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Characteristic responses of a 1,2-di-myristoyl-*sn*-glycero-3-phosphocholine molecular layer to polymeric surfactants at an air/water interface

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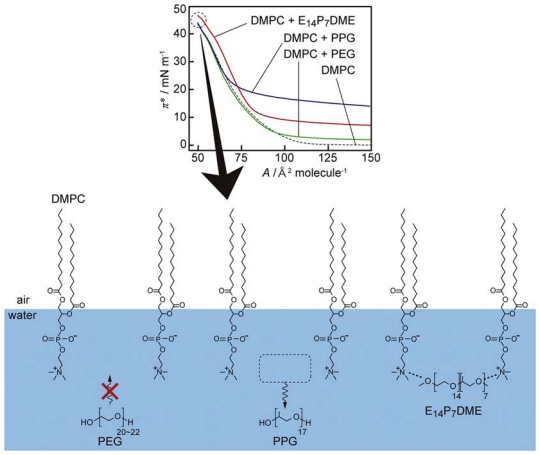
GRAPHICAL ABSTRACT



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ABSTRACT

Phospholipid molecular layers mixed with polymeric surfactants (PS) composed of ethylene oxide and/or propylene oxide monomers were investigated experimentally to clarify the effect of the chemical structure of the PS on the monolayers. The surface pressure (*Π*) – surface area (*A*) isotherm for phospholipid (1,2-dimyristoyl-*sn*-glycero-3-phosphocholine (DMPC)) changed characteristically depending on the chemical structure of the PS. Differential scanning calorimetry and attenuated total reflection Fourier transform infrared spectroscopy were used to evaluate the interaction between DMPC and PS molecules.

1. Introduction

Biological membranes composed of lipid molecular layers have been widely investigated to clarify their properties, including responsiveness, stability, and barrier function, as a closed or tentatively open system [1–3]. Artificial membrane systems, such as monolayers and liposomes,

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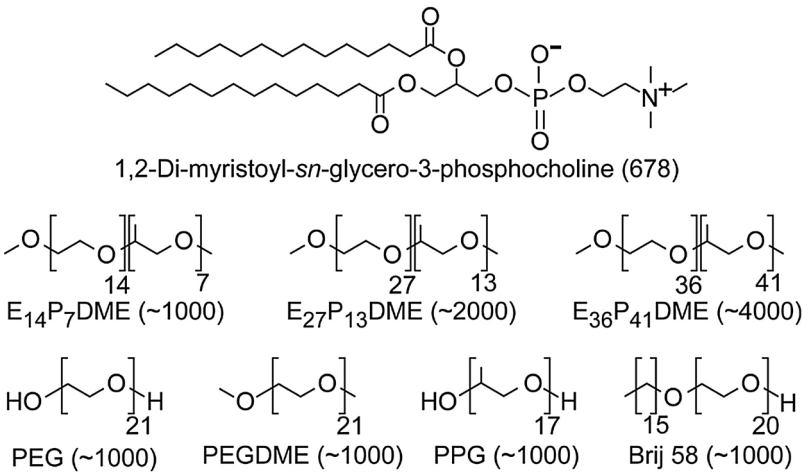

Scheme 1. Chemical structures of DMPC and the PS compounds used in this study. Numbers in parentheses are average molecular weight.

are useful not only for reducing the complexities of biological membranes, but also for elucidating the intrinsic nature of a target molecule [4,5].

Biological membranes are generally damaged by the penetration of amphiphilic molecules into the lipid molecular layers or the solubilization of lipid molecules in amphiphilic micelles [6–13]. In contrast, there are several amphiphilic molecules that adapt to biological membranes, similarly to how a cosmetic adapts to the skin [14,15]. Thus, amphiphilic molecules can be classified into two types: those that induce damage and those that adapt to the biological membrane. For example, there are several reports regarding the interaction between phospholipid and poly(ethylene glycol) (PEG) [16–19]. However, the way in which the chemical structure of an amphiphilic molecule influences that molecule's effect on a lipid membrane has not yet been clarified.

In this study, we examined polymeric surfactants (PS) composed of ethylene oxide and/or propylene oxide monomers of which molecular weight was around 1000 and related PS with higher molecular weight (see Scheme 1) to understand the physicochemical properties of a lipid-amphiphilic mixed monolayer. PC have been well examined as phospholipid molecules. Therefore, we selected DMPC as a general PC. On the other hand, we reported the interaction PC and sodium dodecyl sulfate or fatty acids as anionic substances [11,20]. The artificial model membrane system comprised DMPC and PS, and we examined the surface pressure (Π) – surface area (A) isotherm of DMPC with the addition of PS in the bulk phase. The $\Pi - A$ isotherm provides abundant information on the stability of the mixed monolayer under compression. The interaction between DMPC and PS was evaluated by differential scanning calorimetry (DSC) and attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR). Our experimental results suggest that the combination of ethylene oxide and propylene oxide monomers and the polymer chain length play an important role in the effect of PS on the DMPC monolayer.

2. Experiments

1,2-Dimyristoyl-*sn*-glycero-3-phosphocholine (DMPC), Brij58, and poly(ethylene glycol) dimethyl ether (PEGDME) were purchased from Sigma-Aldrich (St. Louis, MO). Chloroform was purchased from Nacalai Tesque, Inc. (Tokyo, Japan). HEPES was purchased from Dojindo Co. (Kumamoto, Japan). Polyethylene glycol (PEG) and polypropylene glycol (PPG) were purchased from Wako Chemicals (Kyoto, Japan). Three copolymers composed of polyoxyethylene/polyoxypropylene dimethyl ether (E_nP_mDME, (n, m) = (14, 7), (27, 13), or (36, 41)) were synthesized based on previous papers [14,15].

To prepare a DMPC monolayer on water, water was first distilled and then purified with a Millipore Milli-Q filtering system (Direct-Q, Millipore SAS, France; the pH of the obtained water was 6.3 and its resistance was 18.2 MΩ). This water was used to prepare a 0.1 M HEPES buffer solution (pH 7.0), and then 0.01 ~ 5 μM PS was dissolved in the buffer. DMPC was dissolved in chloroform and the chloroform solution was dropped onto this water phase with a micro syringe. The volume of DMPC was several tens of microliters and the amount was 1.62×10^{-8} mol. The $\Pi - A$ isotherm for the DMPC monolayer was measured with a surface pressure meter (Kyowa Interface Science Co. Ltd., HMB, Saitama, Japan) at 298 ± 1 K. The surface area (A) decreased from 210 to 40 cm^2 at a rate of 16.5 $cm^2\,min^{-1}$; i.e., 16 $Å^2$ $molecule^{-1}\,min^{-1}$ for the DMPC monolayer. Compression of the monolayer was started 5 min after injection of the chloroform solution to allow the chloroform to evaporate from the water surface. The concentration of PS in the water phase changed from 0.01 to 5 μM. At least three examinations were performed to confirm reproducibility.

The phase transition temperature (T_p) for DMPC with and without PS was measured by DSC (differential scanning calorimetry; DSC-50, Shimadzu, Kyoto, Japan) at a scan rate of 2 K min^{-1}. Solid or liquid samples (mass: 6–19 mg; amounts of DMPC and PS: both 6 μmol) were placed in an aluminum vessel and measured under a N_2 atmosphere. T_p was defined as the intersection of the baseline with the line extrapolated along the lower-temperature side of the peak signal in the heating scan.

ATR-FTIR spectra were obtained with an FTIR spectrophotometer (Spectrum One, Perkin-Elmer, Waltham, MA) equipped with an ATR diamond cell (Universal ATR Sample Accessory) at room temperature. Measurements were performed on mixtures of DMPC and PS (molar ratio of the mixture: PS/DMPC = 1.0, the amount of DMPC added to the ATR cell: ca. 3×10^{-7} mol). Each sample was prepared by depositing a 10 μL chloroform solution of the PS/DMPC mixture on the ATR plate and then slowly evaporating the chloroform under a stream of N_2 gas. The spectral resolution was 2 cm^{-1} and 100 cumulative spectra were obtained. We have not yet succeeded the measurement of FTIR to evaluate the effect of PS molecules for the DMPC monolayer due to the lower absorbance. Therefore, we measured FTIR for PS-DMPC amorphous aggregates which were obtained from their mixture dissolved in chloroform to evaluate the molecular interaction between them in the present study.

3. Results

Fig. 1 shows the modified surface pressure (Π^*)–surface area (A) isotherm for a DMPC monolayer on an aqueous phase containing different PS compounds ($E_{14}P_7$DME, Brij58, PEG, or PPG). Here, $\Pi^* = \Pi + (\gamma_w - \gamma_{PS})$, where Π denotes the surface pressure for a DMPC monolayer on an