Iridescent Solutions Resulting from Periodic Structure of Bilayer Membranes

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Dilute aqueous solutions of alkenylsuccinic acid (ASA) have been found to exhibit iridescent phenomena in the concentration range of about 1 to 2 wt %. The structures of the iridescent solutions and the more concentrated solutions have been studied mainly by the ultraviolet (UV) and X-ray diffraction techniques. The experimental results of X-ray diffraction for the concentrated C₁₆ASA solutions (10-60 wt %) indicate that the bilayer membranes of 4.1 nm thickness are stacked periodically to form a lamellar liquid crystal. The UV diffraction method was applied to iridescent dilute solutions (0.7-2.4 wt %) of the same surfactant. Strong but broad Bragg reflections corresponding the spacing of 300-150 nm were obtained. Because of the lack of higher order reflections in UV diffraction patterns, the detailed structure of iridescent solutions could not be made clear. A simple model is adopted to estimate the structure of dilute solutions. If the lamellar liquid crystal is uniformly formed in the whole space of the solution, the Bragg spacing, d, is expressed as $d = [((1-c)/c)\rho_1/\rho_2 + 1]d_1$, where c is the weight fraction of surfactant, ρ_1 and ρ_2 are the densities of surfactant and water layer, respectively, and d_1 is the thickness of surfactant layer. The Bragg spacing obtained from both X-ray and UV diffraction increases with decreasing concentration, c, of ASA and is proportional to (1-c)/c, and two lines from different methods are shown to be identical. These results strongly suggest that the iridescent dilute solutions also consist of lamellar liquid crystals having extremely long spacing distance as above and the iridescent color appears by the interference of reflected light by single bilayer membranes of ASA.

Introduction

The iridescent phenomena by ordered structures of monodisperse latexes are well-known and extensively studied,¹⁻⁷ after the pioneering works for Schiller layers.^{8,9} Similar iridescence has been recently found also in the dilute aqueous solutions of some kinds of surfactant and surfactant mixtures.¹⁰⁻¹² This coloration phenomenon of surfactant solutions shows some characteristic features as follows: (1) iridescent color appears only in narrow surfactant concentration range of about 1-2 wt %; (2) the color has beautiful luster; (3) the color changes with concentration of surfactant and/or the angle between the directions of light irradiation and an observer; (4) the color of transmitted light is complementary to that of reflected light; (5) the color disappears by strong agitation such as sonication, etc. These facts may suggest that these colorations are due to the diffraction phenomena of visible light by the ordered structure of colloids in the solutions. This model of solution structure implies that the periodical distance of the structure is of the order of submicrometer (half of the wavelength of visible light), which is a surprisingly long distance from the standpoint of molecular interactions. We have studied the structure of aqueous solutions of alkenylsuccinic acid (ASA) which is newly found to show the above iridescence.

Useful techniques, however, are not established at all to observe the raw structure of solution having a spacing in the range of submicrometer. Electron microscope is a powerful tool to observe the structure of this region, but the specimens must be seriously damaged by the treatment of freezing and/or staining. Actually, the iridescent color vanished even by the rapid cooling to liquid nitrogen temperature, so that this approach is not appropriate to study the structure of iridescent solutions. We have tried to apply

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the UV light diffraction method using a nitrogen gas laser ($\lambda =$ 337.1 nm). N_2 gas laser is a useful light source not only for its strong intensity but also for variability of wavelength when coupled with a dye laser.

Experimental Section

Alkenylsuccinic acids (C_nASA 's; CH_3 -(CH_2)_{n-4}-CH= $CHCH_2CH(COOH)CH_2(COOH)$, n = 12-18) were prepared from the corresponding alkenylsuccinic anhydrides by hydrolysis with concentrated NaOH solutions at 80 °C under strong stirring. Alkenylsuccinic anhydrides were of guaranteed reagent grade and were purchased from Tokyo Kasei Ltd. The acid form of ASA was precipitated by lowering the solution pH to 2.0. The crude ASA samples were washed thoroughly by pure water more than 3 times, and then recrystallized twice from acetone. The purity of used ASA was checked to be more than 99% by gas chromatography. The contamination of sodium ion was shown to be less than 30 ppm from atomic absorption. Deionized and distilled water was used to make the sample solutions.

Iridescent solutions were prepared by dissolving the appropriate amount of ASA in water at 80 °C and kept standing for several hours at 70-80 °C (sufficiently higher than the coagel-liquid crystalline transition temperature) in order to obtain the full brightness of color. The wavelength and the intensity of iridescent color are more reproducible when they were once frozen to coagel phase. All measurements were, therefore, carried out after this cooling treatment. The sample solutions of higher concentrations were prepared in the same way as the above.

The optical system was set up for UV diffraction experiments. Nitrogen gas laser LN 100 (Photochemical Research Associates Inc.) with the wavelength of 337.1 nm was used as a light source and was operated with the spark gap voltage of 17 kV and a repetition rate of about 10 pulses/s. Preliminary experiments were performed with visible light using the dye laser LN102 with a dye type 2A500. Diffraction patterns were recorded on Fuji FG films set in a cylindrical film cassette in which the sample to film distance was 25 mm. The inside and outside diameters of quartz sample holder were 3 and 8 mm, respectively, and the front of the outer surface of the cell was cut flatly to avoid the streak reflection of direct beam. The temperature of the cell was controlled by linear heater coiled on to the cell holder, as illustrated in Figure 1. Refractive index correction of water was made when the periodical spacings were calculated from the UV diffraction patterns.

The color of the solution can be measured quantitatively by the reflection spectrum. The reflection spectra were measured from the reflected light to normal direction with a CMS 1200 fast spectrocolorimetric photometer designed by Murakami Color

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Figure 1. Illustration of sample cell and film cassette. The front of the quartz cell is cut flatly as shaded. Most of the reflected direct beam from the front face of the cell passes through the same hole as the incident beam.



Figure 2. DSC thermograms of nonannealed (a) and annealed (b) samples of the 10 wt % C1₆ASA solution.

Research Lab. Specimens were put in a cylindrical glass cell of 10 mm diameter and were kept constant at 70 °C.

The small-angle X-ray scattering (SAXS) experiments were carried out with a Rigaku rotating anode fine-focus X-ray generator (Type Rotaflex RU 200) equipped with a copper target. Tube voltage and tube current were 50 kV and 60 mA, respectively. The camera used was a Rigaku small-angle-scattering camera with two 0.2 or 0.15 mm diameter pin hole slits. The specimen to film distance was varied from 220 to 270 mm. Diffraction patterns were recorded on the Fuji industrial X-ray films, IX-400. Exposure time of 6 to more than 100 h was necessary depending upon the surfactant concentration of the sample. The specimens were put into a sealed glass capillary and temperature was kept constant at 70 °C during the whole SAXS measurements.

Differential scanning calorimetry (DSC) was carried out with a SSC 540 DSC apparatus designed by Seiko Instruments & Electronics Ltd. The sample solution was put into a 70 or 15 μ L silver capsule and heated at the rate of 0.6 °C/min.

Results

1. Phase Diagram of $C_{16}ASA$ -Water System. Figure 2 shows the typical examples of DSC thermograms for the $C_{16}ASA$ -water systems. The endothermic peak at 34 °C due to the gel to liquid crystalline transition appears only when heating starts just after rapid cooling. When annealed for enough time (i.e., ~10 h) this peak disappears, and only one peak at 63 °C due to the coagel to liquid crystalline transition is observed. These results indicate that the gel phase obtained in the rapid cooling process is a metastable phase.¹³ The phase diagram of $C_{16}ASA$ -water system obtained from the DSC measurements is shown in Figure 3. Over a wide range of surfactant concentrations (from less than 0.5 wt % to more than 70 wt %), the system has liquid crystalline phase, metastable gel phase, and coagel (hydrated crystalline) phase, and

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Figure 3. Phase diagram of the $C_{16}ASA$ -water system. The closed circles (\bullet) indicate the transition points of the nonannealed samples and the open circles (\bullet) the annealed ones. The shaded part in the diagram indicates the iridescent region. The temperatures of coagel-liquid crystalline phase transition of annealed samples are slightly higher than that of nonannealed ones by 2-3 °C.



Figure 4. Reflection spectra of visible light from iridescent solutions. Ordinate indicates the reflectivity relative to that of titanium oxide white board.

the transition temperatures are almost constant at about 63 °C (coagel to liquid crystalline phase transition temperature, T_{c_1}) and at 34 °C (metastable gel to liquid crystalline phase transition temperature, T_{c_2}). Similarly to the case of other hydrophobic surfactants¹⁴ such as dialkyldimethylammonium salts, ¹⁵ lecithin, ¹⁶ etc., aqueous solutions of C₁₆ASA maintain liquid crystalline phase even in the concentration of less than 0.5 wt %. As indicated in the figure by shading, the region of iridescent solutions is very narrow in the phase diagram of C₁₆ASA (1–2 wt % and T > 63 °C(T_{c_1})). When cooled quickly, the iridescent color of the solutions maintains until 34 °C, and changes drastically to the color of shorter wavelength at 34 °C (= T_{c_2}).

2. Observation of the Iridescent Solutions. The C₁₆ASA solutions exhibit bright iridescent colors from red to violet with increasing concentration of the surfactant from 1.2 to 2.0 wt %. Below 0.6 wt % or above 2.0 wt %, the solution is colorless and turbid or transparent and shows opaque and weak violet color at 0.7-1.0 wt %. Figure 4 shows the reflection spectra of C₁₆ASA solutions. The wavelength of maximum reflection, λ_{max} , moves to a shorter wavelength (blue shift) with increasing concentration of the surfactant. The λ_{max} of the red solution (1.2 wt %) is about 670 nm, of the green solution (1.5 wt %) about 550 nm, and of the violet solution (2.0 wt %) about 400 nm.

Iridescent color also changes with observing direction against the irradiating direction of the white light. The color shifts to the blue side as the angle between direct beam and reflected light increases. These facts strongly indicate that the coloration phenomenon obeys diffraction theory described by Bragg's equation, $2d \sin \theta = n\lambda$.

3. UV Diffraction. Some examples of UV diffraction patterns of $C_{16}ASA$ solutions are shown in Figure 5. Strong but broad Bragg reflections of first order were observed. The spacings are calculated to be 245 and 170 nm for the solutions of 1.2 and 1.8

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Figure 5. UV diffraction patterns from the 1.2 (a), 1.8 (b), and preserved 1.5 wt % (c) solutions. Exposure time was 1 s. The center hole is used for the light path of the direct UV beam through the specimen. Streaks imaged on both sides of films are due to the reflection from the face of cylindrical cell could not be avoided even by the flat cut of the cell front.

wt %, respectively. The Bragg distance calculated from the UV diffraction patterns are exactly the same as that from normal reflection spectra. A diffraction pattern of 1.5 wt % solution preserved for 1 year at room temperature is shown in Figure 5c. In this case, a mixed $C_{16}ASA$ sample with another $C_{16}ASA$ derivative (monoamide with glycine) having branched hydrocarbon chain is used to depress the transition temperature, T_{c} , below room temperature. One can see easily from the figure that the Bragg reflections become markedly sharpened and anisotropic. This sharpening of the reflection pattern means that the size of the ordered region and/or the degree of order in each region are grown during preservation. Actually, in this preserved solution, many of crystallike domains of visible size are observed to be oriented to form flow patterns. Bragg reflections of higher order cannot be observed even when the spacing distance between periodic units is long enough to expect the second-order reflection for the UV light, probably because of the considerable extent of disorder in the periodic structure. Consequently, the detailed structure of iridescent solutions cannot be determined unfortunately.

4. X-ray Diffraction. The X-ray diffraction measurements were made for the C₁₆ASA solutions of 2-60 wt %. Figure 6 shows the diffraction patterns from the 10 and 30 wt % solutions. One series of Bragg reflections corresponding to the spacing with an interrelation of 1:1/2:1/3:1/4 and 1:1/2 was obtained from the 10 and 30 wt % solutions, respectively, which indicates a lamellar structure with interplanar spacing, d, of 28.5 and 10.4 nm, respectively. In the whole concentration range of 10-60 wt %, Bragg reflections indicating the lamellar phase are obtained and the spacings are varied continuously from 28.5 to 6.8 nm. Strong anisotropy of diffraction patterns observed in each solution of different concentration indicates the lamellar leaflets are oriented parallel to the axis of a glass capillary. In dilute region from 2 to 5 wt %, neither Bragg reflection nor small-angle scattering pattern was observed even for enough exposure time (~ 100 h). The interplanar spacings of these dilute solutions are too large for the resolution of the SAXS camera (\sim 80 nm) to give Bragg reflections.



Figure 6. X-ray diffraction patterns from the 10 (a) and 30 (b) wt % $C_{16}ASA$. Sample to film distances were 270 and 220 mm and exposure time 48 and 73 h for the 10 and 30 wt % solutions, respectively. Numbers in the photographs indicate the order of Bragg reflection due to lamellar liquid crystal.

Discussion

As mentioned previously, detailed information on the structure of iridescent solutions cannot be obtained from the UV diffraction experiments, since the higher order reflections are not observed. The structures of concentrated solutions, on the other hand, are determined to be a lamellar liquid crystal from the X-ray diffraction measurements. In order to examine whether the lamellar structure is maintained also in the dilute solutions, a simple model is adopted. If the lamellar structure is uniformly formed in the whole space of the solutions, the interplanar spacing, d, can be related to the weight fraction of surfactant, c, as¹⁷

$$d = \left(\frac{(1-c)}{c} \frac{\rho_1}{\rho_2} + 1\right) d_1$$
 (1)

where ρ_1 and ρ_2 are the density of surfactant and water layer, respectively, and d_1 is the thickness of surfactant layers. The square (d^2) or cubic (d^3) of interplanar spacing can be shown by the same manner to be proportional to the value of (1-c)/c in the case of two- or three-dimensional periodicity of the regular structure (two-dimensional hexagonal (middle) phase of threedimensional cubic phase, etc.). The plot of interplanar spacing, d, against (1 - c)/c is shown in Figure 7. Both plots obtained from UV diffraction of the dilute solutions (1-2.2 wt %) and from X-ray diffraction of the concentrated solutions (10-60 wt %) are linearly related to (1-c)/c, and are even identical. Furthermore, the thickness of surfactant layer can be estimated from the yintercept of this plot to be 4.1 nm. These results strongly suggest that the iridescent solutions also consist of the lamellar liquid crystalline phase constructed with the single bilayer membranes of ASA, as schematically illustrated in Figure 8.

The above conclusion is somewhat surprising, because the structure model has the extremely long spacing of the order of

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Figure 7. Plot of the interplanar spacing, d, against (1 - c)/c. Closed circles (\bullet) were obtained from X-ray diffraction, double circles (\bullet) from UV diffraction, and open circles (\bullet) from spectra of reflected light to normal direction. Refractive index corrections of water were made in the calculation of d from UV and visible light. In the shaded region, the spacing of the periodic structure can reflect the visible light to normal direction in water, and the solutions are iridescent.



Figure 8. The structural model of the 1.2 wt % iridescent solution. The interplanar distance and the thickness of surfactant layer are scaled.

submicrometer which is several tens of times longer than the thickness of the single bilayer itself. To substantiate in another way that the unit structure is single bilayer, the carbon-number dependence of the spacing in the iridescent aqueous solutions of ASA was investigated. Equation 1 can be rewritten as eq 2 including carbon number of ASA and the number of bilayer membranes in the unit structure

$$d = 2m \left(\frac{(1-c)}{c} \frac{\rho_1}{\rho_2} + 1 \right) (l_1 g_1 N + l_2 g_2)$$
(2)

where *m* is the number of bilayer membranes, l_1 and l_2 are the maximum lengths of carbon chain per unit C-C bond (0.127 nm) and hydrophilic head group (~0.5 nm), respectively, along the normal direction to the lamellar leaflets, and g_1 and g_2 are the



Figure 9. Interplanar spacing, d, of the 1.2 and 1.4 wt % solutions as a function of the carbon number of alkenyl chain of ASA molecules.

correction factors of thermal motion for l_1 and l_2 , respectively. Figure 9 shows the plots of interplanar spacing d vs carbon number N for the 1.2 and 1.4 wt % solutions. Two series of plots for different concentrations give the value of ρ_1/ρ_2 and mg_1 ; both are about 0.7. The value of 0.7 for ρ_1/ρ_2 is in good agreement with the result from Figure 7. As g_1 can be estimated to be 0.7–0.8 above T_{c} ,¹⁸ m must be unity; i.e., the membrane of ASA is single bilayer.

According to the above structural model, the iridescent color appears by the interference of reflected light by the single bilayer membranes of ASA. Accordingly, the color (the wavelength in the maximum of reflection spectrum) of the solution is determined by the interplanar spacing which is a function of three factors, the ratio of weight fraction, (1-c)/c, density, ρ_1 , and the thickness, d_1 , of surfactant layer. The drastic change of iridescent color with gelation may be also understood by the change of density, ρ_1 , and the thickness of surfactant layer, d_1 . The blue shift of the reflection maximum may indicate that the effect of d_1 decrease is superior to that of ρ_1 increase. If we use a surfactant having similar density and molecular length, their solutions should show iridescent phenomena in the same concentration range from 1 wt % ((1 c)/c = 100) to 2 wt % ((1 - c)/c = 50) as understood from Figure 7, when the surfactant is sufficiently hydrophobic so as to maintain the lamellar liquid crystalline phase even in such a dilute region. To obtain the iridescent solutions, the spacing, d, must increase continuously in direct proportion to (1-c)/c until the dilute region of 1 wt % or less; in other words, the lamellar structure can be simply swelled by water up to about 100 times of surfactant by weight. This fact seems to indicate that only the repulsive interaction is present between two lamellar leaflets to stabilize the periodic structure of ASA solutions.

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