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Role of self-assembled surfactant structure on the spreading of oil on flat solid surfaces

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ABSTRACT

Uniform spreading of oil on solid surfaces is important in many processes where proper lubrication is required and this can be controlled using surfactants. The role of oil–solid interfacial self-assembled surfactant structure (SASS) in oil spreading is examined in this study for the case of hexadecane-surfactant droplet spreading on a flat horizontal copper surface, with triphenyl phosphorothionate surfactants having varying chain lengths (0 to 9). It is shown that the frictional forces (F_{SASS}) as determined by the SASS regulate droplet spreading rate according to surfactant chain length; surfactants with longer chains led to higher reduction in the spreading rate. The extent of such forces, F_{SASS}, depends on the surfactant density of the evolving SASS, and specific configuration the evolving SASS exhibit as per the orientations of the surfactant chains therein. Thus, $F_{SASS} = [k_1 + k_{2(t)}]\,\Gamma_{\delta(t)}$, where $\Gamma_{\delta(t)}$ is the surfactant adsorption density of SASS at time 't' during evolution, and, k_1 and $k_{2(t)}$ are the force coefficients for $\Gamma_{\delta(t)}$ and orientations (as a function of spreading time) of the surfactant chains respectively. As a SASS evolves/grows along with adsorption of surfactants at the spreading induced fresh interface, the $k_1\Gamma_{\delta(t)}$ component of F_{SASS} increases and contributes to reduction in the net spreading force (S). With a decrease in the net spreading force, the existence of a cross-over period, during which the transition of the spatial dynamics of the chains from disordered to realignment/packing induced ordered orientation occurs, has been inferred from the F_{SASS} vs. chain length relationships. Such relationships also suggested that the rate of realignment/packing is increased progressively particularly due the realignment/packing induced decrease in the net spreading force. Therefore, the realignment process is a self-induced process, which spans a measurable period of time (several minutes), the cross-over period, during which the net spreading force decreases essentially due to such self-induced process.

Contents

1. Introduction

An understanding of the mechanisms by which oil–solid interfacial self-assembled surfactant structures (SASS)—surfactant film—impart

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specific oil spreading behavior is fundamentally important to many applications including engine oil lubrication, coating, painting, oil recovery, micro-fluidics, and drug delivery [1–6]. Depending on the concentration of surfactants and their molecular architecture (polarity of the head group, and chain length and branching), interfacial surfactant films attain form such as uniform monolayer or irregular hemicelles [7,8]. SASS formation is not necessarily a spontaneous event but structurally evolves along with adsorption of surfactants at the fresh oil–solid interface generated during spreading and, alignment/packing of the surfactants in the SASS. In spite of interference from structural and configurational dynamics associated with evolution of SASS, possibly spanning the entire spreading duration, the spreading behavior has been seen to follow Tanner's power law [9].

$$R(t) = \Omega^{\frac{3}{10}}(\sigma/\eta)^{\frac{1}{10}}t^{\frac{1}{10}} \qquad (1)$$

where, ‘*R*’ is the radius of a droplet on a surface, ‘*t*’ is the spreading time, ‘σ’ represents surface tension, ‘η’ refers to the droplet viscosity, and ‘Ω’ is the droplet volume. Here, the spreading behavior of the hexadecane droplet (having triphenyl phosphorothionate (TPPT) type surfactants of varying chain lengths) on a flat horizontal copper surface was studied to determine the role of the surfactant structure on spreading behavior. Self-assembly of the surfactants upon their adsorption at the solid–oil (s/o) interface and along the solid/oil/air (s/o/a) contact line can be viewed microscopically as a flexible soft SASS “tray” electrochemically glued to the interface and having wedges at the s/o/a contact line (Fig. 1). The forces (F_{SASS})—frictional forces at the SASS–oil interface—which vary with structural evolution are governed by surfactant density and alignment/packing of surfactants. In order to determine the progressive effects of an evolving SASS on the spreading rate (determined as $n = \ln$ (normalized base area of a droplet)/ln *t*, area/time), particularly with emphasis on structural evolution being unique as per surfactant structures that constitute a SASS, this study focuses on the how variations in surfactant chain lengths from 0 to 9 regulate spreading rate. Typically, for surfactants having similar head groups, adsorption density and alignment of the chains in the SASS are dependent on the surfactant chain length [10].

2. Experimental

2.1. Materials

The non-aqueous solvent used was hexadecane (>99%, Sigma). The copper metal surface of 100 nm thickness was prepared by thermal evaporation (Edwards BOC Auto 306) of 99.99% pure copper (Kurt J. Lesker Co.) from a tungsten boat followed by deposition on a silicon wafer (University Silicon) at a rate of 2 Å/s and at 5×10^{-7} Torr pressure. The surface tension of solid copper is about 1300 mN/m [11]. Triphenylphosphorothionate type surfactants having different chain lengths [triphenyl phosphorothionate (TPPT), butylated triphenyl phosphorothionate (butylated TPPT), nonylated triphenyl phosphorothionate (nonylated TPPT)] were obtained from Ciba (Fig. 2). Solutions of these surfactants were prepared in hexadecane at desired concentrations.

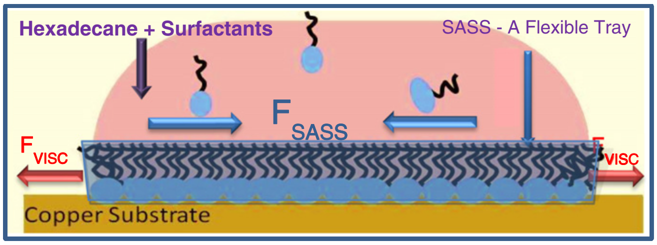

Fig. 1. Illustration of the forces contributing to spreading of a hexadecane-surfactant droplet on a flat horizontal copper substrate. SASS—resembling a flexible tray (blue in color)—can be seen at the ‘substrate Cu’–droplet interface; viscous forces (F_{VISC}) are in the spreading direction and F_{SASS} towards the droplet center. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2.2. Imaging and analysis of oil droplet spreading

The substrate was placed on the stage of a microscope (Nikon) and a 2 μL droplet of the surfactant solution was gently placed onto a stage using a syringe and taking care to avoid any effect due to the loading impact. The ambient temperature was controlled at 25 °C. The images of the droplet during the spreading process were captured by a Hitachi CCD camera from the top and recorded by a Labview program at preset intervals. The base contact area values of the droplets were analyzed from the images with software ImageJ (National Institutes of Health). The droplet area was measured as soon as a pure hexadecane droplet was placed on the Cu metal surface. This area was accounted for in the estimation of the normalized areas of the droplets during spreading.

2.3. Rheological measurements

Kinematic viscosity values of hexadecane-surfactant solutions were measured using an Anton Paar DSR rheometer. 100 mL of solution was poured into a glass cylinder and measurements were taken using a vane type probe, and at 25 °C. Hexadecane density was considered to be 0.77 g/cm^3. Kinematic viscosity values were determined within the shear rate range of 0.1–100 s^{-1}, and using Cannon viscosity standards.

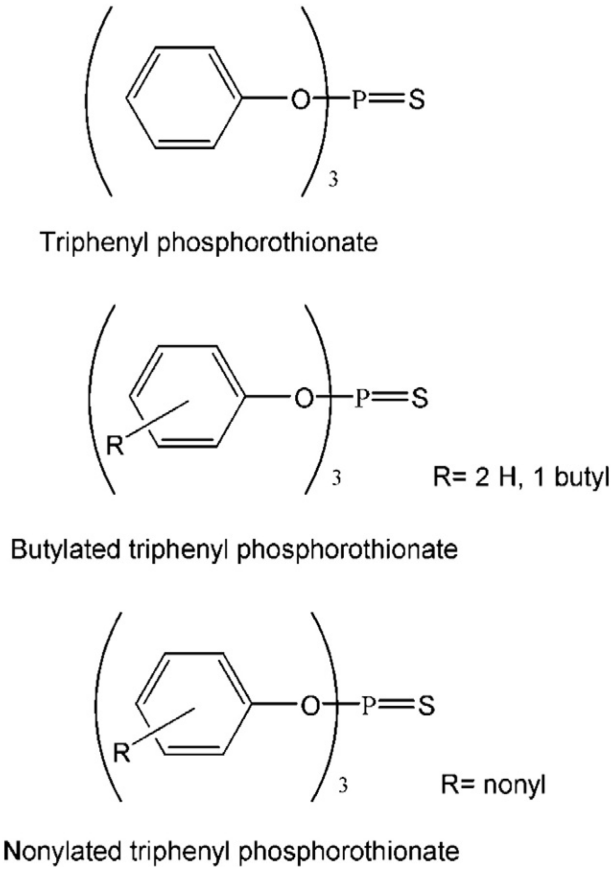

Fig. 2. Molecular structures of triphenyl phosphorothionate (TPPT), butylated triphenyl phosphorothionate (butylated TPPT), and nonylated triphenyl phosphorothionate (nonylated TPPT) surfactants.

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