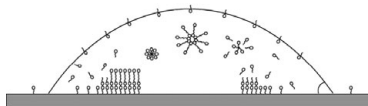$$\mathbb{F}^{ocus}_{on\ luids}$$

On the microhydrodynamics of superspreading

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Droplets of an aqueous phase placed on a very hydrophobic, waxy surface bead-up rather than spread, forming a sessile drop with a relatively large contact angle at the edge of the drop. Surfactant molecules, when dissolved in the aqueous phase, can facilitate the wetting of an aqueous drop on a hydrophobic surface. One class of surfactants, superwetters, can cause aqueous droplets to move very rapidly over a hydrophobic surface, thereby completely wetting the surface (superspreading). A recent numerical study of the hydrodynamics of superspreading by Karapetsas, Craster & Matar (*J. Fluid Mech.*, this issue, vol. 670, 2011, pp. 5–37) provides a clear explanation of how these surfactants cause such a dramatic change in wetting behaviour. The study shows that large spreading rates occur when the surfactant can transfer directly from the air/aqueous to the aqueous/ hydrophobic solid interface at the contact line. This transfer reduces the concentration of surfactant on the fluid interface, which would otherwise be elevated due to the advection accompanying the drop spreading. The reduced concentration creates a Marangoni force along the fluid surface in the direction of spreading, and a concave rim in the vicinity of the contact line with a large dynamic contact angle. Both of these effects act to increase the spreading rate. The molecular structure of the superwetters allows them to assemble on a hydrophobic surface, enabling the direct transfer from the fluid to the solid surface at the contact line.

Key words: capillary flows, contact lines, drops

1. Introduction

Perhaps no example of the remarkable effects that surfactants can exert on interfacial flows is more astonishing than the behaviour of the superspreading surfactants or 'superwetters'. As their name implies, these surfactants can force fluids to move over surfaces in spreading regimes that are unlike any other (Hill 1998). When a millimetre-sized aqueous droplet (of volume V), without dissolved surfactant, is placed on a very hydrophobic solid surface such as a wax or parafilm, the drop settles under gravity, spreading until coming to an equilibrium sessile shape. At the drop edge or three-phase contact line where the air/liquid, liquid/solid and air/solid interfaces intersect, the water subtends a large contact angle θ_{eq}, typically between 90° and 120°. The area that the aqueous drop has spread over the hydrophobic surface is minimal; the water drop has 'beaded-up' and the surface is not wet by the

liquid. Surfactants can cause aqueous droplets to spread over hydrophobic substrates. Conventional surfactant molecules have a common molecular architecture consisting of a long hydrocarbon hydrophobic (non-polar) chain (a string of methylene groups) and a polar group which is larger in cross-section than that of the chain. When these are dissolved in an aqueous droplet (of the same volume V as the surfactant-free drop), and the droplet is placed on a hydrophobic surface, it spreads further at equilibrium than that of the 'clean' drop, retaining a final contact angle which can be as much as tens of degrees less than that of the surfactant-free drop (Stoebe *et al.* 1996, 1997). Thus, the conventional surfactants facilitate partial wetting. Trisiloxane surfactants have a compact non-polar (trisiloxane) group with a cross-section larger in size than that of the polar group. A droplet of volume V with a trisiloxane surfactant spreads rapidly when placed on a hydrophobic surface, forming a pancake shape whose thickness is of the order of tens of microns, and a contact angle at the pancake edge approaching zero (superwetting). The induced spreading rate can in fact be greater than that of an aqueous droplet placed on a surface readily wet by water such as glass. How the superspreaders facilitate this rapid spreading and complete wetting is a puzzle as the interfacial energetics, self-assembly and transport at the contact line of the superspreaders must be fundamentally different relative to the conventional surfactants to account for this dramatic difference. Karapetsas *et al.* (2011) present a new framework and numerical calculations for the interfacial transport of the superspreaders at the contact line, which provides both a starting point for rationalizing their superwetting behaviour and a clue towards understanding how their unique molecular architecture drives the superspreading process.

2. Overview

The droplet spreading model of Karapetsas *et al.* (2011) consists of a two-dimensional Newtonian slender drop in which the hydrodynamic flow and surfactant mass transfer are described by lubrication equations. Crucially, the modelling incorporates both a contact line and a detailed surfactant model for the kinetics, allowing surfactant to co-exist as monomer or aggregate and to absorb to interfaces or the contact line. The modelling retains enough complexity to describe the physics whilst remaining sufficiently tractable for solutions to be found numerically and allow for physical interpretation.

The surfactant modelling assumptions of bulk aggregation and adsorption onto the fluid and solid interfaces are applicable to both conventional surfactants and superspreaders. The central idea which Karapetsas *et al.* (2011) introduce to explain the unique behaviour of the superspreaders concerns their interfacial transport at the contact line. At the air/aqueous interface, all surfactants adsorb with their polar group in contact with the aqueous phase, and the hydrophobic group extending into the air. At the aqueous/hydrophobic solid surface, the non-polar group adsorbs onto the solid surface, allowing the polar moiety to remain in contact with water. For conventional surfactants, the larger cross-section of the polar groups spaces apart the chains when the surfactant adsorbs on the surface in a monolayer configuration, and this is energetically unfavourable as the chains remain in contact with water. Hence, a conventional surfactant, adsorbed at the air/aqueous interface, has no strong affinity to transfer directly onto the solid surface without a complex re-organization (as, for example, to form hemi-cylinders or hemi-micelles analogous to their bulk behaviour). As a result, for the conventional surfactants, the flux along the air/aqueous surface at the contact line is equal to zero, and surfactant can accumulate in front of the contact
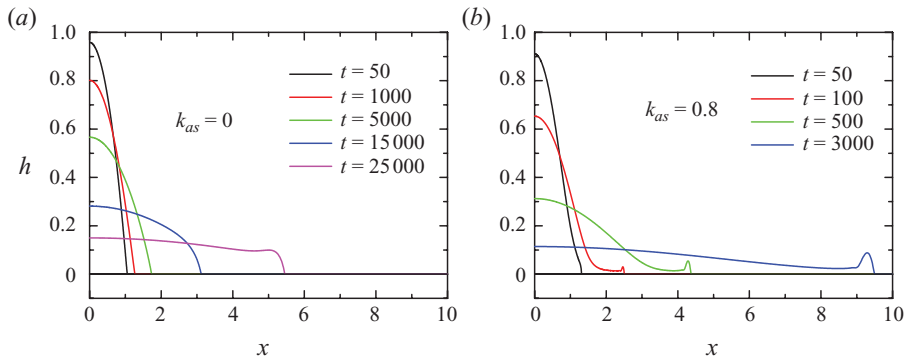
FIGURE 1. The scaled height (h) of the two-dimensional droplet as a function of the scaled distance (x) and time (t) for the case of zero (a) and finite (b) rate of transfer of surfactant from the air/aqueous interface to the hydrophobic solid surface at the contact line. Here k_{as} is the scaled rate of transfer from the fluid surface to the contact line (adapted from Karapetsas *et al.* 2011).

line. For the trisiloxanes, the polar group fits within the footprint of the non-polar group, and as such, dense, water-excluding monolayers can easily assemble along the hydrophobic surface. Therefore, trisiloxanes, adsorbed onto the air/aqueous interface, have a stronger affinity to transfer to the solid surface at the contact line. Studies have suggested (Ruckenstein 1996) that at the contact line, the trisiloxanes self-assemble into a bilayer, with the bottom leaf forming the dense mat (hydrophobic groups down) and the second leaf (hydrophobic group up) tethering this assembly to the air/aqueous interface. This bilayer formation is in analogy with the observed formation of bilayers of these surfactants in an aqueous bulk phase (He *et al.* 1993; Hill *et al.* 1994). Karapetsas *et al.* (2011) formulate new kinetic expressions for the direct transfer of the superspreaders from the air/aqueous interface to the solid surface at the contact line, and from the surface back onto the air/water interface.

Numerical simulations of the drop spreading show clearly how the inclusion of the direct transfer of adsorbed surfactant from the air/aqueous interface to the solid surface at the contact line can result in superspreading behaviour. Consider first conventional surfactants. As the droplet spreads, surfactant adsorbed onto the air/aqueous surface is convected to and accumulates at the contact line. The accumulation reduces the equilibrium advancing contact angle and increases the rate of spreading, which is partially mitigated by the fact that the advected surfactant accumulating at the contact line creates an opposing Marangoni force. The droplet comes to equilibrium with a larger wetting radius due to the decrease in the equilibrium advancing angle. For the conventional surfactants, these effects explain how surfactants facilitate partial wetting of the hydrophobic surface. In the case of the trisiloxane superspreaders, the direct adsorption onto the surface at the contact line from the air/aqueous interface (and adsorption to the solid surface) reduces the surfactant accumulating by advection, and the fluid interface in this vicinity becomes relatively clean. The numerical calculations show that this reduction in concentration increases dramatically the spreading rate (figure 1) as the larger fluid tension near the interface (relative to the apex of the drop) creates a Marangoni force in the direction of spreading. In addition, the larger tension allows the fluid interface to retain a large concave curvature near the contact line in the form of a rim. This rim provides a large contact angle which contributes

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to an accelerated spreading, and the base radius of the drop grows as a power law in time as t. At the later stages of spreading, the direct transfer to the solid surface saturates, the power-law behaviour of the growth of the base radius scales as $t^{1/2}$. Eventually, the fluid interface comes to a uniform surface concentration and the contact angle approaches the (reduced) equilibrium advancing contact angle.

3. Future

The numerical calculations of Karapetsas *et al.* (2011) provide strong evidence that superspreading behaviour derives from the ability of the trisiloxanes to transfer directly from the air/aqueous interface to the solid substrate at the contact line. This transfer process involves a rearrangement or self-assembly of the surfactant at the contact line on the surface to provide a minimum free-energy configuration. For a better understanding of this process, one future challenge is to use molecular dynamics simulations to provide a molecular level view from which insight can be gained into the nature of this re-organization. The molecular dynamics simulations can also provide direction into a more detailed casting of the continuum kinetic equations formulated by Karapetsas *et al.* (2011) to describe the transfer process. The contact line (or point in their two-dimensional simulation) is treated as a singular point in the concentration distribution of the surfactant adsorbed onto the solid surface. A more detailed treatment can model the contact point as a separate phase apart from the fluid and solid interfaces with a concentration distribution (per unit length).

A second challenge for future modelling of the superspreading process involves the nature of the adsorption of surfactant from the bulk aqueous phase to the air/water and water/hydrophobic solid interfaces. To provide enough surfactant from the bulk to drive the surfactant-facilitated spreading, large bulk concentrations are necessary. As such, superspreading concentrations are above the critical concentration for the formation of aggregates. In the current study of Karapetsas *et al.* (2011), the presence of the aggregates is included, but they provide only a passive contribution to the adsorption process – they disassemble in the bulk to provide additional monomer for adsorption onto the fluid and solid interfaces. In fact, because the droplet spreading rate is so large, the adsorption process needs to be necessarily very fast, and the direct adsorption of micelles onto the surface may play a role. In the case of the superspreaders, the bilayer aggregate structures can 'unzip' easily at the air/aqueous and aqueous/solid surfaces, providing an alternate route for adsorption.

References

HE, M., HILL, R. M., LIN, Z., SCRIVEN, L. & DAVIS, H. 1993 Phase behavior and microstructure of polyoxyethylene trisiloxane surfactants in aqueous solutions. *J. Phys. Chem.* **97**, 8820–8834.

HILL, R. M. 1998 Superspreading. *Curr. Opin. Colloid Interface Sci.* **3**, 247–254.

HILL, R. M., HE, M., DAVIS, T. & SCRIVEN, L. 1994 Comparison of the liquid crystal phase behavior of four trisiloxane superwetter surfactants. *Langmuir* **10**, 1724–1734.

KARAPETSAS, G., CRASTER, R. V. & MATAR, O. K. 2011 On surfactant enhanced spreading and superspreading of liquid drops on solid surfaces. *J. Fluid Mech.* **670**, 5–37.

RUCKENSTEIN, E. 1996 Effect of short range interactions on spreading. *J. Colloid Interface Sci.* **179**, 136–142.

STOEBE, T., HILL, R. M., WARD, M. D. & DAVIS, H. T. 1997 Enhanced spreading of aqueous films containing ionic surfactants on solid substrates. *Langmuir* **13**, 7276–7281.

STOEBE, T., LIN, Z., HILL, R. M., WARD, M. D. & DAVIS, H. T. 1996 Surfactant enhanced spreading. *Langmuir* **12**, 337–334.