Dynamic Wetting by Soluble Surfactant Solutions

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Most fluids contain soluble, surface active components, whether by formulation or by contamination. Thus, wetting by fluids containing soluble surfactants is very common in nature and technology. Dynamic wetting by aqueous solutions of soluble surfactants is more complex than wetting by pure fluids. First, the surface tension gradients on the liquid/vapor interface couple to the fluid flow through Marangoni stresses. Second, surfactant can be transported along and to that interface to mitigate concentration gradients and thus Marangoni stresses. Third, surfactant adsorbs to the solid/liquid interface. And finally, as long as the surfactant is nonvolatile, there must be a balance of surfactant flux into and out of the contact line region. Unlike for the case of insoluble surfactants, that balance may involve transport of surfactant through the bulk fluid between the interfaces. In these ways, surfactant transport couples with fluid flow to create rich and varied dynamic wetting behaviors.

When a hydrophilic surface is advanced into a surfactant solution, contact line motion shows a variety of seemingly diverse behaviors. When a solution of an ionic surfactant is spreading across a surface of the same charge, transient dendrites form ahead of the moving contact line. These dendrites arise due to an instability formed when the water from the solution

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is drawn rapidly across the surface causing a surfactant concentration gradient and Marangoni stresses. When a solution of an ionic surfactant is spreading across a surface of the opposite charge, the contact line moves by a stick/jump motion. Here, surfactant is deposited *ahead* of the moving contact line and halts the fluid motion needed to develop the Marangoni stresses. Such carryover of surfactant is responsible for the classic autophobing behavior seen in surfactant solutions with a strong interaction between the surface and the head group of the surfactant. The surfactant barriers developed in this case have a complex structure with erect molecules left behind the spontaneously retreating solution and molecules diffusing across the surface in regions the solution has never touched. Carryover is also present when surfactant solutions spread on hydrophobic surfaces but in this case the structures enhance, rather than inhibit, spreading. When a solution of a nonionic surfactant is spreading across a hydrophilic surface, a combination of the stick/jump and dendritic spreading are observed.

When the surface is pulled out of the solution at speeds below a critical velocity (U_{crit}), the surface emerges dry; at higher receding speeds, a fluid film is entrained on the surface as it emerges from the solution. We have explored both these regimes for a simple system, cetyltrimethyl ammonium bromide (CTAB) solutions receding across SiO_2 and methylated surfaces. Below U_{crit} on SiO_2, the interaction between the surface and the head group of the surfactant demands that a rather well packed monolayer emerge from the contact line. Marangoni stresses are weak and smaller than viscous forces at the meniscus level. However, the mass balance of surfactant moving through the contact line causes drastic changes in the flow field near the contact line compared the case of a pure fluid, reversing the direction of flow on the liquid/vapor interface and inserting a dividing streamline in the liquid. On the methylated surfaces, the solid/vapor interface adsorbs little, if any, surfactant; and this drastic change in the

flow field does not occur. Above U_{crit} where a film is entrained on the surface as it emerges, the stagnation point, present in such cases for pure fluids, is moved off of the liquid/vapor interface and placed in the fluid flow near the meniscus. Mass transport at the contact line at the end of the evaporating films has little impact on the fluid flow. Marangoni stresses are still small compared to the viscous forces in the liquid/vapor interface but they do change the amount of fluid transported into the film. At fixed evaporation rate, the length of the film follows a power law in the withdrawal speed but the power law is different than that of pure fluids and depends on surfactant concentration. As the surface emerges, surfactant is trapped in the entrained film. As the water evaporated from the film, surfactant is deposited in island structures, with heights quantized in units of bilayers with thicknesses similar to crystalline CTAB.