



Deposition of drops containing surfactants on liquid pools: Movement of the contact line, Marangoni ridge, capillary waves and interfacial particles



Xiang Wang^{a,*,1}, Elmar Bonaccorso^{a,2}, Joachim Venzmer^b, Stephen Garoff^{c,**}

^a Center of Smart Interfaces, Technical University Darmstadt, 64287 Darmstadt, Germany

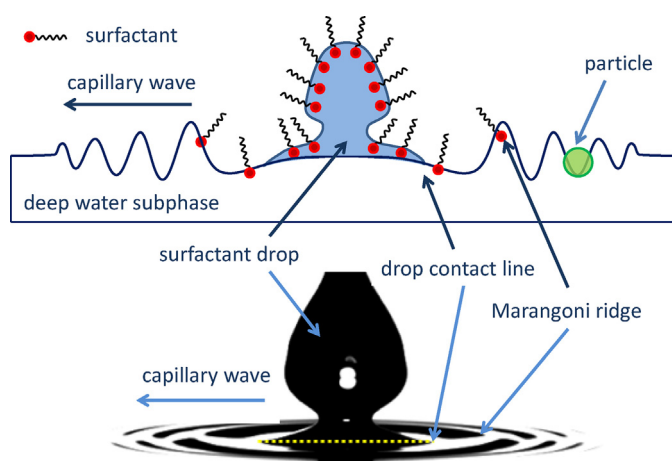
^b Evonik Nutrition & Care GmbH, Goldschmidtstr. 100, 45127 Essen, Germany

^c Physics Department and Center for Complex Fluids Engineering, Pittsburgh, PA 15213, USA

HIGHLIGHTS

- With high speed video microscopy we simultaneously probe the multi-phenomena generated by drop deposition on the subphase.
- The Marangoni ridge propagates slower than the capillary waves, but faster than the drop contact line.
- The pre-deposited particles are mobilized by the Marangoni ridge but not by the capillary waves.
- The propagation speed of capillary waves is influenced by surfactants.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 2 August 2015

Received in revised form 7 September 2015

Accepted 11 September 2015

Available online 14 September 2015

Keywords:

Surfactant solutions

Marangoni ridge

Capillary waves

Interfacial particle transport

ABSTRACT

When a drop of aqueous surfactant solution is placed on a deep subphase of water, multiple phenomena occur. The contact line of the drop spreads until the drop merges with the subphase. A capillary wave train is initiated by the disturbance caused by the drop touching the subphase surface. Marangoni stresses cause the formation and propagation of a localized distortion of the subphase surface (subsequently called the Marangoni ridge). And particles pre-deposited on the subphase surface are propelled by the flow induced by Marangoni stresses. We examine all these phenomena simultaneously at early times (<60 ms). The drop contact line has the slowest propagation speed. The Marangoni ridge propagates slower than the slowest crest of the capillary wave train and the capillary wave speed is affected by the presence of the surfactant. Particle motion is not induced by the capillary waves but is initiated by the passing Marangoni ridge. The particles are rapidly accelerated by the force from surface tension gradient acting on the contact line of the particles and viscous forces acting on the submerged surface of the particles.

© 2015 Elsevier B.V. All rights reserved.

* Corresponding author. Fax: +49 6131 379 100.

** Corresponding author. Fax: +1 412 681 0648.

E-mail addresses: wangxiang@mpip-mainz.mpg.de (X. Wang), sg2e@andrew.cmu.edu (S. Garoff).

¹ Current Address: Max Planck Institute for Polymer Research, 55128 Mainz, Germany.

² Current Address: Airbus Group Innovations, 81663 Munich, Germany.

1. Introduction

Many theoretical and experimental studies have investigated Marangoni driven spreading on liquid surfaces [1–10]. These studies reveal the scientific foundations of numerous applications such as in coating flows [11–13] and drug delivery [14,15]. Most frequently, Marangoni stresses arise from a surface tension gradient due to inhomogeneous interfacial surfactant concentration. The Marangoni stresses can move solid objects (e.g. particles) along a liquid surface [2,6,15–17].

When pure surfactant is deposited as a particle or few monolayers confined to a local region on a liquid subphase, the surfactant escapes from the particle or localized region and moves along the liquid surface. This movement generates a gradient in the surfactant concentration along the liquid surface and thus generates Marangoni flow from regions of lower to regions of higher surface tension on the liquid surface. For many pure surfactants insoluble in the subphase (e.g. oleic acid on water), a molecular monolayer extends ahead of the particle or few layer region and spreads along the liquid subphase [4,17–20]. At the front of the advancing monolayer, there is an abrupt change in the tangential stress boundary condition which causes a deformation in the subphase surface, forming a Marangoni ridge [1,4,21]. This phenomenon, for a pure surfactant particle or localized deposit, has been well studied including the impact of many variables such as subphase thickness, solubility of the surfactant, surfactant surface diffusion, non-Newtonian effects in the subphase, etc. [1,4,10,20,21]. Several authors theoretically predict that under the action of Marangoni stresses, the Marangoni ridge advances with time as $t^{0.75}$ [4,5,18,19]. Experimentally, the spreading of insoluble surfactants on liquid surfaces has been investigated with the aid of talc particles, fluorescent microparticles, Moiré interferometry, or laser shadowgraphy [6,17,19,20,22,23] and the $t^{0.75}$ scaling law has been confirmed [17,18,23–28].

When examining Marangoni driven spreading from a drop of surfactant solution, the solubility of the surfactant and the miscibility of the solvent in the drop with the subphase must be considered. Studies have shown that during the spreading event for low viscosity solvents, the liquid in the drop and that in the subphase do not advectively or diffusively mix even if they are completely miscible [29,30]. The lack of advective or diffusive mixing during capillary driven merging of two fluid bodies has also been seen in the coalescence of sessile drops [31,32]. For spreading of aqueous surfactant solutions on aqueous entangled polymer solutions, the drop remains on the subphase surface for minutes despite the complete miscibility of the drop and the subphase [29]. In this case, the drop contact line lags the experimentally determined Marangoni ridge, as is theoretically predicted [2]. To the best of our knowledge, no other experimental study has examined the movement of the contact line of surfactant drops spreading across a subphase when the solvent is miscible with the subphase.

Lee et al. [30] examined the advancing dynamics of Marangoni ridge when a drop of aqueous soluble surfactant solution spreads on a water surface. They predict that the spreading of such drops with surfactant concentration above the critical micelle concentration (CMC) involved two distinct stages with different power law exponents for the advancing Marangoni ridge. The first stage is rapid and involves the dissolution of micelles in the drop, while the second stage is slower due to surfactant depletion in the drop. The authors [30] show by scaling analysis that the position of the Marangoni ridge in the first stage follows a power law. The scaling with time is $t^{0.75}$ and $t^{0.5}$ for aqueous solutions of insoluble and soluble surfactants, respectively. Their experimental results for surfactants with different solubility and above the CMC agreed relatively well with their theoretical predictions [7,30]. Many other experimental studies examined the spreading dynamics of aqueous

surfactant solutions by measuring the power law exponents associated with the Marangoni ridge [9,16,33,34]. The position of the Marangoni ridge was determined with the aid of tracer particles in many studies [16,23,30,35].

The deposition of surfactant drops on liquid subphase also leads to the formation of interfacial capillary waves, which move out almost immediately following the drop deposition [4,9,23]. However, the propagation dynamics of capillary waves were not quantitatively addressed due to the limited time resolution (0.2 s) of cameras used in those studies. Starov et al. [34] theoretically predicted that these capillary waves should propagate ahead of the Marangoni ridge. Since the amplitude decreases as the wave propagates, the observation of the waves becomes more difficult as time elapses. Using laser shadowgraphy, Berg [8] studied the capillary waves excited by an air bubble impinging with a water/decane interface and obtained a power law exponent ~ 1 for capillary waves.

In this work, we examine microliter scale drops of aqueous surfactant solutions spreading on water subphases of thickness 3 mm. Using two different optical views and high-speed video imaging, we simultaneously track the movement of the capillary wave train, the Marangoni ridge, and the contact line of the drop. In addition, we track the movement of marker particles placed on the subphase away from the point of drop deposition. For control experiments using drops of pure water, we obtain good agreement with models for capillary wave propagation. The capillary waves do not move the particles on the subphase. However, when surfactant drops are used, we observe that the particle motion is initiated by the fluid movement at the Marangoni ridge. This ridge moves slower than the trailing edge of the capillary wave train, but faster than the drop contact line and particles. These results show that using tracer particles in previous studies [16,23,30,35] may not be a reliable method of tracking the position of the Marangoni ridge. It is also found that surfactants affect the velocity of the capillary waves. Our results agree with scaling analyses of the spreading dynamics of the Marangoni ridge.

2. Experimental

2.1. Materials

In the spreading experiments, we used the anionic surfactant sodium dodecyl sulfate (SDS, Acros Organics, purity $\geq 98\%$) and two nonionic trisiloxane surfactants, TSS10/2 and TSS6/3 (denoted as M (D'E_nP_mOH) M, with $n = 10, 6$ and $m = 2, 3$ on average, respectively). M represents the trimethylsiloxy group (CH₃)₃SiO_{1/2}–, D' represents the –O_{1/2}Si(CH₃)(R)O_{1/2}–, R is a mixture of ethylene oxide and propylene oxide (R = –(CH₂)₃–O–(CH₂–CH₂–O–)_n–(CH₂–CH(CH₃)–O–)_m). TSS10/2 and TSS6/3 surfactants (100% undiluted) are commercially available as TEGOPREN[®] 5847 and TEGOPREN[®] 5840. They were synthesized at Evonik Industries AG, Germany, and were used without further purification. Aqueous surfactant solutions were prepared using ultra-pure water (18.2 MΩcm, Merck Millipore, Germany). The concentrations of the SDS and trisiloxanes (TSS10/2, TSS6/3) solutions used were 0.5 wt.% (~ 2 CMC) and 0.1 wt.% (~ 20 CMC), respectively [36]. The surfactant/water mixtures were hand shaken vigorously in order to disperse the surfactants and used within 24 h after preparation. Thus, hydrolytic degradation of the surfactants was minimal and could be neglected.

Flat free water subphases were formed by placing 50 mL of ultra-pure water into 145 mm diameter Petri dishes. The water distributed evenly across the bottom of the Petri dish and the water subphase had a uniform thickness $H_0 \sim 3$ mm. The dimensionless Bond number, G , ($G = \rho H_0^2 g / S$, where ρ is the density of the

Download English Version:

<https://daneshyari.com/en/article/591923>

Download Persian Version:

<https://daneshyari.com/article/591923>

[Daneshyari.com](https://daneshyari.com)