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Mechanism of gelation in the hydrogenated soybean lecithin (PC70)/hexadecanol/water system

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ABSTRACT

The crude phospholipid mixture (PC70) forms a homogeneous gel with hexadecanol (HD) in water, whereas the purified lipid does not. The fact that the crude material PC70 can be utilized for homogeneous gel preparation suits the cosmetic industry very well from the viewpoint of cost performance. In order to clarify the mechanism of the gelation, we investigated the structures and physicochemical properties of the PC70/HD/water system by rheometry, freeze-fracture electron microscopy, differential scanning calorimetry (DSC) and synchrotron X-ray diffraction. Our results suggested that the gelation is induced by change in bilayer morphology from closed vesicles to sheet-like structures with open edges covered by minor lipid components that are stiffened due to intercalation of HD molecules between phospholipids. The morphological change may give rise to homogeneous distribution of the bilayer sheets throughout the solution and formation of water continuum that may work as a network in the gel.

1. Introduction

Hydrogels of amphiphilic molecules are widely used in the cosmetic and pharmaceutical industries. These systems usually consist of surfactants and alcohols and have been applied to formulation of hair conditioners [1,2] and skin moisturizing creams [3–7]. Cationic surfactants employed in hair conditioners adsorb on the hair surface to increase the flexibility of single fibers and reduce the friction between fibers [2,8,9]. On the other hand, nonionic surfactants are favorable for moisturizing creams because of their low stimulative nature [10]. These ternary systems have been characterized by various techniques such as light and electron microscopy [11–13], rheometry [3,6,13–20], differential scanning calorimetry [7,21,22], NMR [23], conductivity and dielectric analyses [24–28], laser Raman spectroscopy [29], and X-ray diffraction [4,5]. Consistency of the surfactant-containing ternary systems can be regulated from a nonelastic fluid to a fairly hard gel by alteration of composition, temperature, concentration and so on. In these systems, the gelation is induced by formation of a viscoelastic network (convoluted bilayer network) throughout the solution. In addition, viscoelastic properties in these ternary systems sometimes exhibit a long-term relaxation, which is closely related to the change in bilayer morphology [30].

In this study, we tried to make a hydrogel using crude mixtures of phospholipids instead of surfactants because phospholipids are natural ingredients and suitable for health care products [31,32]. Crude mixtures of phospholipids extracted from soybean or egg are widely used as liposome materials and emulsifiers in the pharmaceutical, cosmetic and food industries mainly because of their high cost performance. These mixtures contain a fairly wide range of phospholipid species in addition to the major component, phosphatidylcholine (PC) [33–37]. For example, PC70 is a hydrogenated soybean lecithin containing a variety of phospholipids including phosphatidylethanolamine (PE), phosphatidylinositol (PI), phosphatidylglycerol (PG) and so forth in addition to ~70% PC and in common use in cosmetic industries as a commercial raw material. The minor components in a crude phospholipid mixture provide a potential for giving useful properties to the pure material. We found that PC70/hexadecanol bilayers constitute a homogeneous hydrogel in contrast to the pure PC/HD bilayers, which are known to show phase separation instead of gelation [38]. In spite of the difference in viscoelastic properties, PC70/HD and pure PC/HD bilayers had very similar phase transition behavior. In order to make efficient use of the PC70/HD gel as commercial products, we need to understand and regulate its formation process. Hence, we systematically investigated the structures and physicochemical properties of the PC70/HD/water system by rheometry, freeze-fracture electron microscopy, differential scanning calorimetry (DSC) and synchrotron X-ray diffraction. Our results suggested that the gelation was induced by change in bilayer morphology from closed vesicles to sheet-like structures. The morphological change may give rise to homogeneous distribution of bilayer sheets throughout the solution and formation of water continuum that may work as a network in

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the gel. The gelation mechanism we proposed paying attention to the role of water layers highlights the solvent rather than the solute from a new point of view and will provide a useful insight into understanding the hydrogel formation.

2. Materials and methods

2.1. Sample preparation

Hydrogenated soybean lecithin (PC70) and hexadecanol (HD) were purchased from Nippon Fine Chemical Co., Ltd. and Sigma–Aldrich Co., respectively. Hexadecanol is approved for use in cosmetics at any blending quantity. Other reagents used were of analytical grades. All materials were used without further purification. Samples were prepared as follows: All lipids were dissolved in chloroform/methanol (2:1, v/v) to be mixed in a desired weight ratio. The solvent was first removed with a rotary evaporator, and subsequently with a high vacuum pump for about 2 h. The remaining film was dispersed in purified water, vortexed at 80 °C for 10 min, and cooled down to 30 °C. The final lipid concentration was 50 mg/ml.

2.2. Rheological measurements

Rheological measurements were performed using a Physica MCR301 (Anton Paar GmbH) with a cone-plate geometry (50 mm diameter, 0.0174 radian cone angle). We used the strain sweep from 0.01% to 100% at the frequency of 1 Hz to determine the linear region for complex viscosity (η^*) measurements. A solvent trap was used to minimize the drying-out effects (water evaporation) and dust contamination. All measurements were carried out at 25 °C.

2.3. Differential scanning calorimetry

The phase behavior of the PC70/HD mixed bilayers was examined by differential scanning calorimetry (DSC). The sample solution containing about 10 mg lipids was loaded into an aluminum pan and set in a DSC apparatus (DSC6220, SII Nano Technology Inc.). The temperature was increased from 10 °C to 85 °C at the scanning rate of 5 K/min. For convenience, the peak temperatures in the DSC thermograms were measured for analysis of the change in the transition temperature T_m.

2.4. Freeze-fracture electron microscopy

The specimen frozen rapidly in liquid nitrogen slush was placed in a freeze-fracture apparatus (JFD-9010, JEOL Ltd.), and a replica film for the fractured surface was obtained according to a conventional method described elsewhere [39]. The replicas were observed with a transmission electron microscope (JEM-1010, JEOL Ltd.) operating at 80 kV.

2.5. X-ray diffraction

Synchrotron X-ray diffraction experiments were performed at Station BL40B2 of SPring-8, Japan. An aliquot of specimen solution was sealed into a thin glass capillary with a diameter of about 1 mm and equilibrated at the room temperature before the measurement. Two-dimensional diffraction pattern was recorded with an imaging plate detector (R-AXIS VII, Rigaku). The wavelength λ was 0.1 nm, and the exposure time was 30 s. The camera length was set to be about 500 mm so as to be appropriate for simultaneous detection of small and wide-angle diffraction and calibrated using cholesterol powder crystals. One-dimensional intensity profiles as a function of the modulus of scattering vector $s = 2\sin\theta/\lambda$ (2θ is the scattering angle) were obtained by integrating the two-dimensional diffraction patterns along the azimuthal direction and divided by $2\pi r$, where r is the distance from the beam center.

3. Results

3.1. HD-induced gelation in the PC70/HD/water system

The dispersibility and fluidity of the PC70/HD/water system were visually observed. Fig. 1 shows a photograph of the aqueous solutions of PC70/HD with the HD weight fraction W_H from 0 to 0.4. It is clearly visible that a decrease in fluidity (i.e., gelation) takes place above $W_H = 0.24$. In the pure HD dispersion ($W_H = 1$), the HD aggregates were completely separated from the aqueous phase (data not shown).

To quantitatively evaluate the degree of the gel formation, we examined dynamic viscoelastic properties of the PC70/HD/water system by sweeping the strain. Fig. 2 shows the modulus of complex viscosity $|\eta^*|$ calculated from the linear region of the dynamic measurement as a function of W_H. The $|\eta^*|$ rose gradually and leveled off above $W_H \sim 0.2$. These results correlated with the decrease in fluidity shown in Fig. 1.

3.2. HD-induced change in bilayer morphology

To investigate the mechanism of the gelation, we carried out freeze-fracture electron microscopic observations in the

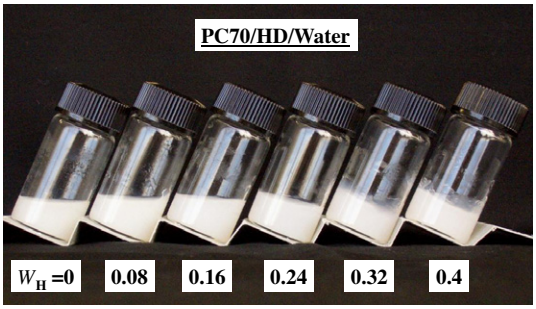

Fig. 1. Gelation induced by addition of HD to PC70 bilayers. The vials were slanted a few minutes before taking the pictures. Prominent decrease in fluidity of the homogeneous PC70/HD/water solution is clearly seen at the weight fractions of HD (W_H) higher than 0.24.

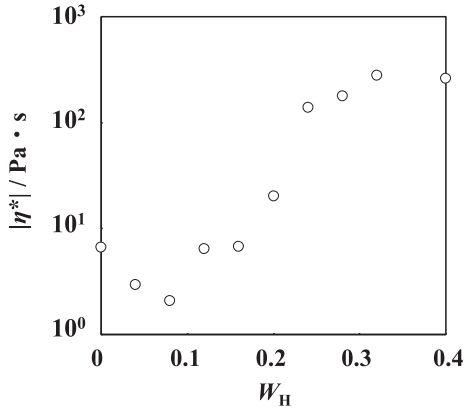

Fig. 2. Dependence of complex viscosity on W_H in the PC70/HD/water system. The modulus of complex viscosity $|\eta^*|$ at oscillation frequency of 1 Hz was taken from the linear region of the strain sweep measurements (see Section 2 for details). The viscosity rises markedly at $W_H > 0.2$ as seen in Fig. 1.