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# Effect of Ionic Surfactants on the Iridescent Color in Lamellar Liquid Crystalline Phase of a Nonionic Surfactant

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A nonionic surfactant, *n*-dodecyl glyceryl itaconate (DGI), self-assembles into bilayer membranes in water having a spacing distance of sub-micrometer in the presence of small amounts of ionic surfactants, and shows beautiful iridescent color. Ionic surfactants have great effects on this iridescent system. We have interestingly found that the iridescent color changes with time after mixing DGI and ionic surfactants and the color in equilibrium state changes greatly with changing concentration of the ionic surfactants. The time dependent color change results from the transformation of DGI aggregate structure after being mixed with ionic surfactant. It is first found that the iridescent color of this nonionic system can be changed from red to deep blue by altering the concentration of ionic surfactants added even though the total concentration of surfactant is almost constant. Such large blue shift of the iridescent color in equilibrium state cannot be fully explained by the ordinary undulation theory applied so far for this phenomenon. The flat lamellar sheets tend to curve by increasing the concentration of ionic surfactants to form separated onion-like and/or myelin-like structures. These separated structures of lamellar system result in the decrease of spacing distance between bilayer membranes because some vacant spaces necessarily appear among these structures.

Keywords: bilayer membrane, iridescent color, Helfrich thermal undulation, liquid crystal, lamellar sheet, lamellar vesicle

## 1. Introduction

Surfactants form a rich variety of self-assembled structures in their dilute aqueous solutions<sup>[1]</sup>. Among them, the highly swollen lamellar phases have been well studied in the past years<sup>[2-5]</sup>. The spacing distance between these bilayer membranes in the swollen lamellar phases can extend to hundreds of nanometers and the solutions show iridescent color<sup>[6-9]</sup>. The iridescent surfactant systems studied so far cover anionic, cationic and nonionic surfactants<sup>[10-14]</sup>. It is well known that this iridescent color can be changed by changing the total concentration of surfactants<sup>[6-14]</sup>.

For the lamellar bilayer membrane systems of a common nonionic surfactant C<sub>12</sub>E<sub>5</sub>, the periodic structure of bilayers is assumed to be stabilized by the Helfrich steric undulations<sup>[15-17]</sup>. Small amounts of ionic surfactants give a significant influence on the behavior of the dilute bilayer solutions of the nonionic agent<sup>[18]</sup>. Small amounts of ionic surfactants suppress the Helfrich undulations, flatten the bilayers and decrease the interplanar distance. Jonströmer and Strey found that a blue shift in scattering spectrum when trace amounts of ionic surfactants were added to this nonionic surfactant system<sup>[18]</sup>. This blue shift in Bragg diffraction peak has been widely explained by the above mentioned Helfrich thermal undulation theory<sup>[19]</sup>, as shown in Eq. [1],

$$\frac{\Phi d}{\delta} = 1 + \frac{\Delta A}{A} \quad (1)$$

where  $d$  is the interplanar distance (between the mid-planes of the neighboring lamellas),  $\delta$  the thickness of the bilayer membrane,  $\Phi$  the volume fraction of surfactant,  $A$  the projected area of undulating membrane on the  $(x,y)$  plane, and  $A+\Delta A$  the average of the true area of the undulating membrane. Taking the bilayer thickness  $\delta$  and the volume fraction  $\Phi$  to be 4 nm and 0.016, respectively, as a typical case in the normal nonionic iridescent systems, the blue shift in interplanar distance is about 20 nm<sup>[17,18]</sup>.

This paper deals with an iridescent solution of a polymerizable nonionic surfactant, *n*-dodecyl glyceryl itaconate [DGI;  $n$ -C<sub>12</sub>H<sub>25</sub>OCOCH<sub>2</sub>C(=CH<sub>2</sub>)COOCH<sub>2</sub>CH(OH)CH<sub>2</sub>OH]<sup>[20]</sup>. DGI forms bilayer

membranes (lamellar liquid crystal) in water and gives iridescent color in the presence of small amount of ionic surfactants such as *N,N*-dimethylbenzylammonium dodecylitaconate, sodium dodecyl sulfate (SDS)<sup>[20]</sup>. We have first found in this work that the iridescent color of DGI solutions can be tuned from red to deep blue by changing the concentration of ionic surfactant added even though its concentration is negligibly small comparing with the total surfactant concentration. In the equilibrium state, we have found in this work a much larger blue shift of about 70 nm by addition of ionic surfactants to the nonionic surfactant system. Such a large blue shift cannot be well explained only by the thermal undulation theory mentioned above, and a new additional mechanism is necessary.

## 2. Materials and methods

**2.1 Materials:** SDS and cetyltrimethyl ammonium bromide (CTAB) with higher purity than 99.0 %, were obtained from MP Biomedicals, Inc.. Millipore deionized water was used to prepare the sample solutions

**2.2 Synthesis of DGI and preparation of DGI iridescent samples.** DGI was synthesized by essentially the same procedures as those in the previous works<sup>20,21</sup>. The crude product was purified by a silica gel column (Silica Gel 60N, KANTO Chemical Co., Inc.). The final product was checked by element analysis to contain 64.39 % C (64.48 % theoretical), 9.83 % H (9.74 % theoretical).

The iridescent solution of DGI with various amounts of ionic surfactants were prepared by fixing DGI concentration at 1.63 wt % (43.65 mmol/L), and changing ionic surfactants from 0.025 to 2.5 mol % (with respect to DGI, concn.= $1.09 \times 10^{-5} \sim 1.09 \times 10^{-3}$  mol/L). The mixed solutions of DGI and the ionic surfactants were kept at 55 °C to obtain the iridescent color since the Krafft point of DGI was 43 °C<sup>[20,21]</sup>.

**2.3 Measurement of light reflection spectrum.** Light reflection spectra of iridescent DGI solutions were measured by a Double-Beam Spectrophotometer (Shimadzu, UV-150-02) and detected at a fixed scattering angle by varying the wavelength. The intensity of reflected light from the samples was calibrated by that from a BaSO<sub>4</sub> white board. In order to keep the temperature, each measurement was

carried out immediately after taking the sample out from the temperature-controlled water bath. The interplanar distance,  $d$ , is calculated by Bragg equation,  $2nds\sin\theta = \lambda$  with  $n = 1.33$ ,  $\theta = 67.5^\circ$ , where  $n$ ,  $\theta$  and  $\lambda$  are the refractive index of water, the angle of incidence and the wavelength of the reflected light, respectively.

**2.4 Investigation of DGI dynamic process.** The dynamic process of the structure change in DGI solution was monitored by the reflection spectra of selected DGI samples after mixed with different concentrations of SDS at some time intervals. The lamellar liquid crystalline droplets of pure DGI with small spacing distance of several nm were also observed at time intervals by an inverted microscope (Olympus IX71) equipped with a hot plate (Tokai Hit, MATS-10002s) to control the temperature. The images of DGI liquid crystalline droplets were recorded by a CCD camera. The size and number of the droplets were averaged from the results measured for over 30 microscopic photographs. The spherical liquid crystalline droplets of DGI were checked to be lamellar liquid crystals by the Maltese cross texture under a polarizing microscopy.

**2.5 Viscosity and viscoelasticity measurements.** The viscosity measurements of dilute DGI solutions were carried out by Ubbelohde capillary viscometers. The samples with different concentrations of DGI and SDS were kept in a water bath at  $55^\circ\text{C}$ , and each sample was tested at least twice, and the average deviation of each viscosity was less than  $\pm 0.2\%$ . The rheological experiments were performed using a Rheometric Scientific rheometer (3ARES-17A) equipped with a temperature-control chamber. The cone-and-plate device was made of titanium. In a series of frequency-sweep tests, an oscillatory shear flow with small amplitude and a constant shear strain of about  $3\%$  was applied to the DGI sample solutions. The elastic modulus,  $G'$ , and the viscous modulus,  $G''$ , were measured in periodical experiments in the angular frequency range between 0.1 and 100 rad/s.

**2.6 Freeze-Fracture Transmission Electron Microscopy (FF-TEM) experiments.** FF-TEM experiments were carried out in JEOL Corporation. The typical processes were as follows: DGI solutions with different concentrations of SDS had been kept in a water bath for 1 day to obtain the equilibrium state, a certain amount of a sample was dropped in the specimen carrier and frozen by liquid

nitrogen. The frozen samples were then fractured at  $-120\text{ }^{\circ}\text{C}$  in a JFD-9010 vacuum chamber. After treating by etching at  $-90\text{ }^{\circ}\text{C}$ , the samples were tilted and coated by platinum and followed by carbon. The replicas were peeled off after the melting of the samples put in ambient conditions. Transmission electron microscopic observation was made by JEM-1011 (voltage at 100 kV), the images were recorded by a CCD camera equipped on this apparatus.

### 3. Results

Pure DGI in water forms lamellar liquid crystalline droplets at  $55\text{ }^{\circ}\text{C}$  with the diameter of several  $\mu\text{m}$ . (A typical image under a polarized microscopy is shown in Supporting Information). The spacing distance between bilayer membranes in these liquid crystals is in several nanometers (See Supporting Information). With the presence of small amounts ionic surfactants, the bilayers are separated apart and the liquid crystalline droplets are no longer observed by polarized microscopy. The swollen bilayer systems thus obtained show the iridescent color.

**3.1 Dynamic process of color change in dilute region of SDS.** It is interestingly found that the kinetic process to attain the equilibrium state after mixing SDS and DGI is dependent on SDS concentration. Figure 1 shows the interplanar distance,  $d$  (calculated from each reflection spectrum by Bragg equation), between bilayer membranes against the SDS concentrations (molar ratio to DGI) obtained at time intervals after mixing SDS and DGI. As seen from the figure, the color (interplanar distance,  $d$ ) shifts with time is remarkable in the lower concentration range of SDS. When the molar ratio of SDS is higher than 1:600, however, the interplanar distance,  $d$ , is almost constant with time. For a pure DGI sample without any ionic surfactants, the lamellar liquid crystalline droplets having small spacing distance of several nm are maintained to be unchanged even after one week in water bath at  $55\text{ }^{\circ}\text{C}$ .

**3.2 Color change of DGI solution with different concentrations of SDS and CTAB.** Figure 2 shows the color photographs of selected iridescent DGI solutions as a function of SDS concentration. One can find that the iridescent color shifts to blue side with increasing concentration of SDS. A cationic surfactant, CTAB, also shows similar effect on DGI solutions. When the molar ratio of SDS to DGI is

1:4000 (SDS concn.=  $1.09 \times 10^{-5}$  mol/L), after being kept in water bath at 55 °C for 3 h, the solution shows pink color appearance, while the ratio is smaller than 1:4000, a turbid, heterogeneous solution is obtained. This indicates that a phase separation into liquid crystalline droplets and almost pure water phase takes place in the absence of SDS<sup>[20]</sup>. As the ratio of SDS increases to 1:30, the solution changes to transparent and colorless one. When the concentration of DGI is fixed to 1.63 wt % and the molar ratio of SDS is increased from 1:4000 to 1:40 (from  $1.09 \times 10^{-5}$  to  $1.09 \times 10^{-3}$  mol/L), the color of the iridescent solution changes from pink to deep blue. This large change of color (Bragg diffraction peak) is quite different from the results reported so far. In  $C_{12}E_5$ /SDS systems<sup>[18, 22-24]</sup>, the largest shift in Bragg peak is just around 30 nm, but in our system, the wavelength of the iridescent solution shifts from 724 to 400 nm, covering almost the whole range of visible light.

The reflection spectra of the equilibrated solutions after keeping the samples in water bath for 27 h exhibit sharp and narrow peaks, and do not noticeably change any more (see the Supporting Information). The plot of the equilibrated interplanar distance,  $d$ , against the molar ratio of SDS to DGI is shown in Figure 3. A good straight line is found when the concentration of SDS is in the intermediate range. However, when the SDS concentration is in the lower range, the blue shift in iridescent color (interplanar distance,  $d$ ) is more remarkable with increasing concentration of SDS. Once the concentration of SDS exceeds the molar ratio of 1:50, the relationship between  $d$  and the SDS concentration seems to be more complex. It should be noted here that the reported phenomena of the effect of SDS on a nonionic surfactant system ( $C_{12}E_5$ ) is quite simple: the interplanar distance,  $d$ , varied a little (from 167 to 181 nm)<sup>[17]</sup> with the SDS concentration change. But in our system, the interplanar distance changes from 240 to 175 nm in the equilibrium state when the concentration of SDS changes from  $1.09 \times 10^{-5}$  to  $1.09 \times 10^{-3}$  mol/L.

**3.3 Viscosity and viscoelasticity change in the solution.** The viscosity change in DGI solution with different ratio of SDS is shown in figure 4. The viscosity of DGI solution first decreases with increasing concentration of SDS, and starts to increase again at the molar ratio of SDS to DGI to be 1:800 (SDS concn.=  $5.45 \times 10^{-5}$  mol/L). Interestingly, the interplanar distance of the sample has an inflection point at

the same molar ratio of SDS to DGI as shown in Figure 3. It should be noted that the sample with the highest viscosity still shows iridescent color, which indicates the existence of swollen bilayer structures. Once the molar ratio of SDS to DGI is higher than 0.1, the samples show as low viscosity as water. This result indicates that the structure of DGI aggregates changes into spherical micelles. The increase in viscosity in a lamellar system has already been demonstrated when the system is under steady shear flow. The formation of onion-like lamellar structures as separated bodies and the interactions between these onions result in the increase in viscosity<sup>[26, 27]</sup>. Figure 5 shows the elastic modulus,  $G'$ , and the viscous modulus,  $G''$ , plotted against the angular frequency. In both samples with DGI concentrations of 2.0 and 3.0 wt % keeping the SDS concentration ratio to be 1:40, one can see that at high frequencies, it behaves elastically ( $G' > G''$ ), while at low frequencies, it switches to a viscous behavior ( $G'' > G'$ ). The increase in elasticity and decrease in viscosity moduli with increasing frequency indicate the existence of some entanglements<sup>[28]</sup> of DGI microstructures in the solutions. Onion-like and/or more complicated structures might form in these solutions. A 1.6 wt % DGI solution with a SDS concentration of 1:40 is also confirmed to be viscous and elastic from the fact that when the solution is slightly shaken and its flow stops, the bubbles in the solution show reverse flow.

**3.4 FF-TEM images of DGI aqueous solution with different concentrations of SDS.** Figure 6 shows the images of freeze-fracture TEM of DGI solutions in which the ratios of SDS to DGI are 1:4000 (SDS concn.=  $1.09 \times 10^{-5}$  mol/L) and 1:40 (SDS concn.=  $1.09 \times 10^{-3}$  mol/L), respectively. The interplanar distances of both samples agree well with those calculated from the wavelength at the maximum light reflection. When the molar ratio of SDS to DGI is 1:4000, the lamellar sheets can be clearly seen in Figure 6 a). The bilayers occupy the whole space of the solution. However, when the molar ratio of SDS is increased to 1:40 (SDS concn.=  $1.09 \times 10^{-3}$  mol/L), the onion-like and/or myeline-like lamellae are interestingly found as shown in Figure 6 b).

#### 4. Discussion

It has been reported that the nonionic surfactant systems of  $C_{12}E_5$  do not need any ionic surfactants to have the swollen bilayers showing the iridescent color<sup>[16-18]</sup>, although this type of nonionic surfactant may contain ionic impurities, in some cases owing to the oxidation of the terminal -COH group to ionizable -COOH group<sup>[29]</sup>. In our DGI systems, it is found that ionic surfactants are necessary to change from the lamellar liquid crystalline droplets of pure DGI having the spacing distance of several nm to the iridescent lamellar phases. For the pure DGI samples without any ionic surfactants, the liquid crystalline droplets are kept unchanged even after being left in water bath at a higher temperature than the Kraff point for a week. This result shows that the electrostatic repulsive force of the headgroup of the ionic surfactant separates apart the DGI bilayers at the initial moment, and DGI lamellar liquid crystalline droplets undergo the transition to swollen lamellar bilayer membranes.

**4.1 Kinetic change in the iridescent color of DGI solutions.** In order to elucidate the mechanism of the color change with time, we have made the microscopic observation of the liquid crystalline droplets of DGI after being mixed with SDS. Figures 7 a) and b) show the change of the number and size of the liquid crystalline droplets. One can find that the number of the liquid crystalline droplets decreases but their size increases dramatically with increasing time as well as SDS concentration. It is evident that higher concentration of SDS can accelerate the transition from liquid crystalline droplets to the iridescent swollen lamellar phase. The penetration of SDS molecules into the DGI bilayer membranes must be governed by the diffusion process, and higher concentration of SDS results in the rapid transformation of DGI aggregate structures. At the very beginning of the experiments, most of the DGI are in the liquid crystalline droplet state and only small fraction of DGI is in swollen state to show a pale red appearance. With longer time standing, more and more DGI bilayers transform to the swollen state to give the large blue shift of the solutions.

**4.2 Large blue-shift in the iridescent color with increasing concentration of SDS in the equilibrium state.** We have first found the large blue shift of iridescent color in a nonionic lamellar phase by increasing the concentration of ionic surfactant. Helfrich thermal undulation theory can only

explain a blue shift of about 20 nm as mentioned before. A 70 nm blue-shift in the iridescent color at equilibrium state can not be well explained only by this thermal undulation effect.

When the concentration of SDS is low, DGI bilayers are separated apart to form lamellar sheets. In this lamellar sheet structure, the thermal undulation plays an important role for the solution to shift to the blue side. Namely, the ionic charge of SDS molecules in a same membrane flattens the bilayers and thus leads to an increase in the surface area. The initial sharp decrease of interplanar distance in Figure 3 may be due to this mechanism<sup>[17-19]</sup>.

It is well known that the increase in SDS concentration results in the increase of ionic strength, and may reduce the electrostatic repulsive force between bilayer membranes. But this situation does not cause the blue-shift in our iridescent system, since the spacing distance between bilayer membranes is not determined by the minimum of the DLVO potential. In the iridescent systems, the distance between bilayer membranes is too large (200 - 300 nm) for the van der Waals attractive force to work. Only the electrostatic repulsive force works between the bilayer membranes, and the spacing distance is determined simply by the concentration of bilayer membranes (total surfactant)<sup>[30]</sup>. So, even if the added SDS reduces the electrostatic repulsion, the spacing distance (the periodic structure) does not change unless the repulsion becomes too small to maintain the periodic structure of bilayer membranes.

According to the packing theory<sup>[31]</sup>, the shape of the surfactant aggregates is mainly governed by the packing parameter of  $v/Ls_o$ , where  $v$ ,  $L$  and  $s_o$  are the volume, the length of the alkyl chain and the effective surface area of the headgroup of surfactant molecule, respectively. DGI molecule may be in truncated conical shape and tends to form flat lamellae, while the molecule of SDS is wedge-shaped and favors to form spherical micelles. When the ratio of SDS is increased, it is reasonable that the structure of DGI bilayers will change from flat lamellar sheets to lamellar vesicles consisting of curved bilayer membranes. Once the separated onion-like vesicles are formed, the bilayer membranes can not occupy the whole space of the solution, resulting in the emergence of some vacant spaces. The interplanar distance between bilayer membranes decreases in the above situation since the space for the bilayer

membranes becomes smaller. Some experimental evidences for this structural change can be given below.

If we plot the interplanar distances against  $(1-c)/c$  (where  $c$  is the weight fraction of DGI) in these solutions, one can see the interesting curve, as shown in Figure 8. When the concentration of SDS is low enough, *i.e.*, the molar ratio of SDS to DGI = 1:4000, the interplanar distances are linearly related to  $(1-c)/c$ . The structures of these solutions can be assumed to be the perfect lamellar sheets which occupy the whole space of the solution<sup>[32]</sup>. However, once the concentration of SDS increased to 1:40, the relationship of the interplanar distance and  $(1-c)/c$  is no longer linear; at the higher concentration of DGI, the more insensitive change is observed in the interplanar distance. It is known that deviations from the ideal dilution law occur in the case of the area per headgroup of surfactant being variable during swelling process and dependent on the surfactant/cosurfactant ratio<sup>[33]</sup>. Since the ideal dilution law works well in the lower SDS concentration case, it can be concluded that the ratio of DGI and SDS and the area per headgroup are almost constant during dilution. The deviation in the higher SDS concentration region can be interpreted as showing that the molecular area of the surfactants, *i.e.*, the curvature of the bilayers varies with the concentration. This result necessarily results in the existence of some unoccupied space in this lamellar system.

From the result of viscosity, one can find that the viscosity decreases and reached to a minimal value, then begin to increases again with increasing the concentration of SDS. The increase in viscosity proves that DGI aggregate structure changes. P. Versluis and co-workers<sup>[26,27]</sup> found that the onion-like structures of the bilayers show a high viscosity in dilute solutions. This may be the case also in our systems as proved by FF-TEM images in Figure 6. Interestingly, myelin structures can be found in the image of FF-TEM. The formation of this structure also results in the increasing in the viscosity and elasticity. The onion-like DGI multilamellae may deform into myelin-like structures under shearing, which results in the entanglement among them.

## 5. Summary

We have systematically studied the effect of ionic surfactants on the iridescent color of a nonionic surfactant. It is first found that i) the iridescent color changes with time after mixing DGI and ionic surfactants, ii) the kinetic process of the above color change depends highly upon the concentration of ionic surfactants, and iii) the iridescent color in equilibrium state changes greatly with changing concentration of the ionic surfactants. The time dependent color change results from the transformation of DGI aggregate structure after being mixed with ionic surfactant. The penetration of ionic surfactants into DGI bilayer membranes is a diffusion-dominated process and depends highly upon the concentration of the ionic surfactants. The flat lamellar sheets tend to be curved by increasing the concentration of ionic surfactants to form separated onion-like and/or myelin-like structures. These separated structures of lamellar system result in the decrease of spacing distance between bilayer membranes because some vacant spaces necessarily appear among these structures. This mechanism of the large blue shift is the first finding, and may provide the new insight for the iridescent surfactant systems.

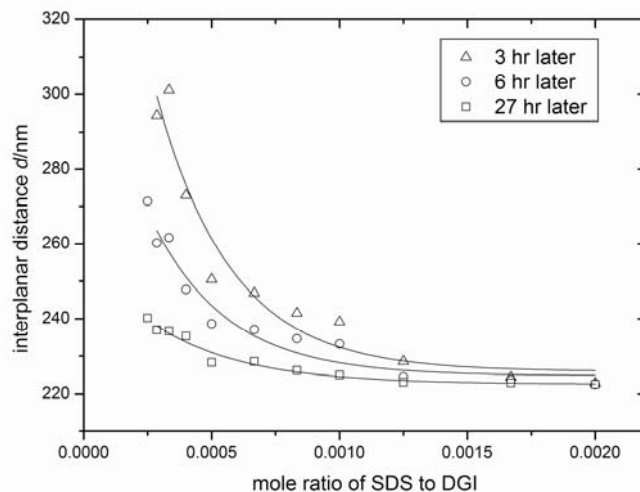
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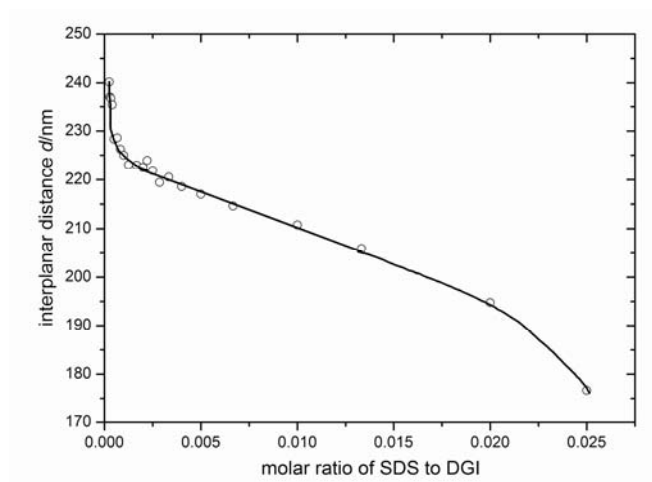
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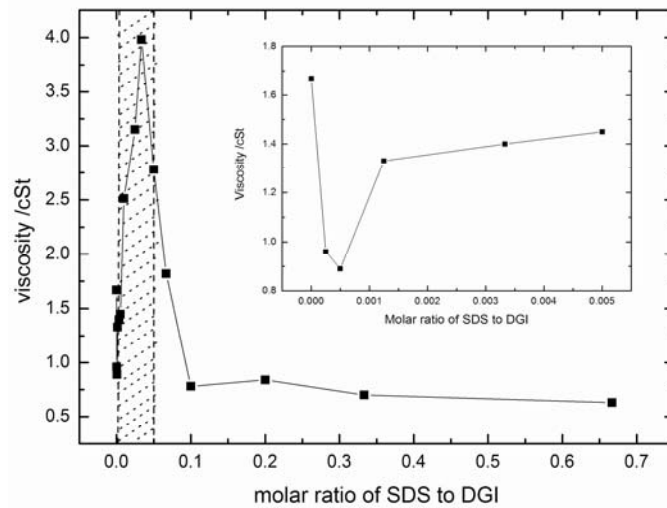
**Figure 1.** Dependence of interplanar distance,  $d$ , on the concentration of SDS, plotted against molar ratio of SDS to DGI at different time intervals. A large blue shift in lower SDS concentration range can be observed. The total concentration of DGI is 1.63 wt %.



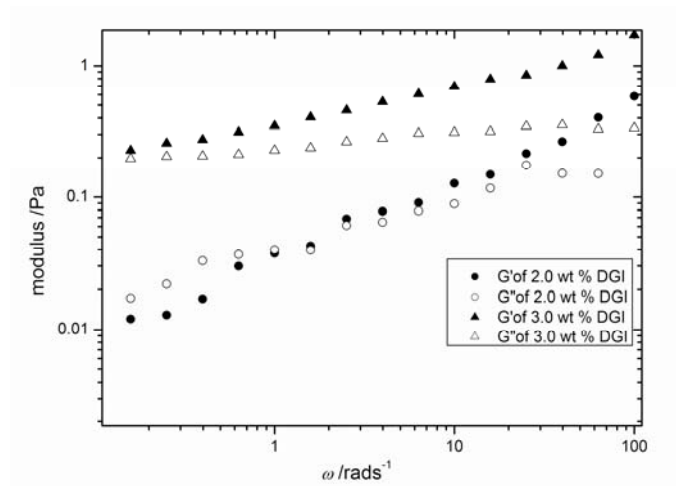
**Figure 2.** Color change from pink to deep blue with increasing molar ratio of SDS to DGI observed at 3 hrs after mixing SDS and DGI (from left to right, the molar ratios of SDS to DGI are 1:4000, 1:2500, 1:1000, 1:600, 1:400, 1:200, 1:100, 1:75, 1:50, 1:40, respectively)



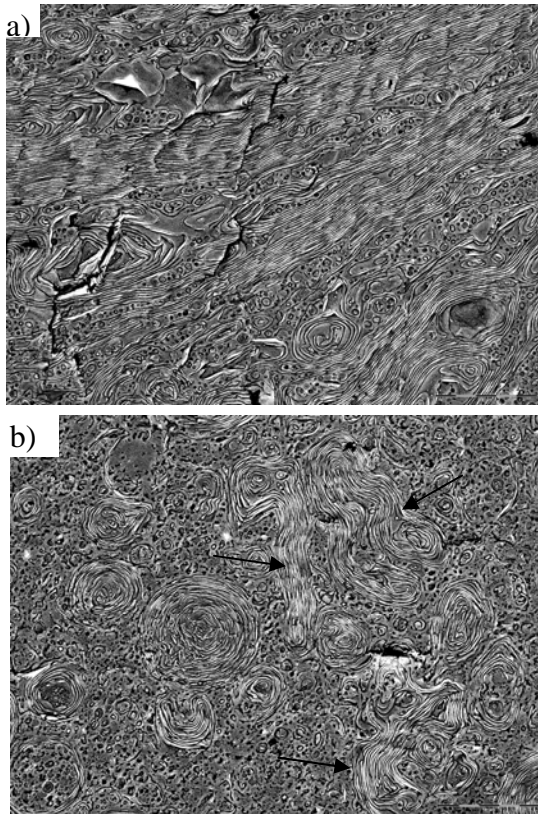
**Figure 3.** Plot of the equilibrated interplanar distance,  $d$ , against molar ratio of SDS to DGI in wide range of SDS concentration. The total concentration of DGI is 1.63 wt %.



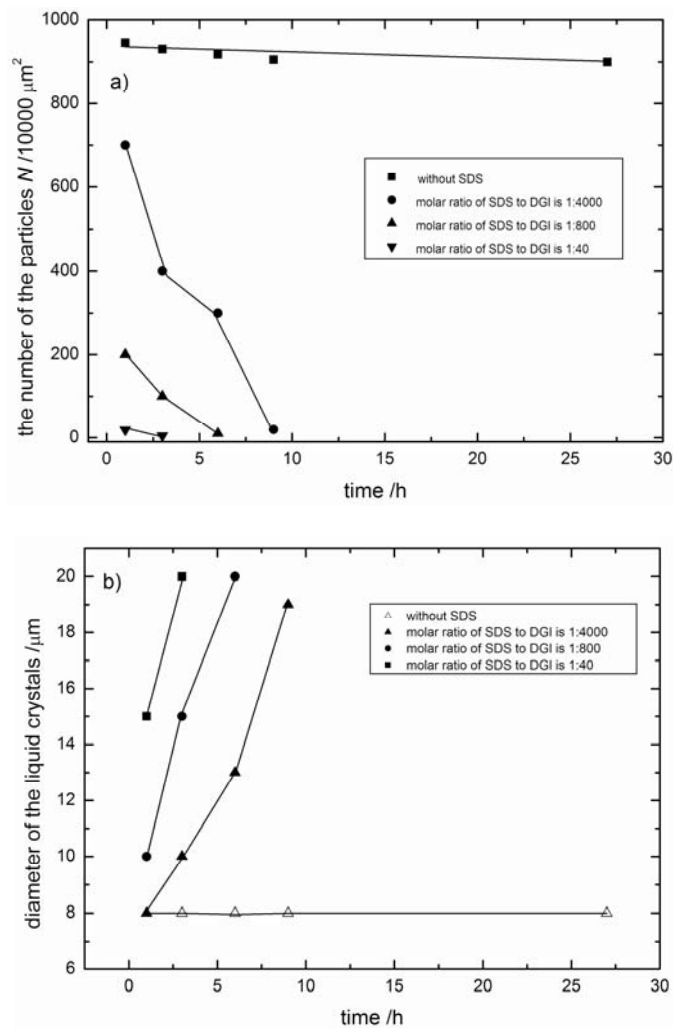
**Figure 4.** The viscosity of 1.6 wt % DGI aqueous solution as a function of the ratio of SDS to DGI. The highest viscosity appears when the ratio of SDS to DGI is 1:40. The cross hatching shows the region where the iridescent color appears. The inserted figure is the expansion of the lower SDS concentration range.



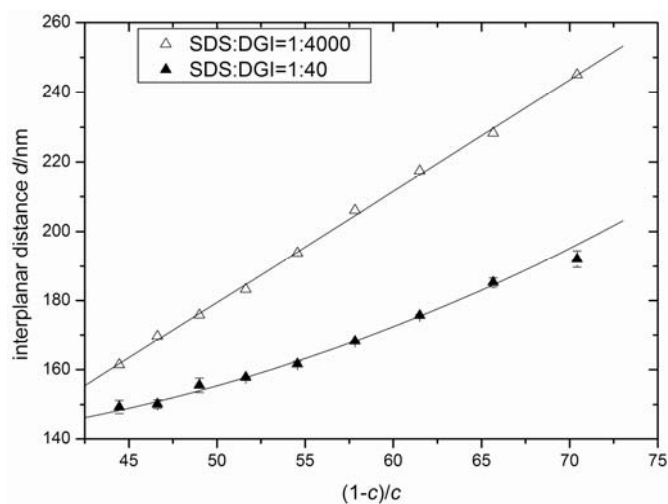
**Figure 5.** The elastic modulus,  $G'$  and the viscous modulus,  $G''$  of DGI solutions at 55 °C as a function of angular frequency  $\omega$ . The molar ratio of SDS to DGI was fixed at 1:40, and DGI concentrations were 2.0 and 3.0 wt %, respectively. The samples have been prepared and kept in water bath at 55 °C for 1 day to obtain the equilibrium state.



**Figure 6.** Freeze-Fracture TEM of DGI aqueous solution with a SDS ratio of 1:4000 a) and 1:40 b). The scale bar is 10  $\mu\text{m}$ . When the molar ratio of SDS is 1:4000, lamellar sheets occupy the whole space. While the molar ratio of SDS is 1:40, DGI lamellae tend to curve to form onion-like and/or myelin-like structures which are separated in the water phase. Myelin structures are shown in the figure by the arrows.



**Figure 7.** Plot of the number of the lamellar liquid crystalline droplets in DGI solution against time a) and the diameter change of the liquid crystalline droplets with time b). For DGI system without any ionic surfactant, the size and the number of the liquid crystalline droplets do not change noticeably even after being kept in water bath at a temperature over the Kraff point for a week.



**Figure 8.** The interplanar distances between the DGI bilayer membranes change against  $(1-c)/c$  (where  $c$  is the weight fraction of DGI). The samples are prepared at the molar ratios of SDS to DGI to be 1:4000 and 1:40, respectively (shown in the figure by  $\triangle$  and  $\blacktriangle$ ). (The experiments at higher SDS concentration were carried out at least three times). The total concentrations of DGI change from 1.4 to 2.2 wt %. All the samples were prepared and kept in water bath for a day at 55 °C to get to the equilibrium state.