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Ability of sodium dodecyl sulfate to transiently stabilize a phospholipid molecular layer

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ABSTRACT

The interaction between sodium dodecyl sulfate (SDS) and a phospholipid (1,2-dioleoyl-*sn*-glycero-3-phosphocholine (DOPC)) molecular layer was investigated experimentally to understand the mixing effect of SDS on biomembranes. Both the SDS concentration-dependencies of the contact angle between a pair of water droplets in oil and the surface pressure of a DOPC phospholipid monolayer changed at 1 ~ 2 mM SDS, which was lower than the critical micelle concentration. Attenuated total reflection Fourier transform infrared spectroscopy was used to evaluate the interaction between DOPC and SDS molecules.

1. Introduction

Studies on biomembranes, such as the intercellular lipid lamellar structure of the stratum corneum, are very important for understanding their functions, such as their barrier function and their responses to chemical stimuli [1,2]. In contrast, biomembranes are damaged by the penetration of surfactant molecules in the lipid bilayers or the solubilization of lipid molecules in surfactant micelles [3–5]. On the other hand, the surfactants are generally used to solubilize biomembranes in biological research [6,7]. Artificial membrane systems such as liposomes are useful for not only simplifying biomembranes but also for understanding the intrinsic nature of a target molecule [8–13].

The mechanism of liposome solubilization proposed by Lichtenberg et al. has been widely accepted and developed [13–16]. This mechanism consists of three stages depending on the concentration of surfactant across the critical micelle concentration (cmc), i.e., penetration of surfactant molecules into the lipid bilayers (stage I), the coexistence of surfactant-saturated vesicles and lipid-saturated micelles (stage II), and mixed micelles (stage III). However, the physicochemical properties of the lipid-surfactant mixed molecular layer have not yet been clarified.

In this study, we investigated the effect of sodium dodecyl sulfate (SDS; $CH_3(CH_2)_{11}OSO_3Na$), which is widely used in medicine, research, engineering, and the home, on a lipid molecular layer. As artificial model membrane systems, we examined water-in-oil (W/O) droplets coated with a 1,2-dioleoyl-*sn*-glycero-3-phosphocholine (DOPC) monolayer and the surface pressure (π) – surface area (A) isotherm of DOPC under the addition of SDS. The W/O droplet system has recently been shown to be useful for evaluating the interaction between the lipid membrane and added chemical stimuli based on the adhesive force between a pair of adhering droplets [17–19]. The surface pressure (π) – surface area (A) isotherm gives us abundant information on the stability or fluidity of the monolayer under compression of the membrane. The molecular interaction between DOPC and SDS was evaluated by attenuated total reflection Fourier transform infrared spectroscopy (ATR FT-IR). Our experimental results suggest that the interaction of SDS with the DOPC monolayer plays an important role in the non-genomic effect of SDS, and that a stable molecular layer, which is composed of a DOPC-SDS mixture, exists at a concentration below the cmc.

2. Experiments

1,2-Dioleoyl-*sn*-glycero-3-phosphocholine (DOPC) and SDS were purchased from Sigma-Aldrich (St. Louis, MO). Mineral oil, chloroform, and methanol were purchased from Nacalai Tesque, Inc. (Tokyo, Japan).

Water-in-oil (W/O) droplets coated with DOPC lipid monolayers were prepared based on the previously reported method [17–19]. A DOPC dry film was made on the bottom of a glass tube, and the mineral oil was added to the DOPC film and homogenized for 90 min with a 90 W sonicator (Yamato Scientific Co. Ltd., B1510J-DTH, Tokyo, Japan) at 333 K. The final concentration of DOPC in the oil was 1 mM. The obtained DOPC-in-oil solution was used within a day. The temperature of the oil and water solutions was adjusted at room temperature, which was higher than the phase transition temperature for DOPC

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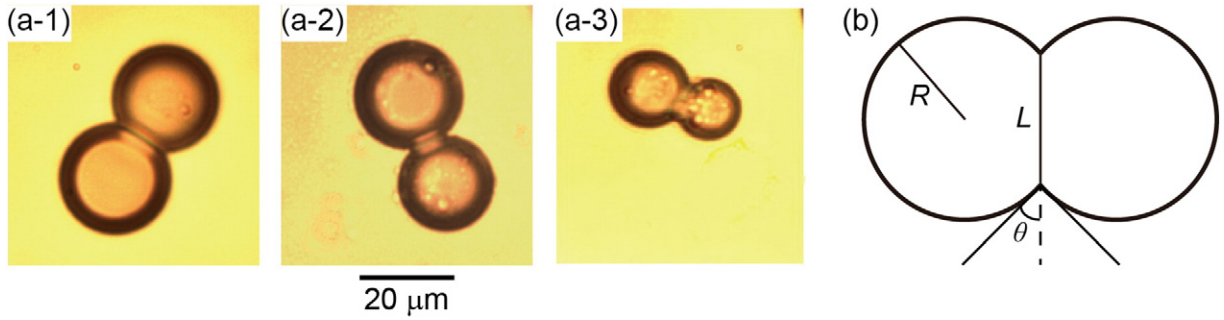

Fig. 1. (a) Snapshots of a pair of DOPC droplets in mineral oil and (b) definition of L, R, and θ. The concentration of SDS in the water phase was (a-1) 0, (a-2) 1, and (a-3) 2 mM.

(~258 K) [20]. Next, about 10 vol% of purified water was added to the DOPC-in-oil solution, and emulsification was achieved via pipetting to obtain adhering droplets. Just after pipetting, an aliquot containing the droplets was placed between two cover glasses (Matsu-nami Glass Ind. Ltd., Osaka, Japan) with a spacer (0.1 mm thick) to prevent the droplets from sticking to the glass plate. 5 min after the preparation, water-in-oil microdroplet pairs reached a steady state and the life time was at least 1 h.

For the preparation of a DOPC monolayer on water, the reagent used (DOPC) was dissolved in chloroform, and the chloroform solution was dropped on water with a micro syringe (volume: several tens of μL). The amount of DOPC dropped on water was 1.62×10^{-8} mol. For the water phase, SDS was dissolved in water. Water was first distilled and then purified with a Millipore Milli-Q filtering system (pH of the obtained water 6.3, resistance > 20 MΩ). The $\pi - A$ isotherm was measured with a surface pressure meter (Kyowa Interface Science Co. Ltd., HMB, Saitama, Japan) at 298 ± 1 K. The surface area (A) was decreased from 210 to 50 cm^2 at a rate of 18.9 cm^2 min^{-1}, i.e., 19 $Å^2$ $molecule^{-1}$ min^{-1} for a DOPC monolayer without additives. The monolayer was compressed beginning 5 min after application of the chloroform solution to eliminate chloroform from the water surface by evaporation. The interfacial tension γ_{ow} at an oil–water interface coated with a lipid monolayer was evaluated using the Wilhelmy plate method (accuracy ± 0.01 mN m^{-1}; DY-300; Kyowa Interface Science Co., Ltd., Saitama, Japan). Here, the inner diameter of the glass chamber to measure the interfacial tension was 58 mm, and the volumes of water and oil phases were 20 and 30 mL, respectively. At least four examinations were performed to confirm reproducibility.

For ATR FT-IR, spectra were obtained with a FT-IR spectrophotometer (Perkin-Elmer Spectrum One) equipped with an ATR diamond cell (Universal ATR Sample Accessory) at room temperature. The measurements were performed for a solid sample composed of DOPC and SDS (molar ratio of the mixture: SDS/DOPC = 0.017, 0.5, 1.0, and 1.7, the amount of DOPC added to the ATR cell: ca 3×10^{-7} mol). The solid samples were prepared as follows: An organic solution (a mixture of 50 vol% chloroform and 50 vol% methanol) of the SDS/DOPC mixture was deposited on the ATR plate and the solid sample was obtained by slowly evaporating the organic solvent under a stream of N_2 gas. The spectral resolution was 2 cm^{-1} and the cumulative number was 100.

3. Results

Fig. 1 shows snapshots of a pair of DOPC water droplets in mineral oil for different concentrations of SDS in the water phase. Here, we focused on water droplet pairs rather than single water droplets in oil to evaluate the adhesive force between the DOPC molecular layer. The relative value of the contact length between the adhering droplets ($2L$) to the radius of a droplet (R), i.e., $2L/R$, for 1 mM SDS was shorter than those for 0 mM (pure water) and 2 mM SDS. Thus, the contact angle between the adhering droplets, θ, for 1 mM SDS was smaller than those for 0 mM and 2 mM SDS. The interfacial tension at the oil-water interface, γ_{WO}, including 1 mM DOPC with the addition of 0, 1, and 2 mM SDS for four examinations was 0.4 ± 0.1, 0.3 ± 0.1, and 0.3 ± 0.1 mN m^{-1}, respectively.

Fifty droplet pairs were analyzed for each SDS concentration to make a histogram for θ, as shown in Fig. 2a. The error value on the contact angle was within 4 degree in the measurement of the circumference line. Only droplet pairs with diameter $2R_n$ ($n = 1$ or 2; $R_1 \geq R_2$) such that 5 μm < $2R_n$ < 25 μm and $1 \leq R_1/R_2 < 1.5$ were selected to prepare the histogram. We selected data under the condition of $1 \leq R_1/R_2 < 1.5$ to prepare the histogram. The force Δf, which is induced by the difference in size between two contacting droplet, is less than ~0.2 γ, as

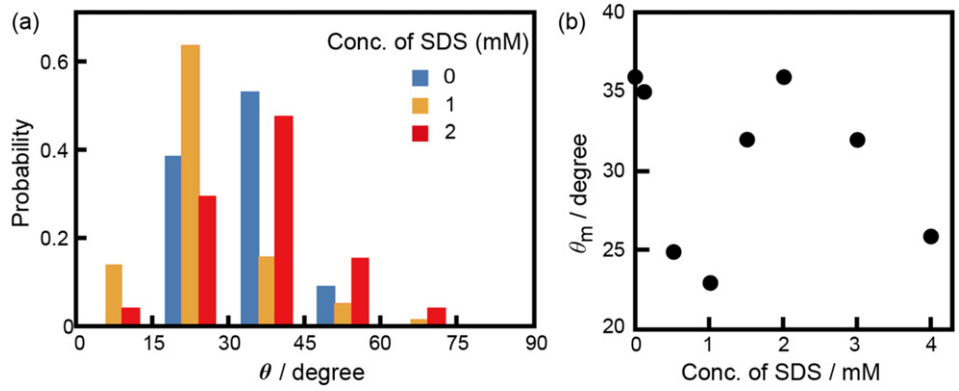

Fig. 2. (a) Histograms of the contact angle, θ, between adhering droplets in mineral oil and (b) mean value of the contact angle, θ_m, depending on the concentration of SDS in the water phase. The concentrations of SDS for the blue, orange, and red bars in (a) were 0, 1, and 2 mM, respectively.