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Friction and adsorption of aqueous polyoxyethylene (Tween) surfactants at hydrophobic surfaces

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Abstract

The nanotribological responses of a series of nonionic polyoxyethylene surfactants (Tween 20, Tween 40, Tween 60, and Tween 80) were investigated after they were adsorbed from aqueous solution onto atomically smooth hydrophobic substrates. The hydrophobic surfaces were composed of a condensed monolayer of octadecyltriethoxysilane (OTE; contact angle $\theta > 110°$). The nanorheological measurements were performed using a modified surface forces apparatus after coating atomically smooth mica with these OTE monolayers, while adsorption measurements were performed using phase-modulated ellipsometry on silicon wafers coated with these same monolayers. The minimum surface–surface separation observed under high load in friction studies agreed quantitatively with the thickness obtained from ellipsometry. For Tweens 20, 40, and 60, the thickness of the adsorbed film increases with increasing alkyl chain length. Systematic investigations of the nanorheological response showed that there is a "solid-like" elastic response from confined surfactant layers, which is the case for the smallest separations to separations up to slightly larger than twice the adsorbed film thickness. In kinetic friction, these confined layers are characterized by a shear stress of approximately 3 MPa with minimal dependence on shear rate. The magnitude of the sliding shear stress is the same as the apparent yield stress at $\approx$3 MPa; it is independent of alkyl chain length within the Tween family of surfactants and corresponds to a nominal friction coefficient of $\mu \sim 1$. A similar friction coefficient is observed for boundary lubrication on the macroscopic scale in a tribometer utilizing hydrophobic surfaces and $\mu \approx 1.1$ for Tweens 20, 40, and 60. These results suggest that while Tween molecules adsorb onto hydrophobic surfaces to form a robust separating layer, the lubricating properties of these layers are dominated by a highly dissipative slip plane, the same for all alkyl chain lengths.

Keywords: Tween; Adsorption; Friction; Hydrophobic; SFA; Micelles; Rheology; Tribology; Contact angle; Surfactant; Shear

1. Introduction

Understanding the complexity of surfactant adsorption at solid–liquid interfaces remains one of the main challenges of colloid science. Furthermore, the dynamic properties of surfactants at surfaces on the nanoscale are poorly understood and the literature is relatively sparse, although the subject has been studied for some time [1–3]. These dynamic properties have a large bearing on the (nano)tribological and lubricating properties of surfaces coated by surfactant layers. This is a subject of considerable relevance to many everyday-life systems, such as foods and personal care products, as well as to industrial processes. Most published nanorheological/tribological studies of surfactants have involved ionic surfactants, such as CTAB [4], but we are not aware of a systematic prior study that investigates the tribological properties of nonionic surfactants. In this paper, we aim to fill this knowledge gap by investigating the adsorption of a series of nonionic surfactants (Tweens) onto hydrophobic surfaces as well as the nanotribological/rheological properties of these surfactant-covered surfaces.

No unifying picture has emerged despite extensive studies on the influence of surfactant charge on the kinetics, morphology, structural properties, and mechanisms of adsorption by cationic [5], anionic [6], nonionic [7], and zwitterionic [8] amphiphiles at the liquid–solid interface. These studies show that, depending on the aliphatic chain length, aqueous electrolyte, and surface chemistry of the substrate, surfactants may adsorb

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as hemicylindrical structures, cylindrical aggregates, monolayers, or bilayers.

In this paper, for simplicity we consider the adsorption of nonionic surfactants onto a hydrophobic surface. Previously, it was found [9] that a monolayer forms in this situation, provided that the solid hydrophobic surface is uniform in topography and chemical composition—in other words, is very hydrophobic. As the length of the hydrocarbon chain increases, the hydrophobic interaction between the surfactant and the substrate increases. Moreover, the hydrophobic interaction between neighboring molecules also increases, giving a more closely packed density on the substrate. The amount of longer chain surfactants adsorbed grows more rapidly than in direct proportion to the alkyl chain length [10]. The series of Tweens 20, 40, and 60 varies only in alkyl chain length, which makes this series a good candidate for investigating the influence of alkyl chain length on adsorbed layer thickness.

In the experiments described below, we use the same hydrophobic surface—a condensed monolayer of octadecyltriethoxysilane (OTE) [11–13], formed on a silicon wafer for the contact angle and ellipsometry measurements and on freshly cleaved mica for the friction measurements. From earlier studies [11–13] it is known that extended OTE monolayers are highly hydrophobic (contact angle >110°) and show extremely low roughness (root mean square ∼3 Å) and the present study confirms this essential premise of the experimental design.

We present contact-angle measurements to establish the quality of hydrophobicity, ellipsometry measurements to determine the adsorbed film thickness, and friction measurements in a modified surface forces apparatus (SFA) to quantify the nanorheological properties of the confined surfactant films. The results of these studies are compared to provide a unifying picture of the adsorption process of a homologous series of polyoxyethylene sorbitans (Tweens). We address the question how monolayers adsorbed onto these hydrophobized surfaces slide past one another in frictional contact. The film thickness and nanorheological results are also discussed in terms of macroscopic tribological measurements in which the same surfactant solutions are used to lubricate compliant hydrophobic surfaces in a tribological setup utilizing macroscopic surfaces that are rough on the molecular scale.

Fragneto et al. [14] quantified how surface coverage grows with solution concentration and went on to show that chains within the adsorbed layer are tilted regardless of surface coverage; the lower the surface coverage, the higher the tilt for all systems that they studied. They concluded that the hydrocarbon chain must lay close to flat on the surface. In contradiction, Cross et al. [15] reported that surfactants with longer alkyl chains form thinner, denser layers when adsorbed to extended hydrophobic surfaces from aqueous solution. This they sought to explain by considering the fluidity of surfactants, which is known to decrease with increasing alkyl chain length [16]. The substrate used in those experiments can be considered as pseudo-hydrophobic, however, as it was prepared through treatment with trimethylchlorosilane. The level of hydrophobicity determined from water contact angle measurements was marginal, with the advancing contact angle of only 71 ± 2°.

2. Experimental

2.1. Materials and sample preparation

The following nonionic surfactants, each of them ethoxylated sorbital esters of fatty acids and a polyoxyethylene unit 20 repeat groups long on average, were studied: (a) Tween 20, in which the headgroup is sorbitan monolaurate; (b) Tween 40, in which the headgroup is sorbitan monopalmitate; (c) Tween 60, in which the headgroup is sorbital monostearate; and (d) Tween 80, in which the headgroup is sorbitan monooleate. Tweens 20, 40, and 60 possess 12, 16, and 18 saturated carbons in the alkyl chain, respectively. Tween 80 possess 18 carbons in the alkyl chain and is unsaturated. All of these surfactants are soluble in water with a high value of hydrophilic–lipophilic balance. These surfactants were purchased from Fluka and were used as received. Key properties for the purpose of this study are summarized in Table 1.

For the fabrication of OTE monolayers, *N*-octadecyltriethoxysilane was purchased from Hüls America, Inc. In the literature, as different groups have reported variable experiences when it comes to making OTE monolayers of good quality [17–20], it is clear that the resulting monolayers depend highly on details of the experimental protocol. A detailed discussion of the experimental protocols that have been found in this laboratory to be most effective will be presented later (manuscript under preparation). Briefly, previous studies from this laboratory showed that the packing density and degree of crys-

Table 1
A summary of the major physical properties of the Tween surfactants used in this study

	Commercial name			
	Tween 20	Tween 40	Tween 60	Tween 80
Chemical name	Polyoxyethylene (20) sorbitan monolaurate	Polyoxyethylene (20) sorbitan monopalmitate	Polyoxyethylene (20) sorbitan monostearate	Polyoxyethylene (20) sorbitan monooleate
Molecular weight	1228 g/mol	1284 g/mol	1312 g/mol	1310 g/mol
Density (g/ml)	1.105	1.080	1.070	1.064
cmc (mM)	0.059 (0.0072%)	0.027	0.0023	0.012 (0.0016%)
HLB	16.7	15.6	14.9	15.0
Cloud point (°C)	76			65
Viscosity at 25 °C (cP)	330	500	550	425
Phase	Clear liquid	Yellow liquid–gel	Liquid–gel	Golden-yellow viscous liquid

Data are taken from Ref. [30].