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Real-time monitoring the adsorption of sodium dodecyl sulfate on a hydrophobic surface using dual polarization interferometry

Ming Duan [a,b,*], Hu Wang [a,c,*], Shenwen Fang [b], Ying Liang [b]

[a] State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu 610500, China
[b] School of Chemistry and Chemical Engineering, Southwest Petroleum University, Chengdu 610500, China
[c] School of Materials Science and Engineering, Southwest Petroleum University, Chengdu 610500, China

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ABSTRACT

The adsorption process of sodium dodecyl sulfate (SDS) at a hydrophobic layer was investigated by dual polarization interferometry (DPI), which provided the real-time information at solid/liquid interface. In dilute solution, the molecules adsorb at the surface as isotropic layer. With the increase in concentration, the molecules aggregate to form hemimicelles and the critical hemimicelles concentration (HMC) is 1 mM. The adsorption of SDS at C18 surface obeys two-step process. The competitive formations of micelles in solution and hemimicelles on C18 surface lead to particular adsorption behavior in higher concentration. We also proposed a four-stage adsorption model of SDS at C18 surface according to bulk concentration.

1. Introduction

Surfactants are used in countless diverse applications for their adsorption performance at surface and interface. As one of the mostly utilized surfactants, sodium dodecyl sulfate (SDS) has been extensively studied in the past few decades [1–3]. Understanding the adsorption behavior of SDS on a hydrophobic surface is important to a variety of fields, such as enhanced oil recovery, mineral flotation, detergency, lubrication and microelectronics [4–6].

The aggregation of SDS at hydrophobic surface exhibits much difference in comparison with bulk phase. It has been found that a greater amount of SDS molecules adsorb at C18 monolayer below the critical micelle concentration (CMC, about 8.1 mM) than above it [7]. The maximum adsorption on C18 surface occurs at about 7 mM bulk solution. It can be ascribed to the presence of hemimicelles below the CMC. However, how aggregation is organized at hydrophobic surface still needs continue investigation. Although some research works suggest that most of the aggregates observed in bulk solution can also appear at the solid/liquid interface as hemimicelles, the structure, shape, and how the aggregates present are still ambiguous.

Understanding more detailed adsorption mechanism requires knowledge of molecular transfer processes between interfacial layer and bulk solution. There have been a lot of experimental techniques explored to study the adsorption of surfactant onto hydrophobic surface, such as ellipsometry, Raman, Vibrational Sum Frequency, fluorescence spectroscopy, FTIR, calorimetry, atomic force microscopy and neutron reflection [8–11]. All of them, however, have their limitations.

Herein we introduce dual polarization interferometry (DPI) to investigate the adsorption of SDS on hydrophobic layer (C18 layer). DPI is an optical, surface analytical technique, which can provide more detailed information in surfactant adsorption and is intensely used in bioscience in the recent year [12–14]. The measurement technique of DPI is based on Yong's two-slit interference [15]. The laser passes through the four layered silicon chip from the inlet side [16]. Two of the layers work as waveguides, one for reference and another for sensing. The interference fringes can be gathered at the outlet. The waveguide in reference layer is stable and will never change. Therefore, any changes occurring at sensing layer will cause the moving of interference fringes. When adsorption within the evanescent field (about 100 nm) occurs on the sensing surface, the refractive index changes and causes a phase change, finally leads to a shift of the interference fringes. The important practical consequence of this approach is that measurements focus on determining the spatial position of fringes and not by measuring their intensity, which can further enhance the stability of the measurement. In practical, the position of the fringe image is monitored on the millisecond time scale to enable changes happening in real time to measure the deposition of materials on the waveguide surface at a resolution level of 10^{-15} g/mm^2.

* Corresponding authors. Address: State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu 610500, China
E-mail addresses: swpua124@126.com (M. Duan), huwang@swpu.edu.cn (H. Wang).

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By involving two orthogonal polarizations, transverse electric (TE) and transverse magnetic (TM), two separate shifts of fringes can also be obtained. In this way, DPI can provide a measurement of molecules at the surface to give the real-time information on the refractive index, thickness, density, and the mass of adsorbed molecules on surface.

In this paper, DPI was introduced to investigate the adsorption behavior of SDS molecules onto C18 surface. Different concentrations of SDS were injected onto C18 surface. Analyzing as isotropic and anisotropic layers yielded out the real-time information of adsorption, like adsorbed mass, thickness, TM/TE, kinetic constants, birefringence, desorption behavior and residual molecules information. Based on all the experiment results, we can obtain a thorough understanding on the adsorption behavior of SDS onto C18 surface in different concentrations.

2. Experimental section

SDS was purchased from Aladdin Chemistry Co. Ltd. and purified before experiment. All the solutions used in the experiments were prepared with deionized water. The DPI experiments were conducted with *Ana*Light Nano 200 (Farfield Group Ltd., Crewe, UK). The silicon chip including a silicon oxynitride surface modified to introduce covalently bound C18 (FB 100 C18 chips, Farfield Scientific Ltd.) were used for all experiments. The fluid (deionized water) flowed over the channel on the chip surface in a speed of 50 μL min^{-1} by an external pump (Harvard Apparatus, PHD2000 Infusion). Before SDS injection, ethanol was injected to the chip surface for calibration. In a consecutive injection experiment, SDS with concentration of 0.2 mM, 0.5 mM, 1 mM, 2 mM, 5 mM, 10 mM and 20 mM were successively injected to the chip surface. While in other measurements, different concentrations of SDS, 0.1 mM, 0.2 mM, 0.3 mM, 0.4 mM, 0.5 mM, 0.6 mM, 0.7 mM, 0.8 mM, 0.9 mM, 1 mM, 2 mM, 3 mM, 4 mM, 5 mM, 6 mM, 7 mM, 8 mM, 9 mM, 10 mM, 20 mM, 30 mM, 40 mM and 50 mM were injected to different pieces of chips, respectively. In all the experiments, the flow rate of the fluid changed to 15 μL min^{-1} and lasted for 6 min when the SDS was injected. The experiment temperature was 20 °C.

3. Results and discussion

DPI provides a novel method to quantitatively investigate the adsorption of SDS on hydrophobic surface. The adsorption behavior of SDS onto C18 was firstly examined with a consecutive injection method, in which different concentrations of SDS were injected onto the same C18 chip for 6 min and allowed to equilibrate with deionized water before the subsequent injection of the next concentration. Fig. 1a shows the real-time changes in TM and TE. It can be seen that the SDS molecules strongly adhere to the surface and there are still some residual phase changes remaining after the flow phase returning to deionized water, which indicates that some SDS molecules are still kept on the surface. The peak values of TM and TE gradually rise with the increase in SDS concentration, which means that more SDS molecules adsorb on the surface in higher concentration.

More adsorption information can be obtained from the real-time behaviors of mass, thickness, refractive index (RI), coverage and birefringence data in SDS injection process, which can be acquired from data analysis. The organic molecules adsorbed on the solid surface from solutions usually form isotropic layer, for example, proteins and polymers [14,17]. However, some molecules can form birefringence (anisotropic layer), like lipid bilayers and surfactants assembly [7,18]. DPI enables analysis for both isotropic and anisotropic layers. For isotropic layer, the RI, thickness, mass

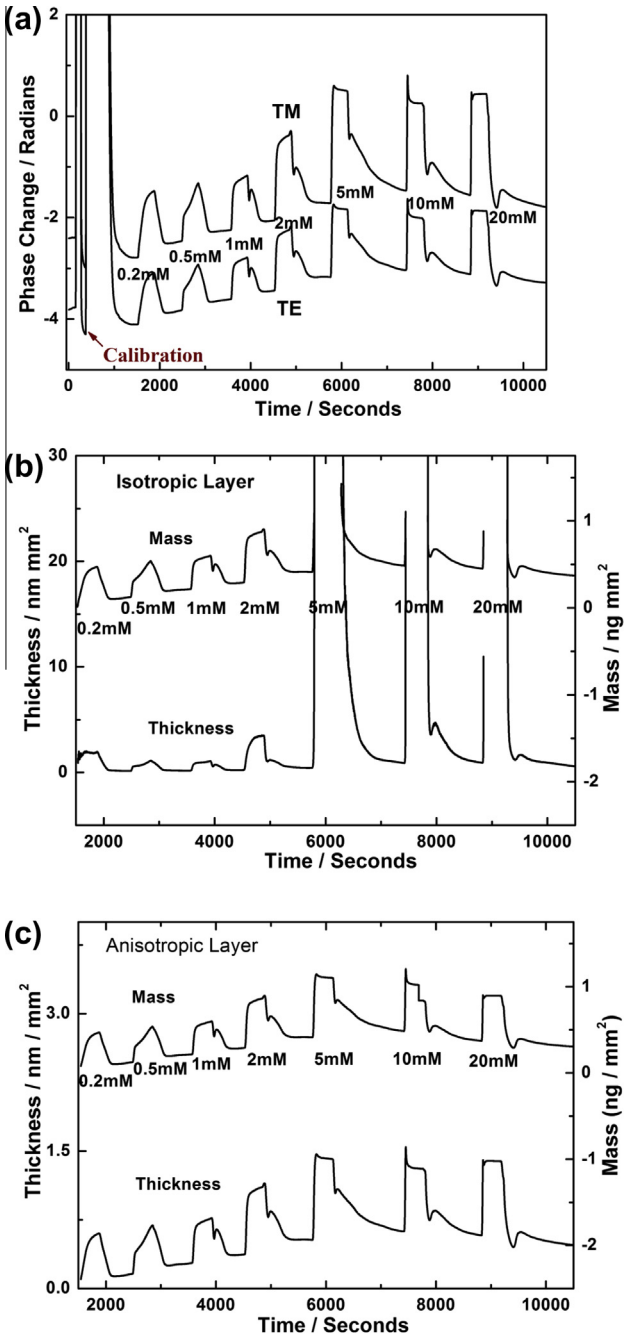

Fig. 1. Real-time data of TM and TE in a consecutive injection experiment and the mass and thickness changes analyzed as (b) isotropic layer and (c) anisotropic layer.

and coverage (density) of SDS layers can be resolved. And the birefringence is regarded as zero. If the layer is anisotropic, it cannot be resolved as an isotropic layer. If using isotropic analysis, the calculation gives errors or unreasonable values. With a fixed RI at 1.45 and RII (refractive index increment, 0.107 ml/g for SDS), the mass and birefringence of the SDS can be resolved as anisotropic layer from TM and TE.

Fig. 1b and c are the calculated thickness and mass data, analyzed as isotropic and anisotropic layer, respectively. Tables 1 and 2 are the corresponding calculated data in each concentration. It is shown that at low concentrations, from 0.2 mM to 2 mM, both isotropic and anisotropic models can give an intact calculated data. However, at higher concentrations, the data could not be resolved as isotropic layer indicating that the layers are anisotropic. There-