Mixed monolayers of Gemini surfactants and stearic acid at the air/water interface

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ARTICLE INFO

ABSTRACT

The properties of mixed monolayers composed of the cationic Gemini surfactant ($[C_{18}H_{37}(CH_3)_2N^+-(CH_2)_3-N^+(CH_3)_2C_{18}H_{37}],2Br^+$, abbreviated as 18-3-18,2Br^{-1}) and stearic acid (SA) at the air/water interface were investigated by using a Langmuir film balance. The excess areas at the different mixed monolayer compositions were obtained and used to evaluate the miscibility and nonideality of mixing. Due to the electrostatic attractive interactions between 18-3-18,2Br^{-1} and SA, the excess areas indicated negative deviations from ideal mixing. Moreover, 18-3-18,2Br^{-1} and SA were miscible at the air/water interface, as was confirmed by atomic force microscopy (AFM) images of the LB films transferred onto mica substrates. The attenuated total reflectance (ATR) infrared spectra showed that SA in the mixed monolayers was ionized completely at a composition $X_{SA} = 0.67$ and formed a "cationic–anionic surfactant," i.e., the carboxylate, with 18-3-18,2Br^{-1} owing to the electrostatic interaction between the head groups.

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1. Introduction

Gemini surfactants consist of two conventional amphiphilic moieties connected by a spacer group near the hydrophilic head groups. Due to their variation in the spacers, head groups, counterions, and the length of hydrophobic chains, Gemini surfactants represent structural diversity and distinctive physicochemical properties [1]. For instance, they provide a superior performance in gene delivery [2], which helps the understanding of the mechanism of the fusion and fission processes in living cells [3], and also serve as gelators [4] and templates for the preparation of nanomaterials [5].

Monomolecular films at the air/water interface have been a considerable focus of recent model systems for biological membranes and two-dimensional pattern formation, photomechanical responses, and molecular recognition systems [6]. It is possible to study monomolecular films containing more than one chemical compound because of their relevance to various interfacial performances. For example, biological membranes are formed of a bilayer of lipid compounds in which the other compounds, such as proteins and sterols, are immersed or bound to the two interfaces, which can perform matter and energy transport [7]. In the past two decades, the mixed systems formed by mixed cationic and anionic surfactants have been investigated extensively owing to their strong synergistic effects on interfacial properties and spontaneous vesicle formation behaviors [8–11]. Particularly, in an aqueous two-phase system, there is an interface composed of cationic and anionic surfactants, which have potential applications in drug separation probably because of the comparatively low cost of raw materials [12,13]. Simultaneously, the spontaneous formation of vesicles or bilayers has been found in mixtures of cationic and anionic surfactants. For the mixtures of cationic Gemini and anionic surfactants, there even appear vesicles with multilayer structures. In these mixed systems of cationic and anionic surfactants, all of the interfacial films are concerned with the molecular interactions or arrangements. So far, in order to have an insight into the physicochemical properties of the mixed cationic and anionic surfactants, a wide variety of monolayers, including Gibbs and Langmuir monolayers, have been investigated. For soluble systems, Gibbs monolayers of mixed cationic–anionic surfactants have been investigated at the air/water interface, while for insoluble systems, Langmuir monolayers of mixed conventional surfactants and other compounds have been reported in the literature [14–21]. In addition, as for mixtures comprising Gemini surfactants, the properties and applications of the soluble surfactants in solution or at interface have been studied, but the behaviors of insoluble monolayers have been explored only in a few works [22–27]. However, details of the molecular arrangement–performance relationship of the mixed cationic and anionic surfactant monolayers, especially the cationic Gemini and anionic one, remain to be clarified.

Therefore, in this work, the miscibility between 18-3-18,2Br^{-1} and SA and the structure of the mixed 18-3-18,2Br^{-1}/SA monolayers were studied at the air/water interface by analyzing the π–A isotherms and the ATR spectra, respectively. The morphology of the

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LB monolayers was characterized by AFM. The schematic molecular structure of the mixed 18-3-18,2Br^{-1}/SA monolayers at the air/water interface is given at $X_{SA} = 0.67$.

2. Materials and methods

2.1. Materials

The cationic Gemini surfactant 18-3-18,2Br^{-1} was synthesized in this laboratory by using the method described by Zana et al. [28] and characterized by elemental analysis and nuclear magnetic resonance. SA was purchased from Ling Feng Chemical Reagent Company, Shanghai (purity > 99%), and used as supplied without further purification. Chloroform was used as the solvent of the spreading solution. Water, purified by means of a Milli-Q plus water purification system with an electric resistance of 18.2 MΩ, was used as subphase. All experiments were carried out at $25 \pm 0.1\,°C$.

2.2. Preparation of the LB film

Stock solution of 5.0×10^{-4} mol/L concentration of 18-3-18,2Br^{-1} and SA in chloroform was spread over pure water to form a monolayer using a microsyringe (Hamilton) and was equilibrated about 10 min to allow the solvent to evaporate completely.

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 on a Model 612D computer-controlled Langmuir film balance (Nima Technology, Coventry, UK). A rectangular polytetrafluoroethylene (PTFE) trough ($20 \times 30 = 600$ cm^2) with two movable barriers moving with the same compression rates was used, which was filled with pure water. The subphase temperature was maintained by circulating water from a thermostat circulated through the base plate of the trough during the experiment. In order to eliminate the influence of contaminant, a PTFE nozzle with an aspirator pump connected was applied to suck the surface of the subphase before each experiment. The surface was deemed to be clean when the fluctuation in surface pressures was found to be less than 0.2 mN/m during a complete compressing of the surface without surfactants.

The monolayer was compressed at a rate of 10 cm^2/min. The surface pressure (π)–area per molecule (A) isotherms were recorded during the compressing process. The LB monolayer was transferred at surface pressures of 10, 20, and 30 mN/m, respectively. The deposition rate was 5 mm/min. In order to measure ATR spectra, a silicon dioxide substrate was used to prepare 10-layer films. The LB films for the AFM investigation were dried in air at room temperature.

2.3. ATR infrared spectrum

ATR infrared spectra were recorded by using an AVATAR360 infrared spectrometer equipped with a Harrick attenuated total reflectance attachment. The 10-layer deposited mixed 18-3-18,2Br^{-1}/SA film used for the ATR spectrum was transferred on the silicon dioxide substrate at a surface pressure of 20 mN/m and $X_{SA} = 0.67$. To obtain ATR spectra, it was placed in a vertical ATR accessory. A total of 500 scans were sufficient to achieve a high signal-to-noise ratio. The spectra were obtained at a resolution of 4 cm^{-1} at room temperature. Prior to ATR measurement, silicon dioxide substrates with the 10-layer deposited LB films were kept in a desiccator with silica-gel desiccant. The silicon dioxide substrate was used to obtain the baseline under ambient conditions.

2.4. AFM observation

The AFM topographic images of mixed 18-3-18,2Br^{-1}/SA LB films were obtained in constant repulsive force mode by AFM

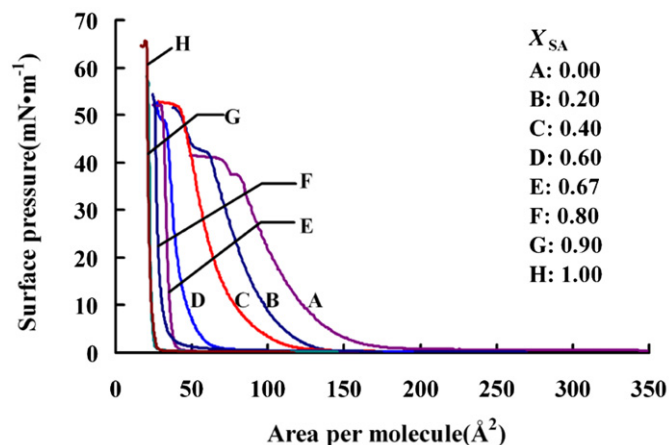**Fig. 1.** Surface pressure–area per molecule isotherms of mixed 18-3-18,2Br^{-1}/SA monolayers of various compositions on water at 25 °C.

(AJ-III, Aijian Nanotechnology Inc., China) with a triangular microfabricated cantilever (Mikro Masch Co., Russia) with a length of 100 μm, a Si pyramidal tip, and a spring constant of 48 N/m. A resonance frequency in the range of 100–190 kHz was used, and resonance peaks in the frequency response of the cantilever typically at 330 kHz were chosen for the tapping mode oscillation. The AFM images were obtained with a scan range of 2×2 μm^2, and scanning frequencies were usually in the range of 0.6 and 2.0 Hz per line. The measurements were carried out under ambient laboratory conditions.

3. Results and discussion

3.1. π–A isotherms at the air/water interface

Fig. 1 shows the π–A isotherms of the mixed 18-3-18,2Br^{-1}/SA monolayers with various compositions at 25 °C on a water subphase. Curves A and H were the isotherms for the monolayers of pure 18-3-18,2Br^{-1} and SA, respectively. It is revealed that the liftoff value of the mean molecular area decreases with the increase of the SA composition. The SA monolayer can be considered as a solid monolayer (as shown in curve H), while there is a phase transition between the liquid-expanded and the liquid-condensed states at about $\pi = 38.4$ mN/m in the monolayer of pure 18-3-18,2Br^{-1} (as shown in curve A). The same phase transition points exist in mixed monolayers as shown in curves B ($X_{SA} = 0.20$), C ($X_{SA} = 0.40$), and D ($X_{SA} = 0.60$) at surface pressures of 42.2, 52.2, and 48.9 mN/m, respectively. However, the mixed monolayer with $X_{SA} = 0.67$ (as shown in curve E) does not exhibit the obvious plateau region, which implies that no phase transition occurs. As for the liquid-expanded and the liquid-condensed monolayer, it is difficult to clarify their phase states only by the π–A isotherm curves because a direct transition from a gaseous to a condensed state might occur, especially at low temperatures. The phase state of monolayers can be determined in terms of the isothermal compressibility κ, which is calculated from the numerical differentiation of the π–A isotherms, $\kappa = (-1/A)(dA/d\pi)$. Harkins [29] pointed out that for the normal long-chain derivatives, the κ value at solid (S) state was in the range from 0.0005 to 0.001 m/mN, whereas the liquid-condensed phase was from 0.004 to 0.01 m/mN. The minimum compressibility κ_{min} values of curves E ($X_{SA} = 0.67$), F ($X_{SA} = 0.80$), and G ($X_{SA} = 0.90$) are 0.0033, 0.0028, and 0.0031 m/mN, respectively, which are relatively close to the latter. Therefore, according to the viewpoint of Harkins, curves E, F, and G are tentatively ascribed to the liquid-condensed phase. In addition, the collapse surface pressure of pure