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Colloids and Surfaces A: Physicochemical and Engineering Aspects



Adsorption kinetics of sodium dodecyl sulfate on perturbed air-water interfaces



OLLOIDS AND SURFACES A

Alvin Casandra^a, Meng-Chen Chung^b, Boris A. Noskov^c, Shi-Yow Lin^{a,*}

^a Department of Chemical Engineering, National Taiwan University of Science and Technology, 43 Keelung Road, Sec. 4, Taipei 106, Taiwan

^b Department of Biotechnology, TransWorld University, 1221, Zhennan Rd., Douliu City, Yunlin County 640, Taiwan

^c Department of Colloid Chemistry, St. Petersburg State University, Universitetsky pr. 26, St. Petersburg 198504, Russia

HIGHLIGHTS

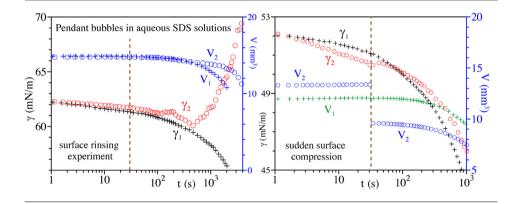
GRAPHICAL ABSTRACT

- A Pendant bubble tensiometer was used to measure the dynamic ST of SDS solutions.
- Processes: surface rinsing, sudden compression, continuous expansion & compression.
- ST increased during surface rinsing, indicating SDS desorbed out of the surface.
- The ST decreased continuously after sudden surface compression.
- The ST remained constant during continuous surface expansion.

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ABSTRACT

A pendant bubble tensiometer was used to measure the relaxation of the surface tensions of aqueous sodium dodecyl sulfate (SDS) solutions for four different perturbed air-water interfaces under surface rinsing, sudden surface compression, continuous surface expansion and compression. The complete set of surface tension (ST) relaxations was monitored to study the adsorption kinetics of SDS. The ST increased in the surface rinsing experiment, and this increase indicated that the SDS that was adsorbed at the air-water interface desorbed from the interface. The ST relaxed continuously after sudden surface compression, and this continuous ST relaxation indicated that the desorption rate of SDS molecules was faster than the surface compression, and this constant ST data indicated that the adsorption and desorption rates were faster than the surface perturbation rate in this study.

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1. Introduction

Surfactant molecules are composed of a hydrocarbon chain bonded to a hydrophilic head group. An unfavorable interaction

* Corresponding author. E-mail address: sylin@mail.ntust.edu.tw (S.-Y. Lin).

http://dx.doi.org/10.1016/j.colsurfa.2017.01.043 0927-7757/© 2017 Elsevier B.V. All rights reserved. between the hydrophobic tail and water molecules makes surfactant monomers dissolve sparingly in an aqueous environment. As a result, surfactant molecules tend to adsorb onto gas-liquid interfaces and reduce the surface tension of the gas-liquid interface [1]. Due to the ability to reduce surface tension of liquid-gas interfaces, surfactants are commonly used in industrial processes [2], including sundry practical applications and products [3]. Determination of the optimal dosage requires specific knowledge of the equilibrium and dynamic properties of the surfactant [4]. Therefore, the study on of surfactant adsorption at the air interface has been an important subject of intense research over the past decades.

For the study of the adsorption/desorption kinetics of surfactant molecules, one would like to know the dynamic properties of the surfactant. The dynamic properties involve how fast the surface tension changes [5,6] and can be extracted by measuring the dynamic surface tension. The dynamic properties of a surfactant have commonly been studied by applying theoretical models to simulate surface tension relaxation. To date, several equations/models on surfactant mass transfer have been introduced in the literature [7–13].

lonic surfactants have attracted much attention in the past decade, as they play essential roles in sanitation and antiseptic agents, germicides, and fungicides and in diverse cosmetic and pharmaceutical applications [14]. Sodium dodecyl sulfate is one of the most widely used surfactants in industry. Hundreds of reports on the application and properties of SDS surfactants have appeared within the past two decades. However, only several of them are focused on the interfacial properties of SDS, such as viscoelasticity and rheological properties of SDS monolayers [15], adsorption/desorption kinetics onto and from solid surfaces [16,17], SDS surfactant molecules film formation [18], and interfacial properties in the presence of proteins [19,20].

Elworthy and Mysels [21] measured the equilibrium surface tension data of pure sodium dodecyl sulfate solutions using the Wilhelmy plate method. Sasaki et al. [22] measured the desorption time of SDS using the capillary wave method. Fang and Joos [23] reported the equilibrium surface tension data of pure SDS solution and in the presence of dodecanol. Corti et al. [24,25] applied laser interferometry on an oscillating bubble to study the desorption of SDS molecules out of the air-water interface. They found that there exists a critical concentration ($C_c = 5 \times 10^{-8} \text{ mol/cm}^3$) below which the exchange of SDS molecules between the air-water interface and bulk was inhibited. Above C_c , the SDS molecules were able to desorb from the interface back to bulk solution when the interface was rinsed with pure water.

To the best of our knowledge, in the literature, much data exist for the experimental dynamic surface tension of SDS, $\gamma(t)$ (listed in Table S1 in the supplementary material) [26–35]. However, hardly any complete $\gamma(t)$ relaxation profiles have been reported for SDS adsorbing onto a fresh air-water interface. Fainerman et al. [31] applied the maximum bubble pressure method and a pendant drop tensiometer to obtain the dynamic $\gamma(t)$ data at 10^{-4} –10 s and $10-10^4$ s, respectively, to obtain complete $\gamma(t)$ profiles for a low concentration SDS solution ($C_0 = 2 \times 10^{-7}$ mol/cm³).

The aim of this study is to study the adsorption kinetics of SDS. A pendant bubble tensiometer was applied to measure the $\gamma(t)$ profiles for four different perturbed air-water interfaces, including surface rinsing, sudden surface compression, continuous surface expansion and continuous surface compression. The outline of this paper is as follows. In Section 2, four different experimental methods using the pendant bubble tensiometer are detailed. The theoretical framework for the mass transport of the surfactant is then given in Section 3. Next, in Section 4, the experimental $\gamma(t)$ relaxation profiles are analyzed to understand the adsorption kinetics of SDS on perturbed interfaces. Finally, a discussion and the conclusion are given at the end.

2. Experimental measurements

2.1. Materials

Ionic surfactant SDS (sodium dodecyl sulfate, M.W.=288.38 g/mol), purchased from Sigma-Aldrich (GC grade,

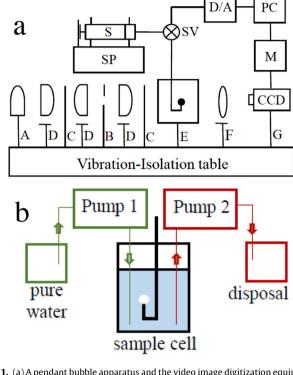


Fig. 1. (a) A pendant bubble apparatus and the video image digitization equipment. A: light source; B: pinhole; C: filter; D: planoconvex lens; E: quartz sample cell and inverted needle inside thermostatic air chamber; F: objective lens; G: video camera; M: monitor; PC: personal computer; D/A: data translation card; S: syringe; SP: syringe pump; and SV: solenoid valve. (b) A pumping system incorporated in the pendant bubble system.

purity \geq 99%), was used without further modification. Acetone (HPLC grade), which was used to calibrate the surface tension measurement, was obtained from Fisher Scientific Co. Aqueous solutions were prepared with clean water purified via a Barnstead NANOpure water purification system, with the output water having a specific conductance of less than 0.057 μ S/cm. The values of the surface tension of air-water and air-acetone using the pendant bubble technique described in the following sections were 72.0 mN/m and 23.1 mN/m, respectively, at 25.0 °C.

2.2. Tensiometer

A video-enhanced pendant (emerging) bubble tensiometer was employed for the measurement of the equilibrium (γ (C)) and dynamic (γ (t)) surface tension of the aqueous SDS solutions at 25.0 ± 0.1 °C. The system creates a silhouette of a pendant bubble, records a video image of the silhouette, and digitizes the image. A collimated beam with constant light intensity passes through the pendant bubble and forms a silhouette of a bubble on a solid-state video camera (MS-4030 charge-couple device (CCD), Sierra, Scientific Co.). The silhouette image was digitized into 480 lines × 512 pixels with a level of gray at 8-bit resolution.

The apparatus (shown in Fig. 1a) and the edge detection routine have been described in detail in a previous study [36]. A calibration procedure using a stainless ball was used to calculate the length between pixels along a row or a column. The calibration procedure yielded a value of 0.01009 mm/pixel. The temperature variation of the aqueous solution was less than ± 0.1 K during the measurement of γ (t). A 16-gauge stainless steel inverted needle (0.047 in. I.D.; 0.065 in. O.D.) was used to generate the bubble.

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