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ORIGINAL CONTRIBUTION

Highly viscoelastic reverse worm-like micelles formed in a lecithin/urea/oil system

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Abstract While lecithin alone can form spherical or ellipsoidal reverse micelles in oil, we found that urea can promote the growth of lecithin reverse worm-like micelles in oil. In a mixed system of urea and lecithin, the urea binds to the phosphate group of lecithin, thus reducing the interface curvature of the molecular assembly and inducing the formation of reverse worm-like micelles. The regions in which these micelles form increased with lecithin concentration. In addition, the zero-shear viscosity (η_0) of the reverse worm-like micelles rapidly increased upon the addition of urea, reaching a maximum of 2 million times the viscosity of *n*-decane. We examined the change in η_0 in detail by performing dynamic viscoelasticity measurements. Values for η_0 increased with urea concentration because the disentanglement time of reverse worm-like micelles increased with micellar growth.

Keywords Reverse worm-like micelle · Urea · Lecithin · Small angle X-ray scattering · Phase diagram · Rheology

Introduction

Surfactants are essential for many industrial applications, including commercial products such as medicines, cosmetics, and foods. In combination with water and oil phases, surfactants, which are amphiphilic molecules with hydrophilic and hydrophobic groups, allow the formation of a great variety of molecular assemblies such as spherical micelles, worm-like micelles, lamellar liquid crystals, hexagonal liquid crystals, reverse spherical micelles, and reverse worm-like micelles. In particular, reverse worm-like micelles have attracted interest because these cylindrically elongated reverse spherical micelles form temporary network structures as well as highly viscoelastic organogels.

The typical three-component system for forming reverse worm-like micelles involves lecithin, water, and a hydrocarbon [1–7]. Lecithin is a zwitterionic phospholipid with two alkyl tails, which forms spherical or ellipsoidal reverse micelles when added to oil. When trace amounts of water are added to this solution, the water molecules form hydrogen bonds with the phosphate group, thus reducing the interface curvature of the molecular assemblies, which is believed to induce formation of reverse worm-like micelles. Substitutes for water have been limited to glycerin, ethylene glycol, and formamide [6]. All of these substances are liquids at 25 °C.

Recently, Raghavan et al. [8–10] reported that bile salts, which are solid substances, induce the formation of reverse worm-like micelles from lecithin in nonpolar organic solvents such as cyclohexane. They proposed that the "facially amphiphilic" structure of bile salts is critical for inducing the growth of lecithin reverse worm-like micelles. Their method for preparing the samples involved homogeneously mixing the lecithin and bile salts in an organic solvent such as methanol and then removing the solvent to produce a solid mixture. A nonpolar solvent such as cyclohexane was then added to the solid with agitation, producing a gel-like substance. Their simple method, which is similar to that for preparing liposomes [11], improved the hydrogen bonding between the lecithin and bile salt.

Based on these previous studies of reverse worm-like micelles [1–10], two conditions are necessary for substances to induce the growth of reverse worm-like micelles: The

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substance must have at least two functional groups that hydrogen bond with the phosphate group of lecithin and the substance must be slightly hydrophobic to penetrate into the reverse micellar palisade layer. Here, urea was used as it satisfies both conditions. In general, urea is added to medicines and cosmetics for the purpose of moisture retention and skin softening. A small amount of urea exists as a natural moisturizing factor in the horny layer of the skin.

The present study investigated the phase state and rheology to find new reverse worm-like micelles composed of lecithin and urea.

Experimental

Materials

Soy lecithin (95%) was purchased from Avanti Polar Lipids (AL, USA). Urea and *n*-decane were purchased from Kanto Chemical (Tokyo, Japan). All chemicals were used without further purification.

Sample preparation and phase diagrams

The required amounts of lecithin and urea were dissolved in methanol in a vial, and then, the solvent was completely removed in a desiccator equipped with a vacuum pump. Following addition of *n*-decane to the vial, the solution was mixed overnight with a magnetic stirrer. The resulting solutions were stored at 25 °C for several days to allow for equilibration. Phase diagrams of the lecithin/urea/*n*-decane systems were obtained by visual observation through crossed polarizers and by small-angle X-ray scattering (SAXS) analysis. SAXS was performed using a Nano-STAR instrument (Bruker AXS , WI, USA) with a CuKα radiation source operating at 45 kV/120 mA. All measurements were obtained at 25 °C.

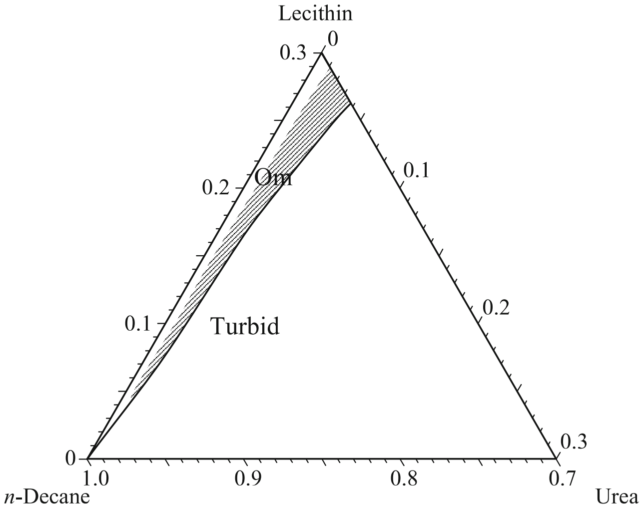

Fig. 1 Partial phase diagram of lecithin/urea/*n*-decane system in the dilute region at 25 °C. The notation Om represents a reverse micellar phase region. The region of high viscosity within the Om phase is shown by the *shading*

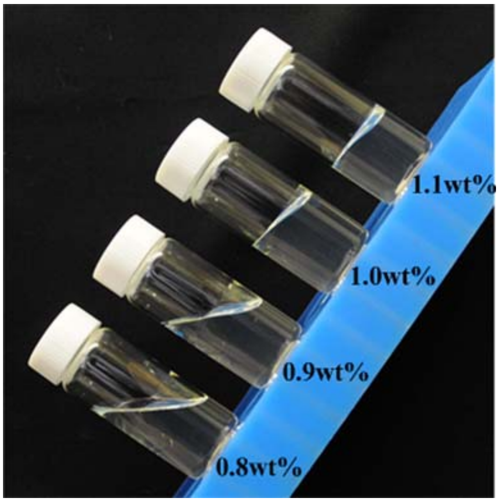

Fig. 2 Change in the surface of lecithin/urea/*n*-decane systems at various urea concentrations when vials were tilted from an upright position. Lecithin concentrations were fixed at 10 wt.%

Rheological Measurements

Steady and dynamic rheological measurements were obtained using a rotational rheometer (HAAKE RS600, Thermo Fisher Scientific, MA, USA) equipped with cone-plate geometry (two sizes, 60 mm and 35 mm diameters, each having a cone angle of 1° and 4°) and a Peltier-based temperature control set at 25 °C. A solvent trap was used to prevent evaporation. Dynamic rheological measurements were obtained using a strain value (γ) from the linear viscoelastic region.

Results and discussion

Phase diagram of a lecithin/urea/*n*-decane system

Figure 1 shows phase diagrams in the dilute region of the lecithin/urea/*n*-decane system. Reverse micelles (Om) formed upon addition of a small amount of urea, and these reverse micellar regions expanded as the amount of lecithin increased. A highly viscoelastic region (shaded area) was also observed in the Om phase, confirming the formation of reverse worm-like micelles. Further addition of urea resulted in a turbid solution.

As shown by tilting the solution vials (Fig. 2), viscosity abruptly increased with added urea at 0.8 wt.% or greater, with gelation occurring at 1.0 wt.% or greater. All of the liquids were transparent and optically isotropic when left stationary, but showed weak birefringence when agitated.

SAXS scattering intensity [$I(q)$] is represented as a function of the scattering vector (q) ($q = (4\pi/\lambda)\sin\theta$ (where λ is X-ray wavelength and 2θ is the scattering angle) for lecithin/urea/*n*-decane systems with different weight ratios (wt/wt/wt). None of the SAXS profiles showed a clear diffraction peak (Fig. 3), indicating the absence of liquid crystals, such as reverse hexagonal liquid crystals or reverse cubic liquid crystals. In the SAXS profile of the lecithin/urea/*n*-decane=1:0.1:98.9 system having the lowest concentrations of lecithin and urea, the slope of the double logarithmic plot in the low-q region was −1. This slope indicates a cylindrical particle, i.e., a reverse worm-like micelle. From cross-section plots (Fig. 4) of SAXS profiles based on the following Eqs. 1 and 2 [12], the section radius (r) of a reverse worm-like micelle was determined to be 21 Å:

$$\ln qI(q) = \ln qI(0) - (1/2)R_\mathrm{c}^2 q^2 \tag{1}$$

$$r = \sqrt{2}R_\mathrm{c} \tag{2}$$

where R_c is the cross-sectional radius of gyration. In addition, contour length (t) of a reverse worm-like micelle was at least 500 Å using the simulation based on Eq. 3 with a fixed r value (21 Å) as shown in Fig. 5. However, calculating an accurate contour length of a reverse worm-like micelle was not possible because of restrictions on the measurement range:

$$I(q) = \int_0^{\pi/2} \frac{\sin^2(q(t/2)\cos\theta)}{q^2(t/2)^2\cos^2\theta} \frac{4J_1^2(qr\sin\theta)}{q^2R^2\sin^2\theta}\sin\theta \mathrm{d}\theta \tag{3}$$

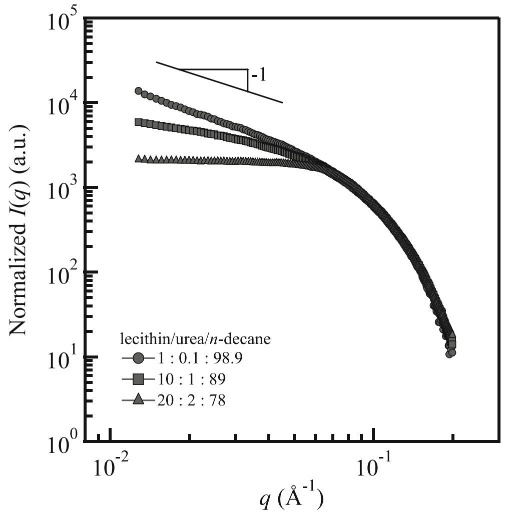

Fig. 3 SAXS scattering intensity [$I(q)$] as a function of scattering vector (q) for lecithin/urea/*n*-decane systems

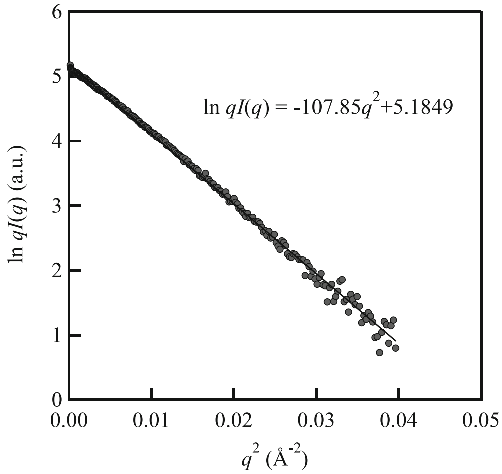

Fig. 4 Cross-sectional plot of an SAXS profile of the lecithin/urea/*n*-decane=1:0.1:98.9 system. The fitting result based on Eq. 1 is shown as a *solid line*

where J_1 is the Bessel function of order 1. Moreover, in SAXS profiles of the lecithin/urea/*n*-decane=10:1:89 and 20:2:78 systems, the scattering intensity and slope of the low-q region decreased, indicating that the number of reverse worm-like micelles per unit volume increases with lecithin and urea concentrations. Thus, the scattering intensity of the low-q region decreases as the structure factor strengthens by adjoining reverse worm-like micelles.

We suggest the following mechanism for the formation of reverse worm-like micelles in this system. While lecithin alone can form spherical or ellipsoidal reverse micelles in oil, a combination of urea and lecithin forms reverse worm-like micelles through binding of the carbonyl and amino groups of urea to the phosphate group of lecithin, which

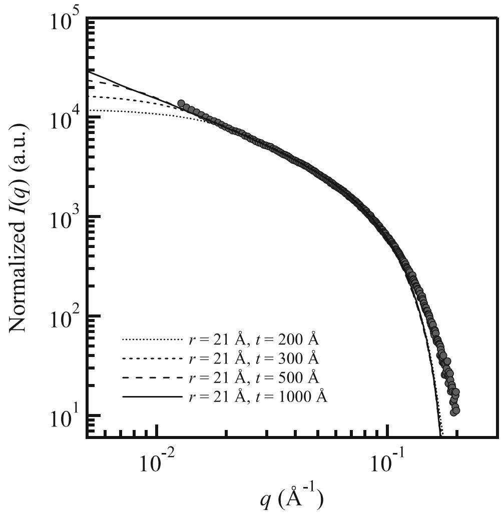

Fig. 5 Simulation using an equation involving cylindrical particles to a SAXS profile of the lecithin/urea/*n*-decane=1:0.1:98.9 system. The results of fitting based on Eq. 3 are shown by *solid* and *broken lines*

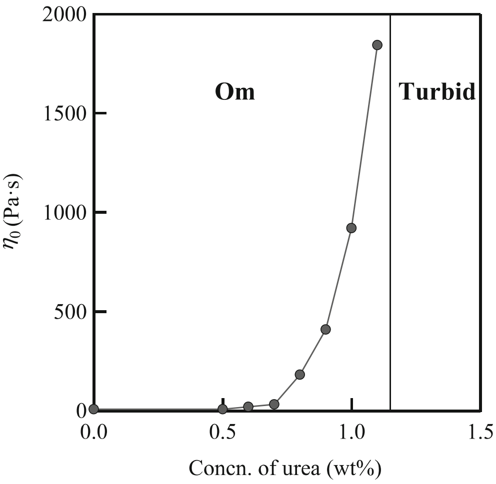

Fig. 6 Relation between zero-shear viscosity (η_0) and urea concentration in lecithin/urea/*n*-decane systems at 25 °C. Lecithin concentrations were fixed at 10 wt.%

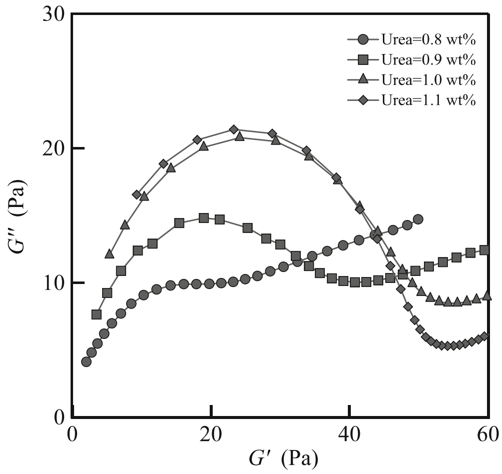

Fig. 8 Cole–Cole plots of G' and G'' at different urea concentrations in the lecithin/urea/*n*-decane system at 25 °C. Lecithin concentrations were fixed at 10 wt.%

reduces the interface curvature of the molecular assembly. This reverse worm-like micelle is stable without phase separation for at least 1 year, and its formation has been confirmed in *n*-hexane, *n*-octane, and liquid paraffin (data not shown).

Rheological behavior of a lecithin/urea/*n*-decane system

After confirming the formation of reverse worm-like micelles in the reverse micellar phases (Om) of the phase diagram (Fig. 1), the rheological properties were examined. The reverse micellar solutions were prepared at a fixed lecithin concentration of 10 wt.% at varying urea concentrations. Figure 6 shows the relation between zero-shear viscosity (η_0) and urea concentration, where η_0 is obtained by the extrapolation of the steady shear viscosity curve to zero-shear rate. The η_0 of solution abruptly increased with added urea, reaching a maximum of 2 million times the viscosity of *n*-decane, thus resulting in the growth of reverse worm-like micelles. To examine the change in η_0 in greater detail, dynamic viscoelasticity measurements were performed.

Figure 7 shows the variation in storage modulus (G') and loss modulus (G'') as a function of frequency (ω) for the lecithin/urea/*n*-decane system. The G' and G'' values represent elasticity and viscosity, respectively. These values intersect at a certain ω, where at high frequencies the elasticity component was predominant ($G' > G''$) and at low frequencies the viscosity component was predominant

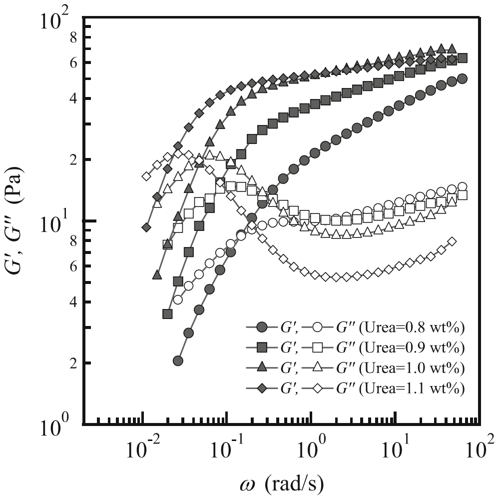

Fig. 7 Variation in G' and G'' as a function of ω obtained by oscillation frequency sweep measurements at different urea concentrations in the lecithin/urea/*n*-decane system at 25 °C. Lecithin concentrations were fixed at 10 wt.%

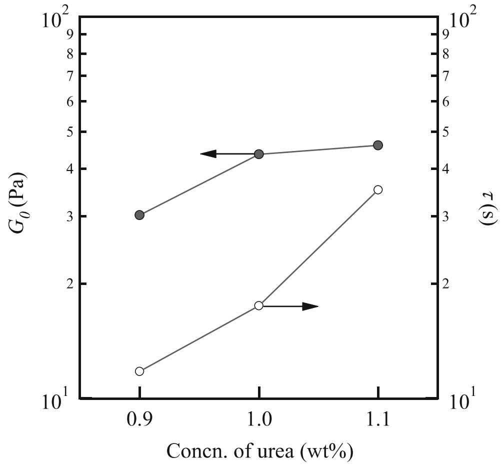

Fig. 9 Variations in G_0 and τ at different urea concentrations in the lecithin/urea/*n*-decane system at 25 °C

(G''> G'). The value of G' increased with urea concentration, suggesting that the elasticity of the solution strengthens upon reverse worm-like micelle formation as urea concentration increases. Figure 8 shows the Cole–Cole plots (relation between G' and G'') based on oscillation frequency sweep measurements (Fig. 7). In general, the Cole–Cole plot shows a complete semicircle when viscoelastic behavior corresponds to the Maxwell model with a single relaxation time [13], which is a simple way to confirm results that are consistent with the single Maxwell model. Relaxation time is the amount of time required for the stress of the entanglement of reverse worm-like micelles to relax and reflects the disentanglement time of reverse worm-like micelles. In general, the relaxation time of linear polymers varies greatly because the polymers disentangle via reptation (i.e., through a reptile-like motion) and is proportional to the third power of the molecular weight [14–17]. In contrast, the rheological behavior of reverse worm-like micelles is determined by the balance between reversible breakage and reptation of the micelles, and single Maxwellian behavior is generally observed when the reversible breakage time is sufficiently shorter than reptation time [8, 18]. In this situation, the relaxation time is represented by the geometric mean of the breaking time and reptation time. Figure 8 shows the Cole–Cole plot of reverse worm-like micelles approaching to a semicircular curve upon an increase in urea concentration and demonstrates increased contribution of reversible breakage relative to reverse worm-like micelles elongation. Thus, assuming that the reverse worm-like micelles formed in this system follow a single Maxwell model, curve fitting can be performed based on Eqs. 4 and 5 [18]:

$$G' = \frac{\omega^2\tau^2}{1+\omega^2\tau^2}G_0 \tag{4}$$

$$G'' = \frac{\omega\tau}{1+\omega^2\tau^2}G_0 \tag{5}$$

where G_0 is the plateau modulus reflecting the volume fraction of the entangled reverse worm-like micelles [8, 18], and τ is the relaxation time of the reverse worm-like micelles. Figure 9 shows variations in G_0 and τ as a function of urea concentration in the lecithin/urea/*n*-decane system. Both G_0 and τ increased with urea concentration. When a sample follows a single Maxwell model, η_0 can be defined as:

$$\eta_0 = G_0\tau \tag{6}$$

Here, η_0 is decided by the balance between the volume fraction and disentanglement time of the entangled reverse worm-like micelles. The η_0 values calculated using this equation were consistent with those obtained by steady-flow viscosity measurements (Fig. 6). These results suggest that η_0 increases with urea concentration because the disentanglement time of reverse worm-like micelles increases with volume fraction of the entangled reverse worm-like micelles.

Conclusions

This investigation into phase states and rheological properties aimed at finding new reverse worm-like micelles composed of lecithin and urea. Reverse worm-like micelles with high viscoelasticity formed upon addition of trace amounts of urea to lecithin. The zero-shear viscosity of reverse worm-like micelles abruptly increased depending on the quantity of urea added, reaching a maximum of 2 million times the viscosity of *n*-decane. The viscoelastic behavior of reverse worm-like micelles formed in this system resembled that seen in the Maxwell model, a basic model of viscoelastic bodies, indicating that these reverse worm-like micelles have a single relaxation time.

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