rate of surfactant diffusivity on the LV surface and from the bulk to the surface, the surface activity (i.e. ability to reduce the LV surface tension), solubility in the aqueous medium, and adsorption on the SL interface and the SV surface [19]. Moreover, Marangoni flow requires fast adsorption kinetics to maintain a sufficiently large surface tension gradient underlining the role of surfactant diffusion in the spreading process [21]. However, it has been shown by Kumar et al. [27] that this rate of adsorption is not high enough to sustain droplet spreading. Despite the latter conclusion, invoking the importance of Marangoni flow has provided a satisfactory explanation for the linear increase of the spreading area with time [8]. Also, the role of a precursor film at the spreading edge of the droplet, where

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