Current opinion in superspreading mechanisms

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ABSTRACT

Background: An aqueous solution of trisiloxane-ethoxylate surfactants (superspreaders) has fascinating surface properties that promote rapid spreading over a large area of difficult–to-wet substrates. The overall spread area achieved by an aqueous droplet containing superspreaders can be as much as 50 times greater than water, and 25 times more effective than a conventional surfactant on a leaf's surface. The phenomenon that drives superspreading is still not well understood and it is under continuous discussion.
Concepts and models: The goal of this paper is to review the data published to elucidate the concepts and mechanisms presented in the literature and to propose a model for superspreading.
Conclusions: A simple model was proposed concerning the surface tension gradient (or Marangoni flow) over the curved droplet surface when the value of the wetting angle was considered. The model predicted the optimum rate of spreading vs. angle at $\theta = 60°$ and was in a satisfactory agreement with the experimental observations.

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1. Introduction

We would like to dedicate this work to Dr. Reinhard Miller, a long-time friend with whom we have had many fruitful scientific discussions on colloid science. He devoted his research to bridge the gap between scientific theory and practice.

An aqueous solution of trisiloxane–ethoxylate (siloxane) surfactants (known as "superspreaders" or "superwetters") has fascinating surface properties: it spreads rapidly over the substrate with a low surface energy and an intermediate wettability (e.g., 60°–70°; referred to as the "water phase"), and efficiently reduces the surface tension (e.g., the air/aqueous solution surface at room temperature from 72 mN/m to 21–22 mN/m at low concentrations of superspreaders).

Since the discovery of superspreaders in the 1960s by Schwartz and Reid [1], and despite their importance to many technological applications, the phenomenon that drives superspreaders to spread so quickly over hydrophobic surfaces is not well understood and is still under discussion. Silicone polyethers are nonionic surfactants and they have a variety of commercial and industrial applications, such as solid modifiers, adjuvants, and surface cleaners. They can also be used in fabric manufacturing as well as pharmaceutical and cosmetic formulations. For information about the applications of siloxane surfactants, see the recently published papers by Somasundaran et al. [2], Mehta et al. [3], Hill [4], and Liles [5]. Superspreader trisiloxane–ethoxylate surfactants are mainly used as adjuvants; this type of spreading is depicted in the photos shown in Fig. 1. For commercial applications, it is important to reveal when the superspreader will wet a large area.

The attached video clip depicts the spreading dynamics of a 20 μL droplet of Silwet L-77 at a concentration of 0.1 wt.% on the surface of an optically smooth polystyrene substrate at a room humidity of 55–

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60% and temperature of 25 °C. The pure water drop wettability on the polystyrene surface was about 60°–75°. The spreading dynamics went in three stages: they were faster during the first 4–5 s with a constant rate of spreading of 0.18 cm/s; then, the rate of spreading slowly decreased; at the end, the contact line spreading became unstable and broke into regular fingers. The initial value of the spreading wetting angle during first few seconds was large (about 45°–50°) before it started decreasing to a value of approximately 1° at the end of the spreading when the advancing line broke into regular fingers. After 27 s of spreading time, the 20 μL droplet of Silwet L-77 covered an area 42 times larger than its initially-wetted area. The sequence of micrographs taken from the side view in Fig. 2 depicts the initial spreading drop shape with a disk-like geometry and the spreading angle.

Fig. 3 depicts the radial radius of spreading and the spreading contact angle vs. time of the 20 μL of droplet 0.1 wt.% Silwet L-77 on the substrate of an optically smooth polystyrene substrate, at a humidity of 55–60%, and a wettability, referred to as the "water phase", of 65°–70°. The faster rate of spreading occurred when the spreading angle was large; as the spreading angle decreased, the rate of spreading also decreased, but it was slower than the value of the spreading contact angle.

Our goal is to review the data in the literature and to discuss what drives the initial fast rate of spreading vs. surfactant concentration and substrate surface energy (e.g., wettability).

The initially-faster spreading rate on a substrate with an intermediate wettability (referred to as the "water phase") requires understanding. Most research conducted on trisiloxane–ethoxylate surfactants was done using commercially available samples from Momentive (formerly Witco), Dow Corning, and Evonik (formerly Degussa/Goldschmidt). Such samples were not pure substances and contained by-products. Aqueous solutions of superspreaders are not stable and slowly hydrolyze over time, at high temperatures, or at a low or high pH; their stability also depends on the method of solution preparation (e.g., dissolved or dispersed by sonication). These are just a few of the possible reasons the data obtained by different research groups were not compatible.

Over the years, scientists have struggled to provide a comprehensive understanding of the superspreading phenomenon. This review discusses and elucidates the concepts and mechanisms presented in the literature on superspreading. We hope to provide answers concerning the main features of superspreading. Challenging questions arise: Why does the spreading rate have an optimum value vs. concentration? Why do superspreaders have the unusual spontaneous spreading rate on substrates with an intermediate wettability of 60°–65°? Why is the value of the concentration corresponding to the optimum of the rate of spreading the same vs. substrate wettability? What are the roles of the molecular structure and vesicle-type aggregates in superspreading? In the literature, superspreading has been attributed to the surfactant molecules' unique molecular structure, as well as the superspreader's ability to lower the liquid–air surface tension to low value, the fast kinetics of adsorption at the liquid–air and solid liquid interface, and/or the surfactant molecules' ability to aggregate and form a vesicle-type of structure (Ananthapadmanabhan et al. [6], Stoebe et al. [7], Ruckenstein [8,9], and Karapetsas et al. [10]). The surfactant molecules from the air/surfactant solution tend to transfer and adsorb into the bilayer at the air/solid substrate interface in order to trigger the spreading (Ananthapadmanabhan et al. [6], Stoebe et al. [7], Ruckenstein [8,9], and Karapetsas et al. [10]). The surfactant diffusion at the subsurface is the key factor for superspreader-enhanced wetting Radulovich et al., [11,12]). The role of the Marangoni flow along the droplet's stretching surface during spreading contributes to the superspreading phenomenon (Nikolov et al. [13], Nikolov et al. [14], Nikolov and Wasan [15], and Rafai et al. [16]).

The proposed concepts and models in the literature will be discussed, and their validity in regards to the superspreading phenomenon will be elucidated based on the relevant published experimental data. The data presented in Fig. 4 depict the superspreaders' spreading rate vs. surfactant concentration and substrate energy defined by the water phase's substrate wettability (Hill [17]). Overall, the spreading rate for M(D'E$_8$OH)M had an optimum of 0.5 cm/s (or 80 mm^2/s) at a surfactant concentration of 0.45 wt.% and at a substrate wettability between 60° and 65°. Based on our knowledge, no concept or model has been presented in the literature that satisfactorily explains the optimum rate of spreading vs. substrate wettability.

Here, we briefly review the data published on superspreading and the views and models presented on superspreading mechanisms in the literature. We will later discuss the concepts and models presented in the literature on superspreading, as well as summarize and provide possible explanations. We believe that this review will help readers gain knowledge about the superspreading phenomenon and some of the important concepts and mechanisms related to superspreading. The goal is to stimulate researchers to explore the superspreading phenomenon and utilize it for novel applications. The fundamentals of wetting and spreading presented in the literature will briefly be discussed.

2. Fundamentals of wetting and spreading on solids

The phenomenon of liquid wetting and/or spreading on solids and the displacement of fluid from a substrate occurs every day in a wide variety of natural and industrial settings. When a droplet of pure liquid is placed in contact with a smooth solid surface, a dynamic phenomenon occurs. The droplet's fluid, driven by the hydrostatic (gravitational), capillary, and adhesion forces, tends to cover the solid or liquid substrate before achieving an equilibrium shape (for simplicity, it is assumed that the three-phase contact line was freely moving over the substrate). The rate of spreading is governed by the balance of the surface and gravitational energies and viscous dissipation near the contact
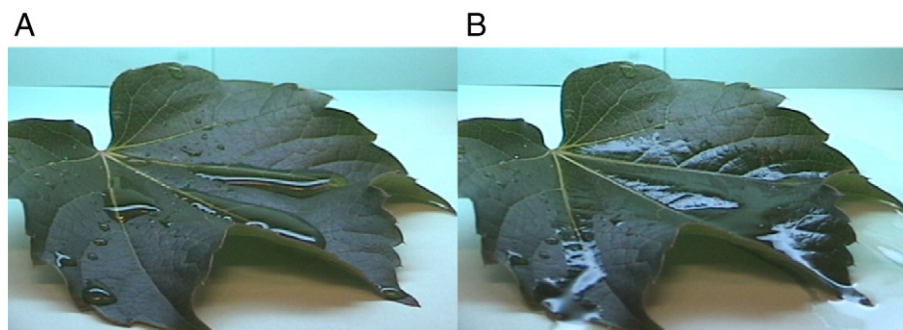

Fig. 1. Photographs depict the spreading of water droplets on a velvetleaf's surface (A) and the aqueous solution of superspreader Silwet L-77 at 0.1 wt.% (B). Published with the kind permission of *The European Physical Journal* (EPJ).