VEM Observation of Molecular Assemblies in Iridescent Surfactant Solutions

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Aqueous solutions of alkyldimethylamine oxides ($C_n DAO$, n = 14, 16, 18), hexadecenesuccinic acid ($C_{16}SA$), and diglycerol isostearyl ether ($C_{18}DGE$) were observed with the video-enhanced differential interference contrast microscope (VEM). Flat plate-like assemblies were seen in iridescent solutions of $C_{16}DAO$ and $C_{18}DAO$, while globular vesicle-like assemblies were formed in iridescent solutions of $C_{14}DAO$ mixed with hexanol and decane, $C_{16}SA$, and $C_{18}DGE$. Similar assemblies were also observed in the dilutions of iridescent solutions which displayed no iridescence. Whereas plate-like assemblies of $C_{16}DAO$ disappeared above 30°C, assemblies of $C_{18}DAO$ changed above 50°C from plate-like to globular. The relation of the iridescence to the molecular assemblies in surfactant solutions is discussed. © 1991 Academic Press, Inc.

INTRODUCTION

The phenomenon of dilute aqueous solutions of surfactants presenting iridescent colors has been found in several systems. These include polyoxyethylene oleyl ether (POE) mixed with a small amount of sodium dodecyl sulfate (SDS) (1), diglycerol alkyl ethers (2), and alkenesuccinic acids (3). The color was observed at dilute surfactant concentrations between 1 and 4%, and it varied from red to violet as the surfactant concentration increased. This iridescence was explained by the interference of light arising from the Bragg reflection between multilamellar layers (1-3).

Lamellar layers in an iridescent solution of POE mixed with SDS were observed on a scanning electron microscope (1). Also, the electron micrograph for an iridescent solution of C_{18} DGE suggested the existence of lamellar layers in a particle ca. 10 μ m in diameter (2). The distance between the layers increased from 200 to 400 nm as the concentration of C_{18} DGE decreased.

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Iridescent solutions of $C_{16}DAO$ and $C_{18}DAO$ were obtained at surfactant concentrations of 0.3-2 wt% at temperatures lower than 23°C for $C_{16}DAO$ and 46°C for $C_{18}DAO$ (4). Although an aqueous solution of $C_{14}DAO$ did not display any iridescence (4), the addition of hexanol and decane induced iridescence (5).

In this paper, we observed the iridescent solutions with the video-enhanced differential interference contrast microscope (VEM). Molecular assemblies were seen in all the solutions, although assemblies of $C_{16}DAO$ and $C_{18}DAO$ had different shapes than those of the other surfactants. The origin of the occurrence of iridescence is discussed and compared for two types of surfactant solutions.

EXPERIMENTAL

Samples of $C_n DAO$ (n = 14, 16, 18), $C_n H_{2n+1}N(CH_3)_2O$, and $C_{16}SA$, $C_{13}H_{27}CH$ ==CHCH₂CH(COOH)CH₂COOH, were the same as previously used (4, 6, 7). $C_{18}DGE$, $C_{18}H_{37}$ OCH₂ CH (CH₂ OCH₃) OCH₂ CH -(CH₂OH)OH, was a generous gift from Drs.

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0021-9797/91 \$3.00 Copyright © 1991 by Academic Press, Inc. All rights of reproduction in any form reserved. Y. Suzuki and H. Tsutsumi of Kao Corporation, Inc., Tokyo. Hexanol and decane were commercial products.

An aqueous solution of $C_{14}DAO$ was mixed with a small quantity of hexanol and decane. The concentrations of $C_{14}DAO$, hexanol, and decane in the solution were 20, 65, and 10 m*M*, respectively. The mixed solution yielded the iridescent color at room temperature. The other surfactants were dissolved in water at high temperature and kept at the desired temperature. Aqueous solutions of $C_{16}DAO$ and $C_{18}DAO$ at 0.5×10^{-2} g cm⁻³ and of $C_{18}DGE$ at 1.5×10^{-2} g cm⁻³ were iridescent at room temperature. The iridescent color for an aqueous solution of $C_{16}SA$ at 10^{-2} g cm⁻³ was obtained at temperatures above $63^{\circ}C$.

Visual observation of the molecular assemblies was carried out on the VEM (8-10). The microscope was equipped with the differential interference contrast optic (Nomarski prism). attached to a video camera, and cabled to a real-time digital image processing computer system. Therefore, low-contrast objects were enhanced and distinguished from the background solution, resulting in improved image quality. The assemblies were observed through a Nikon DIC objective, relayed to the Dage Model NC 68 television camera by a Nikon zoom lens, and photographed from the video monitor using a Polaroid camera. Measurements at high temperature or of temperature dependence were performed using an indiumtin oxide coated conductive microscope slide. The temperature of the slide was adjusted by the applied voltage, and it was measured by a thermocouple connected to a digital thermometer.

RESULTS

Aqueous Solution of C16DAO

Figure 1a shows a VEM photograph for an iridescent $C_{16}DAO$ solution of 0.53×10^{-2} g cm⁻³ at room temperature. Large molecular assemblies with various shapes and sizes co-existed with small particles which were less than a micron in diameter. The large assem-

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blies were very flat or plate-like, and they sometimes enclosed a large number of small particles. They were 5-50 μ m across and assumed many shapes: round, hexagonal, pointed, etc. The small particles were always moving around in and out of assemblies.

When an iridescent solution of C₁₆DAO was heated on the conductive microscope slide, temperature-dependent changes were observed, as shown in Fig. 2. In this experiment, the temperature was raised from room temperature to 42°C within a period of 0 to 5 min. Assemblies began to melt with heating: almost all of the assemblies melted after 60 s. At 90 s. plate-like assemblies disappeared but a globular assembly entrapping some smaller assemblies still existed. Although the globular assembly increased in size until 274 s. it started to disappear afterward: the globular assembly broke first and, in turn, the capsulated smaller assemblies broke. The destruction of the globular assembly and the encapsulated smaller assemblies was finished within 5 s. As the solution was cooled from 42°C to room temperature, the plate-like assemblies reappeared below 30°C.

Aqueous Solutions of $C_{18}DAO$

The aqueous $C_{18}DAO$ solution of 0.51 $\times 10^{-2}$ g cm⁻³ and its $\frac{1}{10}$ dilution were observed with the VEM at room temperature, and the micrographs are shown in Figs. 1c and 1b. In the $\frac{1}{10}$ dilution which displayed no iridescent color, large plate-like assemblies of 5–20 μ m were observed along with small particles, similar to the iridescent solution of C₁₆DAO. Assemblies were separated from each other and were pointed like crushed pieces.

On the other hand, plate-like assemblies in an iridescent C_{18} DAO solution of 0.51×10^{-2} g cm⁻³ were overlapped and it was not easy to find individual assemblies. While some small particles moved around in and out of the assemblies, others appeared from the edge of an assembly.

A freshly prepared solution of 10 wt% C_{18} DAO was not iridescent but was birefrin-



FIG. 1. VEM photographs of aqueous solutions of C_{16} DAO and C_{18} DAO at room temperature. (a) C_{16} DAO at 0.53×10^{-2} g cm⁻³; (b) $\frac{1}{10}$ dilution of (c); (c) C_{18} DAO at 0.51×10^{-2} g cm⁻³; (d) C_{18} DAO at 10 wt%. The bar represents 10 μ m.

gent. Individual plate-like assemblies were no longer distinguishable, but a pile of them was observed, as seen in Fig. 1d.

Figure 3 represents the temperature dependence for the $\frac{1}{10}$ dilution of the aqueous $C_{18}DAO$ solution at 0.51×10^{-2} g cm⁻³. The

temperature was increased from room temperature to 50°C during a period of 0 to 8 min. Plate-like assemblies started melting at 43°C after 170 s and vanished at 330 s. Coexisting small particles moved vigorously at temperatures above 44° C.



FIG. 2. VEM photographs of the temperature dependence of assemblies in an aqueous $C_{16}DAO$ solution at 0.53×10^{-2} g cm⁻³. The temperature was increased from room temperature to 42°C within a period of 0 to 5 min. Time (s): (a) 0; (b) 10; (c) 60; (d) 90; (e) 274; (f) 276; (g) 277; (h) 278; (i) 279. The bar represents 10 μ m.

IRIDESCENT SURFACTANT SOLUTIONS



FIG. 3. VEM photographs of the temperature dependence of assemblies in a $\frac{1}{10}$ dilution of an aqueous C₁₈DAO solution at 0.51 × 10⁻² g cm⁻³. The temperature was increased from room temperature to 50°C within a period of 0 to 8 min. Time (s): (a) 0; (b) 170; (c) 240; (d) 300; (e) 330; (f) 470. The bar represents 10 μ m.

As the plate-like assemblies melted, they changed into globular assemblies. The globular assemblies grew to $5-10 \mu m$ in diameter as the plate-like assemblies melted. Some of the assemblies enclosed small assemblies or particles, but others did not. At 48°C, all the plate-like assemblies had disappeared, and a large number of globular assemblies now filled the solution. They flowed due to the temperature

gradient on the conductive microscope slide, as seen in Figs. 3d-3f.

VEM photographs of various types of assemblies formed at 50-55°C in the $\frac{1}{10}$ dilution are shown in Fig. 4. The relatively huge assemblies of up to 100 μ m across coexisted with smaller assemblies and small particles. Larger assemblies entrapped smaller assemblies and/ or small particles. Although tubular assemblies



Fig. 4. VEM photographs of various types of assemblies formed at 50-55°C in a $\frac{1}{10}$ dilution of an aqueous C₁₈DAO solution at 0.51 × 10⁻² g cm⁻³. The bar represents 10 μ m.

were observed in the streaming specimen, they were not observed in the static specimen.

While cooling to room temperature after being heated to 55°C, the plate-like assemblies were regenerated and coexisted with the globular assemblies. After being kept overnight at room temperature, the specimen was full of plate-like assemblies only.

Fusion, Shrinkage and Destruction of Globular Assemblies

At high temperature, the globular assemblies fused, shrank, and were destroyed. Figure 5 shows micrographs which display the movement of assemblies in the $\frac{1}{10}$ dilution of the aqueous C₁₈DAO solution at 0.51×10^{-2} g cm⁻³ as the specimen was heated from 48 to 61°C. Two globular assemblies approached each other and began to fuse. After the fused part was broken, the resultant ellipsoidal assembly became spherical. The process was

over in a period of only 2 s. It may be noted that a capsulated smaller assembly seems to go through the membrane of the larger assembly, as seen in Fig. 5f.

As the temperature rose further, the shrinkage of assemblies was observed. In Figs. 5a-5j, a globular assembly on the left decreased to $\frac{1}{3}$ its diameter after 850 s which corresponds to an increase in temperature from 48 to 61°C. The destruction of globular assemblies was also instantaneous, as illustrated in Fig. 6. A smaller assembly marked by the arrow in a larger globular assembly vanished within 1 s.

Aqueous Solutions of $C_{14}DAO$ in the Presence of Hexanol and Decane

 $C_{14}DAO$, hexanol, and decane were dissolved in water with concentrations of 20, 65, and 10 m*M*, respectively. The solution was diluted to $\frac{1}{2}$, $\frac{1}{3}$, and $\frac{1}{4}$ with water. The undiluted solution presented the iridescent color,



FIG. 5. VEM photographs representing the fusion and shrinkage of globular assemblies in a $\frac{1}{10}$ dilution of an aqueous C₁₈DAO solution at 0.51 × 10⁻² g cm⁻³. The temperature was changed from 48 to 61°C within a period of 0 to 850 s. Time (s): (a) 33; (b) 33.5; (c) 34; (d) 34.5; (e) 35; (f) 67; (g) 69; (h) 310; (i) 550; (j) 850. The bar represents 10 μ m.



FIG. 6. VEM photographs representing the destruction of globular assemblies above 50°C in a $\frac{1}{10}$ dilution of an aqueous C₁₈DAO solution at 0.51 × 10⁻² g cm⁻³. Time (s): (a) 42; (b) 42.5; (c) 43. The bar represents 10 μ m.

while the dilutions did not display the color. VEM photographs at room temperature are given in Fig. 7.

Small globular assemblies with a diameter of ca. 5 μ m existed in all the dilutions. Al-

though the number of assemblies decreased with dilution, their size was maintained. In the concentrated iridescent solution, globular assemblies gathered closely together, and the structure of each assembly could not be elu-



FIG. 7. VEM photographs of aqueous solutions of C₁₄DAO in the presence of hexanol and decane at room temperature. (a) $\frac{1}{4}$ dilution of (d); (b) $\frac{1}{3}$ dilution of (d); (c) $\frac{1}{2}$ dilution of (d); (d) C₁₄DAO in the presence of hexanol and decane at 20, 65, and 10 mM, respectively. The bar represents 10 μ m.

cidated in detail. Tubular assemblies were temporarily formed in a streaming solution, as well as seen in aqueous C_{18} DAO solutions at high temperature. They were sometimes transformed into small particles. Even if the temperature of the solution was raised from room temperature to 50°C, globular assemblies of C_{14} DAO in the presence of hexanol and decane did not change significantly, although they moved around vigorously.

Aqueous Solutions of C₁₆SA

An aqueous solution of $C_{16}SA$ at 1.01 $\times 10^{-2}$ g cm⁻³ and its $\frac{1}{4}$ dilution were heated to 65–70°C. Figure 8 represents VEM photographs which were taken at high temperature. The micrographs are full of globular assemblies of various sizes, the maximum of which was ca. 20 μ m in diameter. The large assemblies in the undiluted iridescent solution seemed to be composed of a multilamellar layer structure, while in the $\frac{1}{4}$ dilution without the iridescent color there were globular assemblies which sometimes enclosed the smaller assemblies.

Aqueous Solutions of $C_{18}DGE$

Figure 9 shows VEM photographs of an iridescent C_{18} DGE solution of 1.53×10^{-2} g cm⁻³ and its noniridescent $\frac{1}{10}$ dilution at room temperature. Globular assemblies and small particles existed in the $\frac{1}{10}$ dilution. The globular assemblies had a diameter of less than 5 μ m. In the iridescent solution, globular assemblies were thickly aggregated and coexisted with tubular assemblies.

DISCUSSION

Aqueous C_{16} DAO solutions of 0.3–1.9 wt% were iridescent at temperatures below 23°C, turbid at 23–30°C, and transparent above 30°C (4). For aqueous C_{18} DAO solutions, the iridescent region was below 46°C at 0.3–2.2 wt%. The solutions were turbid at 46–49°C and transparent at higher temperature. A bright birefringent color was observed for aqueous C_{18} DAO solutions above 9 wt% and below 50°C. The iridescence changed from yellowish red to blue with an increase in the surfactant concentration.



FIG. 8. VEM photographs of aqueous solutions of C₁₆SA at 65–70°C. (a) $\frac{1}{4}$ dilution of (b); (b) C₁₆SA at 1.01 × 10⁻² g cm⁻³. The bar represents 10 μ m.



FIG. 9. VEM photographs of aqueous solutions of C₁₈DGE at room temperature. (a) $\frac{1}{10}$ dilution of (b); (b) C₁₈DGE at 1.53 × 10⁻² g cm⁻³. The bar represents 10 μ m.

In iridescent solutions and their dilutions, flat plate-like assemblies of $C_{16}DAO$ and $C_{18}DAO$ existed. While plate-like assemblies of $C_{18}DAO$ in the dilution without iridescent color were seen as individuals, those in the iridescent solution overlapped partly. In birefringent solutions, piles of plate-like assemblies were observed.

It has been suggested previously (1-3) that the iridescence is induced by the interference of light arising from the Bragg reflection between the multilamellar layers. Analogous interpretation is possible to the iridescent solutions of C₁₆DAO and C₁₈DAO.

In dilute solutions below 0.3 wt% the platelike assemblies exhibit no iridescence because the large quantity of water included between the flat plate-like layers may keep the distance greater than 400 nm. As the surfactant concentration increases, the distance between the layers decreases, owing to the narrowing of the water layers, from 400 to 200 nm, which is half the wavelengths of red and violet lights, respectively. Then the interference of visible light at 400–800 nm arising from the Bragg reflection between the layers in an assembly is visual. Thus, we can detect the iridescent colors from red to violet for aqueous solutions of $C_{16}DAO$ and $C_{18}DAO$ at 0.3–2 wt%. As increasing surfactant concentrations, the distance between the layers decreases to less than 200 nm and the iridescent color disappears.

At surfactant concentrations above 9 wt%, the overlapping of plate-like assemblies increases until each assembly was no longer recognized, a lamellar liquid crystal was formed in the solution, and birefringence occurred.

At the temperature where the iridescent color disappears, the plate-like assemblies began to melt, and they transformed into globular assemblies in turbid solutions. In the transparent region at high temperature, although assemblies disappeared in the aqueous $C_{16}DAO$ solution, the globular assemblies remained in the aqueous $C_{18}DAO$ solutions. The interference of visible light does not result from such globular assemblies, thus the iridescent color does not arise in the turbid and transparent regions.

Aqueous solutions of C_{14} DAO presented the iridescent color when hexanol and decane were added at appropriate proportions (5). On the

other hand, the aqueous $C_{16}SA$ solution of 1.2–2.0 wt% and the aqueous $C_{18}DGE$ solution of 1–2% were iridescent above 63°C and at room temperature, respectively (2, 3). When these iridescent solutions were diluted, the iridescence disappears, and the globular assemblies existed as individuals. Such situation of assemblies does not produce the interference of visible light. Since globular assemblies of $C_{14}DAO$, $C_{16}SA$, and $C_{18}DGE$ are very concentrated in iridescent solutions, the information about individual assembly structure is poor.

It may be noted that the VEM images of globular assemblies of C_nDAO , $C_{16}SA$, and $C_{18}DGE$ are very similar to those of the cationic and anionic double-chained surfactants (8–10). Moreover, large globular assemblies of $C_{16}SA$ in an iridescent solution were composed of multilamellar-layer structure. In addition, the formation of lamellar layers was previously certified by an electron-microscopic examination for iridescent solutions of POE mixed with SDS and of $C_{18}DGE$ (1, 2). Therefore, globular assemblies of $C_{n}DAO$, $C_{16}SA$, and $C_{18}DGE$ may be vesicles.

Since such layers of vesicle-like assemblies are arranged like a lamellar liquid crystal and transform to lamellar liquid crystal, the solutions exhibit birefringence in addition to iridescence. Then, in iridescent solutions, the interference of reflected light between multilamellar layers is the probable origin of the iridescence, as already suggested (1-3). Concerning the globular assemblies of C₁₄DAO, they may be a microemulsion because they are formed in the mixed solution with hexanol and decane, although this cannot be demonstrated in the VEM observation.

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