

## Cationic Gemini surfactant at the air/water interface

Chen Qibin, Liang Xiaodong, Wang Shaolei, Xu Shouhong, Liu Honglai\*, Hu Ying

State Key Laboratory of Chemical Engineering and Department of Chemistry, East China University of Science and Technology, Shanghai 200237, China

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### Abstract

The surface properties and structures of a cationic Gemini surfactant with a rigid spacer, *p*-xylyl-bis(dimethyloctadecylammonium bromide) ( $[(C_{18}H_{37}(CH_3)_2N^+-CH_2-C_6H_4-CH_2-N^+(CH_3)_2C_{18}H_{37}]_2Br^-$ , abbreviated as 18-Ar-18,2Br<sup>-1</sup>), at the air/water interface were investigated. It is found that the surface pressure–molecular area isotherms observed at different temperatures do not exhibit a plateau region but display an unusual “kink” before collapse. The range of the corresponding minimum compressibility and maximum compressibility modulus indicates that the monolayer is in the liquid-expanded state. The monolayers were transferred onto mica and quartz plates by the Langmuir–Blodgett (LB) technique. The structures of monolayers at various surface pressures were studied by atomic force microscopy (AFM) and UV–vis spectroscopy, respectively. AFM measurements show that at lower surface pressures, unlike the structures of complex or hybrid films formed by Gemini amphiphiles with DNA, dye, or inorganic materials or the Langmuir film formed by the nonionic Gemini surfactant, in this case network-like labyrinthine interconnected ridges are formed. The formation of the structures can be interpreted in terms of the spinodal decomposition mechanism. With the increase of the surface pressure up to 35 mN/m, surface micelles dispersed in the network-like ridges gradually appear which might be caused by both the spinodal decomposition and dewetting. The UV–vis adsorption shows that over the whole range of surface pressures, the molecules form a J-aggregate in LB films, which implies that the spacers construct a  $\pi$ – $\pi$  aromatic stacking. This  $\pi$ – $\pi$  interaction between spacers and the van der Waals interaction between hydrophobic chains lead to the formation of both networks and micelles. The labyrinthine interconnected ridges are formed first because of the rapid evaporation of solvent during the spreading processes; with increasing surface pressure, some of the alkyl chains reorient from tilting to vertical, forming surface micelles dispersed in the network-like ridges due to the strong interaction among film molecules. © 2007 Elsevier Inc. All rights reserved.

**Keywords:** Gemini surfactant; LB film

### 1. Introduction

Gemini surfactants are made up of two amphiphilic moieties connected by a spacer group at or near the head groups. They are a new class of surfactants, having aroused much interest since the early 1990s of the previous century because of their unique properties, such as lower CMC (critical micelle concentration) and  $C_{20}$  (the surfactant concentration where the surface tension is decreased by 20 mN/m), stronger biological activity, and better solubilizing ability, wetting, foaming, and lime-soap dispersing properties compared to conventional surfactants [1].

Monomolecular films spread on liquid surfaces and gases adsorbed onto the surfaces of solids have long been used as

model systems for the study of the behavior of matter in two dimensions. At an air/water interface, surfactants arrange themselves with their hydrophilic head groups immersed in water and the hydrocarbon tails displayed outward in the air. Those formed by amphiphilic molecules at the air/water interface are either Gibbs or Langmuir monolayers, i.e., soluble or insoluble monolayers [2]. For the latter, the structure and properties are usually characterized experimentally by utilizing the classical surface pressure ( $\pi$ )–molecular area ( $A$ ) isotherms, neutron and X-ray diffraction, X-ray reflection, polarized fluorescence microscopy, Brewster angle microscopy (BAM), phase contrast transmission microscopy, scanning transmission electron microscopy, scanning electron microscopy, scanning tunneling microscopy, and atomic force microscopy (AFM), including in situ and ex situ investigations [3,4]. AFM is special in that it can be used to image surface areas from the molecular scale up to hundreds of micrometers in size, because of their

\* Corresponding author.

E-mail address: [hlliu@ecust.edu.cn](mailto:hlliu@ecust.edu.cn) (L. Honglai).

high lateral resolution and the simplicity of sample preparation. It is an ideal tool for macroscopic and microscopic studies on submicrometer morphological changes, which are crucial in the phase transitions of Langmuir–Blodgett (LB) films. At present, atomic force microscopy and its derivative friction force microscopy are frequently used to study phase separation of Langmuir–Blodgett films by imaging them after transferring them to solid substrates [5–8].

The existence of surface micelles in insoluble monolayers has repeatedly been discussed since Langmuir first proposed it in the 1930s, but it has not been well established because of experimental difficulties [9]. Since the emergence of microscopy, especially AFM, it has become possible to investigate surface micelles directly. The formation of surfactant hemimicelles adsorbed onto hydrophobic solid surfaces in aqueous solutions observed by AFM, or transferred onto silicon wafers by the LB technique studied by AFM and X-ray reflectivity, has been reported [10,11]. Surface micelles at the air/water interface formed by nonionic diblock copolymers have been found [12,13]. It has been observed that stearic acid monolayers exhibit a phase transition from a liquid-expanded to a condensed state on the subphase containing polycations and the existence of grains with a diameter of 20–100 nm in the liquid-expanded phase [4,14]. The formation of monodisperse two-dimensional surface micelles by partially fluorinated long-chain acids has been investigated by AFM and infrared spectroscopy [3,15–17]. In addition, the existence of surface micelles can be investigated by other tools, such as grazing incidence small-angle X-ray scattering, X-ray reflectivity, and transmission electron microscopy (TEM) [15,18].

So far, many studies have reported the properties and applications of soluble Gemini surfactants in solution or at interfaces, while only a few papers [19–24] have dealt with their insoluble monolayer behavior. The mixed monolayer of cationic Gemini surfactant with methylene spacers and sodium dodecyl sulfate was investigated by Wang and Marques [25]. The complex or hybrid films formed by a Gemini amphiphile, a bis-(imidazolium salt) with methylene spacers, with DNA [22], dye [19], inorganic materials [26,27], and TPPS [28] were extensively investigated by Liu and his colleagues. The properties of nonionic Gemini surfactant were studied by Mandal and co-workers [29]. However, to our knowledge, no reports concerned direct investigation of the morphologies of Gemini surfactants, especially bis-(quaternary ammonium salt) with a rigid spacer, at air–water interfaces. In this work, the  $\pi$ - $A$  isotherm of a cationic Gemini with a rigid spacer, *p*-xylyl-bis(dimethyloctadecylammonium bromide) ( $[C_{18}H_{37}(CH_3)_2N^+-CH_2-C_6H_4-CH_2-N^+(CH_3)_2-C_{18}H_{37}]_2Br^-$ , abbreviated as 18-Ar-18,2Br<sup>-1</sup>), was determined by using an LB trough. The corresponding morphologies of the monolayers transferred onto mica were studied by AFM. Due to two tail chains and the spacer group in this molecule, it is important to investigate the orientation of the former and the arrangement of the latter with increasing surface pressure or surface molecular density at the air/water interface. In addition, because there is a benzene ring in the molecule, we take advantage of this chromophore to investigate its performances

in LB films by UV–vis spectroscopy, which can offer information about the aggregation effect, and therefore on the structure characterization. To perform the study by UV–vis spectroscopy, the monolayer was transferred onto quartz plates.

## 2. Experimental

### 2.1. Materials

The Gemini surfactant 18-Ar-18,2Br<sup>-1</sup> was synthesized in this laboratory using the method described by Zana et al. [30] and characterized by elemental analysis and nuclear magnetic resonance (NMR). The details of the typical synthesis and the characterization are given in the supporting materials.

### 2.2. Preparation of monolayer and Langmuir–Blodgett film

The surface pressure measurements were performed on a Model 612D computer-controlled Langmuir film balance (Nima Technology, Coventry, UK). The rectangular polytetrafluoroethylene (PTFE) trough (20 × 30 cm) with two movable barriers moving with the same compression rates was used. It was filled with water purified by means of a Milli-Q Plus water purification system with an electrical resistance of 18.2 M $\Omega$ . The subphase temperature was controlled in the range of 5–40 ± 0.05 °C by flowing water from a thermostat (Phoenix P1 Circulator, Thermo Haake, Germany) circulated through the base plate of the trough during the experiment. To eliminate the influence of the contaminant, a PTFE nozzle with an aspirator pump connected was applied to suck the surface of the subphase before experiments. The surface was deemed to be clean when the fluctuation in surface pressures was found to be less than 0.05 mN/m during complete compression of the surface without the Gemini surfactant. The surface pressure was measured by the Wilhelmy method using a low-ash filter paper plate (10 × 23.5 mm) with the aid of a template and a razor knife.

A chloroform solution of 18-Ar-18,2Br<sup>-1</sup> with a concentration of 1.0 × 10<sup>-3</sup> mol/L was used as the spreading solution for the formation of Gemini surfactant monolayer. 20  $\mu$ l of this solution was spread on the subphase with a micrometer syringe. After waiting for 10 min to let the solvent evaporate entirely, the compression curves were recorded. All of the compression rates adopted were 15 cm<sup>2</sup>/min.

The films were transferred to mica or quartz plates by a vertical dipping method while the monolayer was held at constant surface pressure. The subphases were controlled at a constant temperature of 15 °C when the monolayers were transferred. The substrate surface was set to be perpendicular to the direction of the moving barrier. Mica substrates were freshly cleaved immediately before use, while the quartz substrates were initially treated with saturated K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>/concentrated H<sub>2</sub>SO<sub>4</sub> solution for 6 h and then carefully washed with pure water. Thereafter, the quartz substrates were cleaned by successive sonification in chloroform, acetone, ethanol, and pure water for 5 min and again washed with pure water each prior to transfer. The

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