

# A Transient Network Structure in Sucrose Stearate/Water Systems

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The rheological properties of an industrial-grade sucrose stearate aqueous solution were studied. This solution at 1 to 8 wt % appeared translucent or turbid from 20 to 48 °C; however, it became transparent above 48 °C and its viscosity increased. Furthermore, the apparent viscosity of the sample solution increased with temperature, and showed peak value at 48 °C for all such samples. On the other hand, small angle laser-light scattering studies revealed that the molecular-assembly size of the surfactant abruptly decreased at the same temperature. The dynamic modulus of the sample at approximately 48 °C was successfully analyzed with a bimodal Maxwell model, which showed that sucrose stearate formed several types of molecular assemblies and the shape was dependent on temperature. In particular, the rheological properties at approximately 48 °C strongly suggest that the surfactant formed thread-like molecular assemblies.

**Key Words:** Sucrose fatty acid ester / Molecular assemblies / Transient network / Rheology / SALS

## 1. INTRODUCTION

Physical gels with mechanically weak network structures are used in foods, cosmetics, and other personal care products, where they are supposed to be fractured during use. The reversible gels are particularly interesting. Soft materials such as these gels exhibit a transient network structure. Transient network systems can be found in two types of materials. The first type of material that forms a transient network system is the associating polymers group. The telechelic polymers (TPs), a typical example of a system with transient network<sup>1-4)</sup>, show unique rheological properties when in aqueous solution. The most remarkable characteristic is that the mechanical spectrum, the frequency dependency of the dynamic modulus can be analyzed by a simple Maxwell model. In this case, the relaxation time is the lifetime of the crosslink of the transient network. Theoretical studies have revealed that the lifetime of the transient network of TP aqueous solutions is governed by the tension of the effective elastic chain and the affinity of the hydrophobic chain to the micelle-like crosslink point.<sup>5,6)</sup> This theoretical exception has been confirmed by experimental studies on a TP aqueous solution.<sup>7,8)</sup> The second

type of material having a transient network system is thread-like molecular assemblies formed by low-molecular-weight amphiphilic molecules. Certain classes of surfactants form thread-like micelles in water. Many studies on ionic surfactant/salt/water ternary systems have been published.<sup>9)</sup> The thread-like micelle solutions also show Maxwellian behavior in their rheological properties. It is somewhat surprising that these completely different types of molecular systems show similar rheological properties.

Thread-like molecular assembly is quite interesting from both academic and industrial viewpoints.<sup>10)</sup> The mechanism of stress relaxation in this system is still under debate. Cates et al.<sup>11)</sup> proposed a reptation model that assumes that the transient entanglement of the thread-like molecular assemblies is relaxed by reptation. Another idea is a phantom network theory that assumes that the thread-like molecular assemblies slip through at the transient entanglement.<sup>12)</sup> Because the mechanism of the mechanical relaxation of temporally entangled thread-like molecular assemblies is not well understood, further studies on a wide range of such materials are required.

From the perspective of industrial application, the thread-like molecular assemblies are a promising candidate for novel drug delivery system on account of their relatively large hydrophobic space.<sup>10)</sup> If we can engineer the system to have a stimuli response property, it could become a smart delivery

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system for a wide industrial field. The system is also an interesting prospect for the food industry as a texture modifier. It is quite important to control the rheological properties of foods in order to make them feel more satisfying in the mouth and easy to swallow<sup>13-15</sup>, and hence, a new type of rheological control agent is required.

We focused on sucrose stearate, which is a popular edible emulsifier. This nonionic surfactant forms several types of molecular assemblies depending on the temperature of the aqueous binary system.<sup>16-18</sup> The properties of fatty acid esters in industrial-grade sugar are quite complicated owing to impurities. Samples of sugar fatty acid esters, mainly a food ingredient, generally consist of *mono*, *di*, and *tri* esters.<sup>16</sup> The shape of the molecular assembly strongly depends on the shape parameter (SP) described Eq. (1).

$$SP = \frac{v}{a_0 l_c} \quad (1)$$

where  $v$ ,  $a_0$ , and  $l_c$  denote the volume occupied by the hydrocarbon tail, the area on the surface of the aggregate that the head group occupied, and the tail's "maximum effective length," respectively. A surfactant having small SP ( $<1/3$ ) tends to create spherical micelles. If the value is greater than  $1/3$ , the micelle grows linearly and makes a thread-like micelle. Sucrose mono-stearate has a small SP value; therefore, it is expected to make spherical micelles. However, as mentioned above, industrial-grade samples contain *di*-ester and *tri*-ester. In fact, the sample used in this study also contains impurities (see experimental section). A SAXS study reveals that industrial-grade sucrose stearate forms a multilayer system in water.<sup>16</sup> There are several reports on the phase behavior or rheological properties of the sucrose stearate/water binary system. Calahorra et al.<sup>17</sup> report that sucrose stearate solution showed a micelle solution phase above 43 °C; however, this micelle solution never showed rheological properties similar to those of worm-like micelles. Sadtler et al.<sup>18</sup>, in another study on a sucrose stearate/water binary system, report that a viscous phase above 45 °C is the  $L_\alpha$  + water phase; however, they did not perform dynamic modulus measurements (just showed the steady-state viscosity). Both these studies were conducted on samples from the same distributor (Mitsubishi Kagaku Foods, Tokyo). Since we recently found that the surfactant formed thread-like molecular assemblies without any additives, the details of the rheological properties and some results of small-angle laser-light scattering (SALS) studies for the molecular assemblies are reported in this study.

## 2. MATERIALS AND METHODS

### 2.1 Materials

Sucrose stearate (Ryoto Sugar Ester S-1670) was obtained from Mitsubishi Kagaku Foods (Tokyo, Japan). Fig. 1 shows the chemical structure of the *mono*-ester. S-1670 consists of 77 % *mono*-ester, 20 % *di*-ester, and 3% *tri*-ester.<sup>16</sup> The sample was used without further purification. The sample solutions were prepared with distilled water. Since the surfactant does not dissolve in chilled water, the sample solution was heated at around 70 °C to completely dissolve the surfactant.

### 2.2 Phase Behavior

Samples were prepared for phase analysis by weighing the proper amount of sucrose stearate and water (from 1 to 8 wt % of surfactant). The sample solutions, which were sealed in test tubes, were immersed in a water bath to maintain their temperature. The temperature of the sample was controlled within an accuracy of  $\pm 0.5$  °C. The phase behavior of the binary system was checked by observation with the naked eye.

### 2.3 Rheological Measurement

Rheological measurements were performed with a strain-controlled rheometer (ARES, TA instrument, USA) equipped with a water bath temperature control system having a Couette geometry with a cup diameter of 18 mm, a bob diameter of 16 mm, and a bob length of 16 mm. The temperature sweep of the dynamic modulus at constant frequency and strain was measured to check the consistency of the change behavior at various temperatures. The samples were first heated at 70 °C and then cooled (1 °C/10 min) during the measurement. The frequency dependence of the dynamic modulus was also investigated at various temperatures and concentrations.

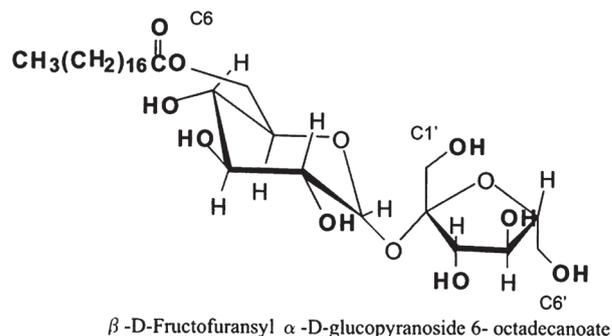


Fig. 1. Chemical structure of sucrose *mono*-stearate.

## 2.4 Small-Angle Laser-Light Scattering

SALS measurement was performed with a homemade apparatus. A He–Ne laser source (5 mW,  $\lambda = 635$  nm) (LDU33; Sigma Koki, Tokyo) was used as the light source. The sample solution was sealed up in a quartz cell (thickness: 1 mm) and its temperature was controlled with a homemade temperature control unit equipped a circulator. The digital images of the projection of the scattering light on a screen were taken with a digital camera (D-5100; Nikon, Tokyo), and then analyzed with free image analyzing software (Image J, and Calib CCD).

## 3. RESULTS

### 3.1 Phase Behavior

The appearance of the S-1670 aqueous solutions, whose concentrations ranged from 1 to 8 wt %, was observed with the naked eye at various temperatures ranging from 20 to 60 °C. The phase behavior is shown in Fig. 2. The most remarkable point is that all the samples changed in appearance from translucent (bluish) /turbid (white) to transparent at approximately 48 °C. It is expected that the samples contain discrete micelles or vesicles (translucent phase) or somewhat large-sized molecular assemblies (turbid phase); however, it is difficult to describe the details of these phases from the result because this observation was performed only by the naked eye. Since the transparent phase exhibited high viscosity (checked by the titling method), the viscosity change behavior of the samples was investigated. Dynamic measurement was performed at constant frequency ( $\omega = 10$   $\text{rads}^{-1}$ ) and strain ( $\gamma = 0.1$ ) at various temperatures to obtain the dynamic modulus, and then, the dynamic viscosity was calculated according to Eq. (2).

$$\eta'(\omega) = \frac{G''(\omega)}{\omega} \quad (2)$$

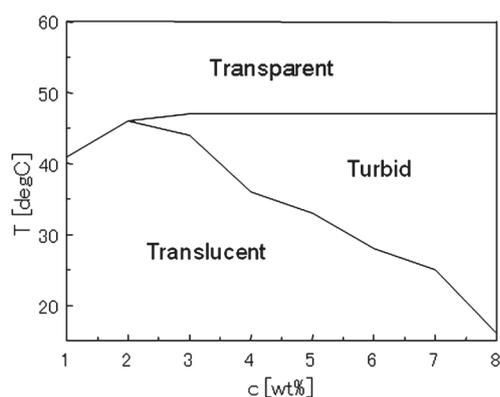


Fig. 2. Phase diagram of S-1670/water binary system.

The 3D plot (Fig. 3) shows the dynamic viscosity for various concentrations and temperatures. As can be seen, there is a peak at around 48 °C for all concentrations of samples. The temperature is in agreement with the phase transition temperature (translucent / turbid to transparent). The viscosity of the samples decreased with increasing temperature above the transition temperature. In general, amphiphilic molecules tend to form a molecular assembly in aqueous solution. The details of the viscosity change were checked on a 4 wt % S-1670 solution, as shown in Fig. 4. The viscosity of the sample started to increase at approximately 40 °C, at which point the appearance changed from turbid to opaque. The viscosity continued to increase with the temperature until approximately 48 °C. The peak value of the viscosity was approximately 10 Pa·s, which is an incredibly high value for an aqueous solution of low-molecular-weight matter. This temperature is also the critical temperature at which the appearance became transparent. Because the relative

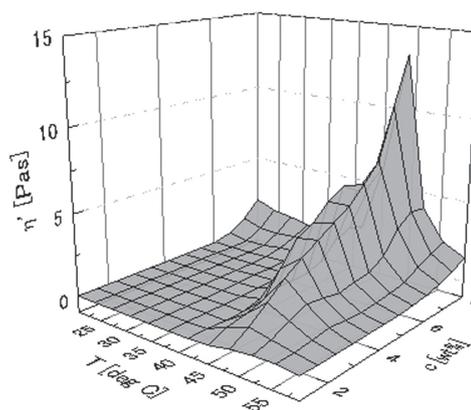


Fig. 3. Apparent viscosity change behavior for the S-1670/water binary system.

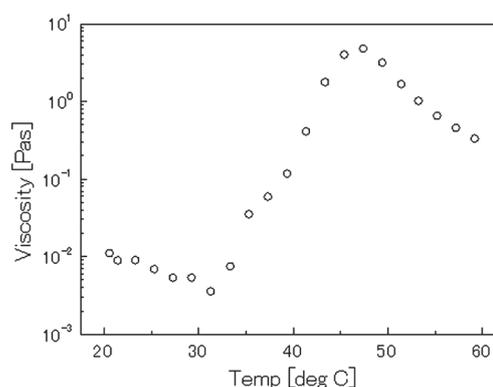


Fig. 4. Temperature dependence of the dynamic viscosity measured at  $\omega = 10$   $\text{rads}^{-1}$  for the 4 wt % S-1670 aqueous solution.

viscosity of a colloid dispersion depends on the concentration, shape, or size of the disperse phase, these behaviors indicate that the size or structure of the molecular assemblies began to change at approximately 40 °C, and that another change occurred at around 48 °C. As shown in Fig. 4, this viscosity change behavior agreed with the phase behavior (Fig. 2). We are particularly interested in the transparent viscous phase. Such high viscosity must be due to well-formed molecular assembly; therefore, we assume that the transparent viscous phase would be a thread-like molecular assembly phase.

### 3.2 Rheological Properties

#### 3.2.1 Temperature dependence of the dynamic modulus

To investigate the structure of the molecular assemblies of the S-1670 solutions at various temperatures, the frequency dependence of the dynamic modulus was measured. As a typical result, the mechanical spectra of the 4 wt % S-1670 aqueous solutions at 40, 44, 48, and 50 °C are shown in Fig. 5 (a, 40 °C; b, 44 °C; c, 48 °C; d, 50 °C). In particular, the result at 44 °C, just below the critical temperature, is quite interesting. The mechanical spectrum (Fig. 5 b) shows bimodal relaxation behavior; namely there is a fast mode and a slow mode. When we focused on the slow mode, the relaxation time shortened with increasing temperature. This result indicates that the microscopic structure of the molecular assembly in S-1670 solution changed depending on the temperature. Above the transition temperature, 48 °C, the mechanical spectrum is Maxwellian (Figs. 5 c and d). We analyzed the experimental data at 48 °C and 50 °C by using a bimodal Maxwell model [Eqs. (3), (4)]:

$$G'(\omega) = G_s \left( \frac{\omega^2 \tau_s^2}{1 + \omega^2 \tau_s^2} \right) + G_f \left( \frac{\omega^2 \tau_f^2}{1 + \omega^2 \tau_f^2} \right) \quad (3)$$

$$G''(\omega) = G_s \left( \frac{\omega \tau_s}{1 + \omega^2 \tau_s^2} \right) + G_f \left( \frac{\omega \tau_f}{1 + \omega^2 \tau_f^2} \right) \quad (4)$$

where  $G_s$  and  $G_f$  are the equilibrium moduli and  $\tau_s$  and  $\tau_f$  are relaxation times, respectively.

The lines in Figs. 5 c and 5 d are the best fit results of the analysis. The fitting lines obviously agree well with the experimental data. That is, S-1670 solution behaved as a Maxwellian viscoelastic liquid above the critical temperature.

#### 3.2.2 Concentration dependence of the dynamic modulus

The effect of S-1670 concentration on the mechanical properties was also investigated. The dynamic modulus of the samples (3 – 8 wt %) were measured at 50 °C and the data were analyzed by using Eqs.(3) and (4). As typical results, Fig. 6 shows the mechanical spectra of 3 wt % (Fig. 6a),

5 wt % (Fig. 6b), and 7 wt % (Fig. 6c) S-1670 solutions at 50 °C, respectively. The entire results are listed in table. We focused on the slow mode relaxation in these results, since it would be directly related the change from the elastic region to the flow region. The relation between  $G_s$  and  $c$  is shown in Fig. 7 and Fig. 8 shows the relation between slow mode relaxation time ( $\tau_s$ ) and concentration. It is clear that the slow mode relaxation time ( $\tau_s$ ) depend on concentration. Since the slope of Fig. 7 is about 1.7, it is expected that the stress would be occurred from the entanglement of a thread-like molecular assemblies in the system. Although the data points are scattered, we cannot consider any correlation between  $\tau_s$  and  $c$  in Fig.8.

### 3.3 SALS

To obtain information on the structure of the molecular assembly, an SALS study was conducted. Since the molecular assembly is expected to be of submicron or micron order, SALS is a suitable method of investigation. The projection images of the light scattering from the samples are shown in Fig. 9 (a, 40 °C; b, 48 °C). It is clear that the scattering intensities at the small-angle region vary widely. The

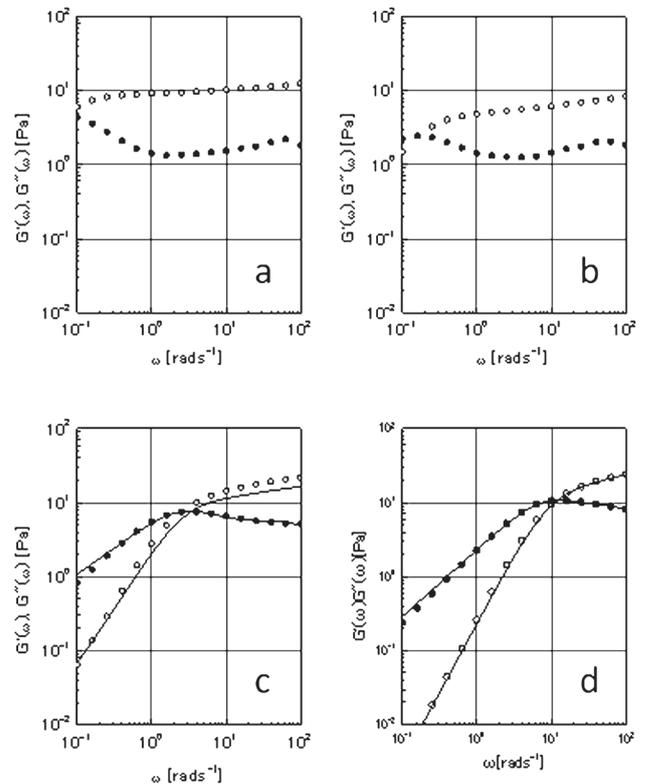


Fig. 5. Dynamic modulus of 4 wt % S-1670 aqueous solution at various temperatures; a, b, c, and d denote the results at 40, 44, 48, and 50 °C, respectively. Open circles and closed circles denote storage modulus and loss modulus, respectively. The lines in c and d denote the best fit results of the analysis using Eq. (3) and (4).

scattering profiles, which are analyzed from the projection image, are shown in Fig. 10 for the 4 wt % S-1670 solution at 40, 45, 47, 48, and 50 °C. We can see strong scattering intensity at the low  $q$  region below the critical temperature (48 °C); however, the scattering intensity was reduced above the critical temperature. This result indicates that relatively large molecular assemblies existed in the turbid phase (see Fig. 2); however, the size of the molecular assemblies abruptly decreased at approximately 48 °C. As you can see, there are the peaks,  $q_m$ , in the scattering profiles obtained below 48 °C in Fig. 10. It is clear from Fig. 10 that the position of the peak shifts to the lower scattering angular with increasing temperature. It is reported that the reciprocal of  $q_m$  is the characteristic length of concentration fluctuation,  $\xi$ , in a phase separation system.<sup>19)</sup> It is believed that this characteristic length represents the distance between the discrete molecular assemblies. The estimated values of  $\xi$  from the scattering

profile were 300 nm, 564 nm, and 862 nm for 40 °C, 45 °C, and 47 °C, respectively. Although the exact shape of the molecular assembly is unknown, it changed depending on the temperature. Above the transition temperature, we cannot analyze the scattering profile because the intensity is too low. This indicates that the size of the molecular assemblies above the temperature would be sufficiently smaller than the wavelength of the laser light (635 nm). If we wish to study the shape or size of the assemblies, we will need to employ a shorter wavelength beam (e.g., x-ray or neutron).

## 4. DISCUSSION

As mentioned before, there are several reports<sup>16-18)</sup> on the molecular assemblies of S-1670; however, there are some discrepancies in the phase behavior or the temperature dependence of the rheological properties. We consider that

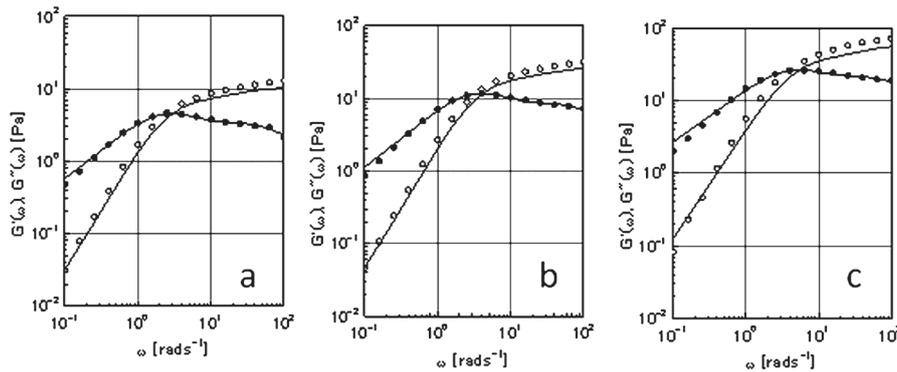


Fig. 6. Dynamic modulus for samples of S-1670 at 50 °C; a, b, and c denote the results for 3, 5, and 8 wt % S-1670 aqueous solutions, respectively. Open circles and closed circles denote storage modulus and loss modulus, respectively. The lines in the Figs denote the best fit results of the analysis using Eq. (3) and (4).

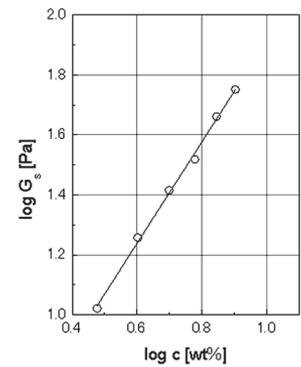


Fig. 7. Relation between the plateau modulus ( $G_s$ ) of the slow mode and S-1670 concentration at 50 °C. The slope of the line is 1.7.

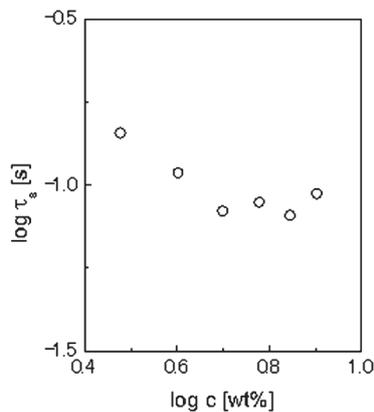


Fig. 8. Relation between the relaxation time ( $\tau_s$ ) of the slow mode and S-1670 concentration at 50 °C.

Table I. The viscoelastic parameters obtained from the analysis using a bimodal Maxwell model. The experimental results measured at 50 °C were used for the analysis.

S-1670 conc. (wt %)	Slow mode		Fast mode	
	$G_s$ [Pa]	$\tau_s$ [s]	$G_f$ [Pa]	$\tau_f$ [s]
3	10.5	0.144	7.2	0.0175
4	18.1	0.109	13.3	0.0134
5	26.0	0.0837	19.5	0.0126
6	33.0	0.0889	25.5	0.0123
7	45.8	0.0812	37.8	0.0112
8	56.4	0.0944	44.9	0.0119

there are at least two reasons for such discrepancy. First of all, since the material is industrial grade, the purity of the mono-ester would be different in each sample. It is considered that the contents of *di*- or *tri*-ester seriously affect the shape parameter (SP), and hence, the solution properties would vary depending on the sample. Second, because ester bonding is sensitive to hydrolysis, part of the fatty acid would be eliminated, and free fatty acid may affect the value of SP. As far as we know, this study is the first to report the observation of a transparent viscous phase without any co-solution or co-surfactant. A simple observation of the appearance revealed that the S-1670 aqueous solution showed a two-step structure transition. The first step was the transition from translucent to turbid. The translucent phase may contain discrete micelles or vesicles because its viscosity was quite low (some  $10^{-3}$ – $10^{-2}$  Pa·s). The translucent phase transitioned to the turbid phase between 20 °C and 40 °C (Fig. 2). The viscosity increased with temperature (Figs. 3 and 4); moreover, the light-scattering intensity was quite high at the low- $q$  region (Fig. 10). Viscoelastic properties also appeared (Figs. 5 a and b). These results indicate that the growth of the molecular assemblies is temperature dependent.

The most interesting phase is the transparent viscous phase above 48 °C. The transparent appearance indicates that the molecular assemblies were sufficiently smaller than the wavelength of visible light, and the SALS result (Fig. 10) supports this finding. The mechanical spectrum and the frequency dependency of the dynamic modulus can be analyzed with a Maxwell model, although it is a bimodal model. Many studies on the rheological properties of worm-like micelle solutions have been published, and they show that the mechanical spectrum follows the Maxwell model.<sup>9)</sup> We can obtain the characteristics of the model, namely the plateau modulus and the relaxation time. The plateau modulus occurs from the entanglements of polymer or thread-like molecular

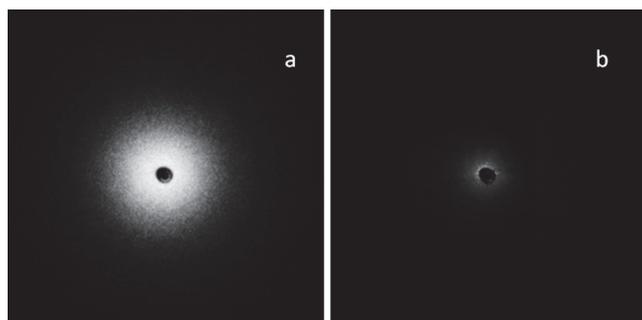


Fig. 9. Projection image of light scattering from 4 wt % S-1670 aqueous solution at 40 °C (a) and 48 °C (b).

assemblies, and the relaxation time of the time constant of the entanglement's relaxation—in other words, the lifetime of the entanglement. Since we observed such Maxwell-type mechanical relaxation in S-1670 solution (Figs. 5 c and d; Fig. 6), the entanglements consisted of thread-like molecular assemblies. It is believed that the slow mode relaxation time ( $\tau_s$ ) indicates the lifetime of the transient networks that occurred in the plateau modulus of this system. On the other hand, it is unclear whether the mechanism of the fast mode relaxation time is of order  $10^{-2}$  s, which would be related to the molecular perturbation in/out of molecular assemblies.<sup>12)</sup> The relation between the plateau modulus and the concentration supports the notion that the modulus occurred from the entanglement of the thread-like molecular assembly since the scaling factor was about 1.7.<sup>20)</sup> The result, which shows that slow mode relaxation time was independent of concentration, can be considered to indicate that the transient network was relaxed in the same manner as that in a phantom network model.<sup>12)</sup>

## 5. CONCLUSION

The results of this study obviously show the existence of thread-like molecular assemblies in the sucrose stearate / water binary system under certain conditions. However, it is difficult to determine whether they are thread-like micelles or vesicles. We consider that further study on the system is needed for confirmation, such as by using a scattering technique with a short wavelength (x-ray or neutron) beam. It is quite unique to find that the shape of the molecular assembly can be controlled

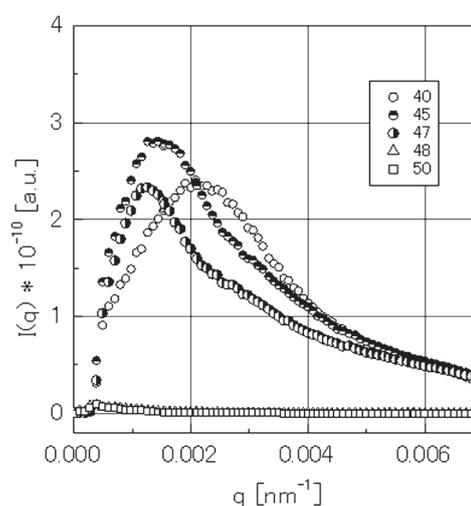


Fig. 10. Scattering profile for 4 wt % S-1670 aqueous solution at various temperatures. Symbols and numbers denoted in the upper-right corner are the measurement temperatures.

by merely adjusting the temperature, without any requirement of additives. Although the temperature of transition from a discrete assembly to a thread-like one was somewhat high (48 °C), we can possibly tune the transition temperature by adding a co-solution or cosurfactant<sup>21,22</sup> or physical stimuli<sup>23</sup> for actual application in the food or pharmaceutical fields. We believe that this material is a promising candidate for use as a temperature-sensitive smart material.

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