



## Effect of the spacer group on the behavior of the cationic Gemini surfactant monolayer at the air/water interface

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### ABSTRACT

Surface properties of the insoluble cationic bis-(quaternary ammonium halide) surfactants (Gemini) with polymethylene spacer at the air/water interface were investigated. The monolayers were transferred onto mica by the Langmuir–Blodgett (LB) technique and the corresponding LB films were characterized by the atomic force microscopy (AFM) and the contact angle of water. For the Gemini surfactants with the different spacer length, it was found that the surface pressure–molecular area isotherms resemble to each other. The limiting area increases rapidly and almost linearly with the increase of spacer length for the short spacers, but reaches a maximum at  $s=10$  and decreases slightly at  $s>10$ . The AFM images show that the surface micelles and the multilayer aggregates gradually appear with the increase of surface pressure. No matter what the surface pressures are, the main structure of the monolayer almost keeps the same, which suggested that the major molecules lie nearly flat on the water surface, while the increase of surface pressure forces the minor alkyl chains to turn only partly or completely vertical to the water surface and even to overturn. This is the cause that the contact angle of water on LB film increases slightly with the surface pressure.

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### 1. Introduction

Gemini surfactants are made up of two amphiphilic moieties connected by a spacer group at or near the head groups, which have aroused many interests since the early 90s of the last century because of their unique properties [1]. Due to the presence of a hydrophilic or hydrophobic and rigid or flexible spacer group and two identical or different amphiphiles in a Gemini molecule, it is possible to synthesize the dimeric surfactants with an enormous variety of chemical structures resulting in a great difference in their properties. The bis-(quaternary ammonium halide) surfactants, in particular with a polymethylene spacer,  $[C_mH_{2m+1}(CH_3)_2N^+-C_sH_{2s}-N^+(CH_3)_2C_{m'}H_{2m'+1}], 2X^-$  ( $X^-$  = counterion), abbreviated as  $m-s-m'$  (if  $m=m'$ ,  $m-s-m$ ), where  $m$  or  $m'$  and  $s$  denote the number of carbon atoms in the alkyl chains and the spacer, have extensively been investigated in literatures [2]. The qualities of the spacer groups, such as their length, flexibility and chemical structure, have been investigated and it has been shown that the spacer group is of the great importance in determining the solution properties of aqueous surfactants [1,2]. However, the details of their structure–performance relationship remain elusive, though this kind of surfactants has been investigated for over two decades.

A monolayer formed at the air/liquid interface by insoluble amphiphilic molecules is called Langmuir monolayer, which is different from a Gibbs monolayer resulted from the preferential

adsorption of soluble amphiphilic molecules in the bulk phase. The knowledge of the surface area per surfactant molecule in the Gibbs monolayers is very important in surfactant science, because it is directly related to the surface excess concentration. On the basis of the variation of the surface tension with the concentration for a surfactant solution, it is possible to determine the surface excess concentration and the surface area occupied by a surfactant molecule at the air/water interface [3–5]. In principle, there is no difference between the soluble and insoluble monolayer, because no molecule is completely insoluble. Insoluble monolayers merely represent an extreme case of adsorption [3]. However, for the insoluble surfactants with very long alkyl chains, the molecular area is usually determined by the surface pressure ( $\pi$ )–molecular area ( $A$ ) isotherms, which have several similarities to the pressure–volume ( $p$ – $V$ ) isotherms of three-dimensional systems. If a liquid-condensed (LC) or a solid phase is observed in the isotherm, the value of the limiting area, an empirical parameter approximating the area occupied by the molecules at zero surface pressure, is conventionally obtained by the extrapolation of the steepest portion of the  $\pi$ – $A$  curves to  $\pi=0$  [3–5]. For a liquid-expanded (LE) phase, because the monolayer might collapse upon compression, the value of the limiting area is usually calculated by the regression analysis of the equation proposed by Menger et al., which was established by a two-dimensional variation of an imperfect gas law [6].

So far, only a few papers [7–12] were concerned with insoluble monolayer behaviors of Gemini surfactants at the air/water interface. The mixed monolayer of cationic Gemini surfactant with methylene

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spacers and sodium dodecyl sulfate was investigated by Wang and Marques [13]. The complex or hybrid films formed by the Gemini amphiphile, a bis-(imidazolium salt) with polymethylene spacers [14], with DNA [10], dye [15], inorganic materials [16,17] and tetrakis-(4-sulfonatophenyl)porphine [18] were extensively investigated by Liu and his colleagues. The properties of nonionic Gemini surfactant were studied by Krishnan et al. [19]. In our previous works, the surface properties and structures of a cationic Gemini surfactant with a rigid spacer, *p*-xylyl-bis (dimethyloctadecylammonium bromide), hereafter referred to as 18-Ar-18, at the air/water interface and the adsorption of collagen on the LB films of propanediyl-bis (dimethyloctadecylammonium bromide) transferred at low surface pressures were investigated [20,21].

In the present work, the  $\pi$ -*A* isotherms of bis-(quaternary ammonium bromide) with a polymethylene spacer consisting of different carbon number, 18-*s*-18 (*s*=3, 4, 6, 8, 10 and 12), were investigated. A single layer was transferred onto mica and the corresponding morphologies were observed by AFM. The contact angles of water on this LB film were also measured. Due to the presence of two tail chains and a spacer group in a molecule, it is important to investigate the orientation of the former and the arrangement of the later with the increasing surface pressure or the surface molecular density, and the effect of the spacer on the properties at the air/water interface. The attractive structures of the aggregates would be formed both in solution and at the air/water interface in virtue of the molecular configurations and the sizes of Gemini surfactants. This study aimed to give an insight into the structures of these Gemini surfactant molecules at the air/water interface.

## 2. Materials and methods

### 2.1. Materials

Gemini surfactant 18-*s*-18 was synthesized in this laboratory using the method described by Zana et al. [22] and characterized by elemental analysis and nuclear magnetic resonance.

### 2.2. Preparation of monolayer and LB film

The surface pressure measurements were performed on a computer-controlled Langmuir film balance (model 612D, Nima Technology, Coventry, UK). The rectangular Polytetrafluoroethylene (PTFE) trough (20×30=600 cm<sup>2</sup>) with two movable barriers with the same compression rates was used. The trough was filled with water purified by means of a Milli-Q plus water purification system (Millipore Inc.) with an electric resistance of 18.2 M $\Omega$ . The temperature of the subphase was controlled at 25±0.1 °C from a thermostat using water flow that circulates through the base plate of the trough during experiment. In order to eliminate the influence of contaminants, 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 a complete compressing cycle 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. The whole apparatus is mounted on an anti-vibration table to minimize ripples on the water surface.

Chloroform solutions of 18-*s*-18 with a concentration of 5.0×10<sup>-4</sup> mol L<sup>-1</sup> were used as the spreading solution for the formation of the Gemini surfactant monolayer. 40  $\mu$ L of the solution was spread on 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<sup>-1</sup>.

The films were transferred onto mica by vertical dipping method at the constant surface pressure. The substrate surface was set to be perpendicular to the direction of the moving barrier. Mica substrates

were freshly cleaved and immediately used. The substrates were submerged into the subphase before spreading the monolayer. The deposition rate was 5 mm/min.

### 2.3. AFM observation

AFM images of one-layer LB films of 18-*s*-18 on the mica were measured with AJ III AFM apparatus (Aijian nanotechnology Inc., China) in a tapping mode under the ambient laboratory conditions. Noncontact silicon cantilever NCS11/50 with the nominal radius of curvature less than 10 nm was used. To avoid damage of the surface, the imaging force was adjusted and kept as low as possible to reduce the applied force to a minimum. Images were obtained from at least five macroscopically separated areas on each sample. At least two individual samples under the same conditions were prepared and imaged. Representative images are presented below.

### 2.4. Measurements of contact angle of LB film

As for the measurement of the contact angle, the usual method is to observe a sessile drop with a telescope or microscope and measure the angle with a goniometer. In this work, contact angle measurements were carried out and water was used as the test liquid. A drop of 1.0  $\mu$ L volume was formed with the use of a micrometer syringe and placed directly onto the sample. The liquid drops were observed with microscopy using 5 $\times$  magnification and recorded with a charge-coupled-device. In this experiment, the experimental error in the contact angle measurements is  $\pm 1.0^\circ$ .

## 3. Results and discussion

### 3.1. The properties of 18-*s*-18 at the air/water interface

The cationic Gemini surfactants, 18-*s*-18 (*s*=3, 4, 6, 8, 10 and 12), are sufficiently water-insoluble at room temperature to permit standard film balance studies. The  $\pi$ -*A* isotherm of 18-*s*-18 at 25 °C is shown in Fig. 1. These curves have been measured more than five times to confirm their reproducibility. It shows that with regard to the isotherms of the Gemini surfactants with the different spacer length, the shapes resemble to each other. The curves move right with the increase of the carbon number of the spacer groups, *s*, indicating that the molecular area under the same surface pressures increases with *s*, except for *s*=12. On the whole, the curves do not exhibit a plateau region characterizing the definable sharp phase transition. The compression of the 18-*s*-18 monolayer is going on to the high surface pressures of 37.5±2.5 mN m<sup>-1</sup>, where there is a break in each curve, indicating the collapse of the monolayer and the formation of multilayers. This result is closely consistent with that of 18-Ar-18 in our previous work [20].

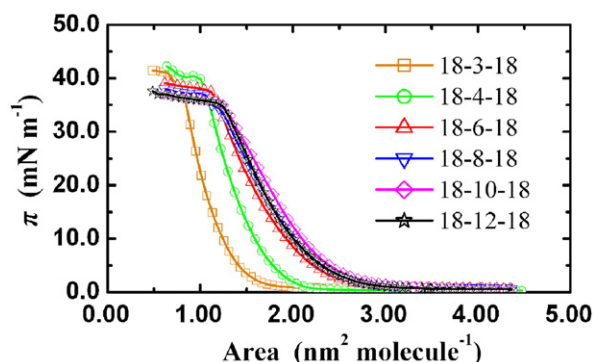


Fig. 1. The  $\pi$ -*A* isotherm of 18-*s*-18 (*s*=3, 4, 6, 8, 10 and 12) at 25 °C.

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