LETTERS TO THE EDITOR

Electron Microscopic Observation of Molecular Assemblies in Iridescent Surfactant Solutions

Aqueous solutions of octadecyldimethylamine oxide (C_{18}DAO), diglycerol isostearyl ether (C_{18}DGE), and tetradecyldimethylamine oxide (C_{14}DAO)/hexanol/decane were observed by transmission electron microscopy. While plate-like assemblies, unilamellar vesicles, or globular microemulsions are formed in dilute solutions of C_{18}DAO, C_{18}DGE, or C_{14}DAO/hexanol/decane, multilamellar layers, multilamellar vesicles, or multilamellar microemulsions, respectively, exist in their iridescent solutions. On the other hand, lamellar liquid crystal is formed in concentrated solutions of C_{18}DAO and C_{18}DGE.

An iridescence phenomenon has been observed for aqueous surfactant solutions of 1–4% surfactant concentrations (1–4) and for aqueous solutions of amine oxide surfactants (C_nDAO) mixed with organic media (5–7). The iridescent colors changed with surfactant concentrations and illumination angles.

Recently, video-enhanced differential interference contrast microscopic (VEM) observations were carried out for iridescent surfactant solutions (8). Globular vesicle-like assemblies existed densely in the iridescent solutions of diglycerol isostearyl ether (C_{18}DGE), hexadecenesuccinic acid (C_{16}SA), and tetradecyldimethylamine oxide (C_{14}DAO) mixed with hexanol and decane. On the other hand, flat plate-like assemblies, which were stacked, were observed in the iridescent solutions of hexadecyl- and octadecyldimethylamine oxides (C_{16}DAO, C_{18}DAO).

In this paper, we investigate aqueous surfactant solutions by transmission electron microscopy (TEM) and clarify the fine structures of molecular assemblies in iridescent solutions and the concentration dependence of the assembly structure.

Samples of C_nDAO (n = 14, 18) and C_{18}DGE were the same as previously used (8). C_{18}DGE was a generous gift from Drs. Y. Suzuki and H. Tsutsumi of Kao Corporation, Inc., Tokyo. Hexanol and decane are commercial products.

Solutions were prepared at room temperature (~25°C) as previously described (8). The electron microscopic observation was carried out on a Hitachi H-800 electron microscope. The replica films were prepared on a freeze fracture apparatus, Balzers BAF 400, according to the freeze fracture method (9). A droplet of solution for freeze fracture was rapidly vitrified in liquid freon at its freezing point in order to avoid contamination by artifacts of the freezing process.

Figure 1 shows electron micrographs of aqueous C_{18}DAO solutions. The images of the multilamellar layer structure with 200 ~ 300 nm separation distance are observed in an iridescent 1% solution, as seen in Fig. 1b. Such layer structure is observable even in a 10 wt% solution which displays birefringence but no iridescence (Fig. 1c), although the separation between layers (~50 nm) is shorter than that in an iridescent solution. On the other hand, Fig. 1a reveals the existence of plate-like assemblies with different sizes and shapes in a 1/10 dilution of iridescent solution. These may be fragments of lamellar layers.

Electron micrographs of aqueous C_{18}DGE solutions are also given in Fig. 1. A photograph from an iridescent 1.5% solution presents vesicular images with multilamellar layers at separation distance more than 170 nm and with various diameters below 9 μm (Fig. 1e). The vesicles diminish in number with increasing surfactant concentration, and the multilamellar layer liquid crystal develops. In a birefringent 4% solution, a small number of vesicles coexist with abundant lamellar layers of ~160 nm separation distance (Fig. 1f). The disordered texture in Fig. 1f may be the purturbed structure of lamellar layers. The multilamellar layers are not observed in a 1/10 dilution of iridescent solution, but unilamellar vesicles exist in it (Fig. 1d). The vesicles have various diameters below 2.5 μm, and the larger vesicles enclose small ones.

An iridescent C_{14}DAO solution was prepared at the mixing ratio of 30 mM C_{14}DAO:60 mM hexanol:60 mM decane. As shown in Fig. 2a, an electron micrograph from a 1/3 dilution of iridescent solution presents the images of globular assemblies with 25 ~ 250 nm diameter which may be globular microemulsions or unilamellar vesicles. In an iridescent solution, multilamellar assemblies (microemulsions) with 400 ~ 500 nm separation of layers coexist with globular microemulsions and/or unilamellar vesicles some of which enclose small assemblies (Fig. 2b). It should be noted that the lamellar layers oscillate more than those of C_{18}DAO and C_{18}DGE do. This suggests that the lamellar layers including cosurfactant (hexanol) and oil (decane) are more liquid-like than those without cosurfactant and oil.

The concentration dependence of the assembly con-

0021-9797/92 $5.00

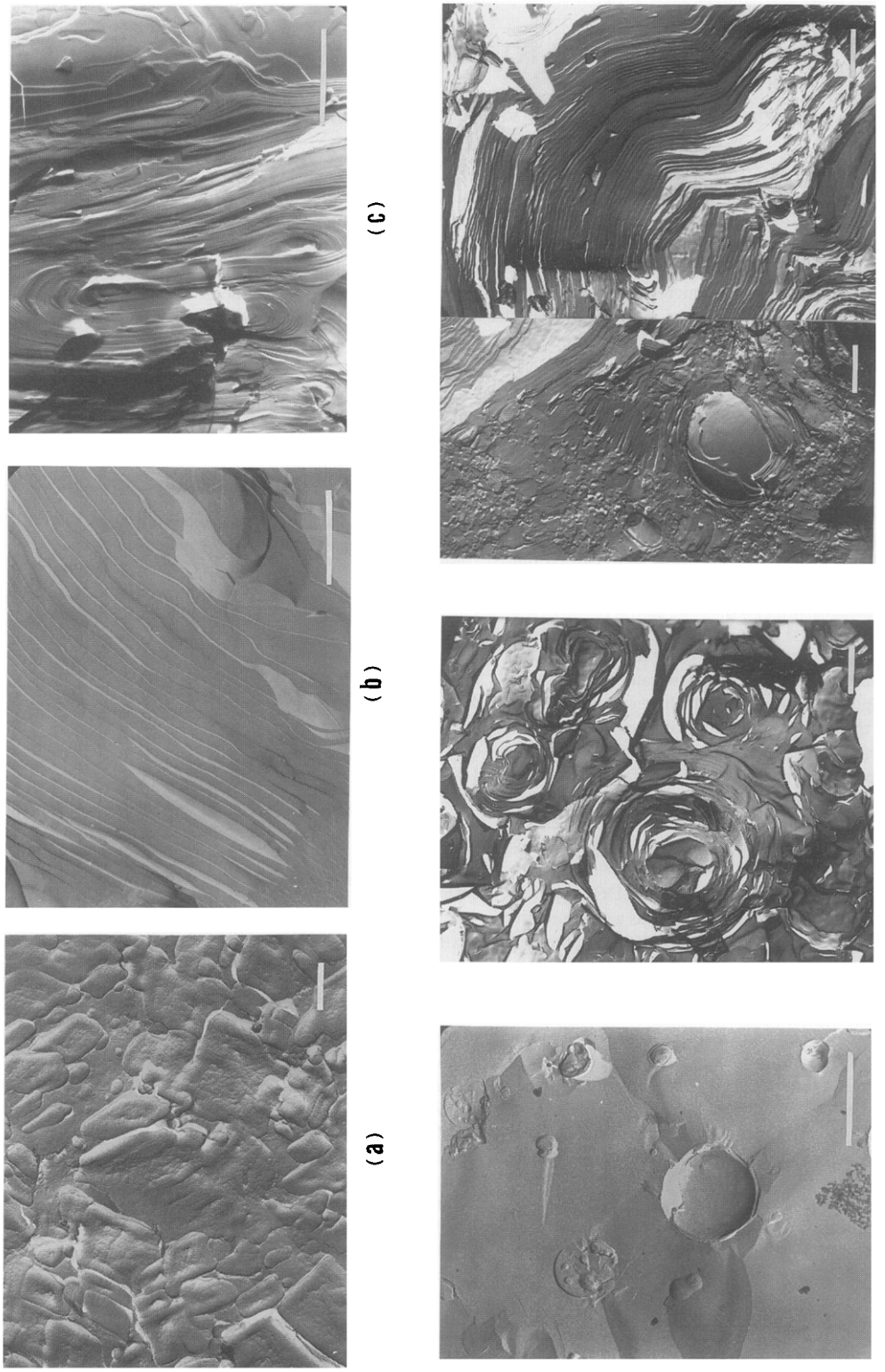

FIG. 1. TEM photographs of aqueous solutions of C_{18}DAO and C_{18}DGE. (a) 1/10 dilution of (b); (b) 1% C_{18}DAO; (c) 10 wt% C_{18}DAO; (d) 1/10 dilution of (e); (e) 1.5% C_{18}DGE; (f) 4% C_{18}DGE. The bars represent 2 μm.

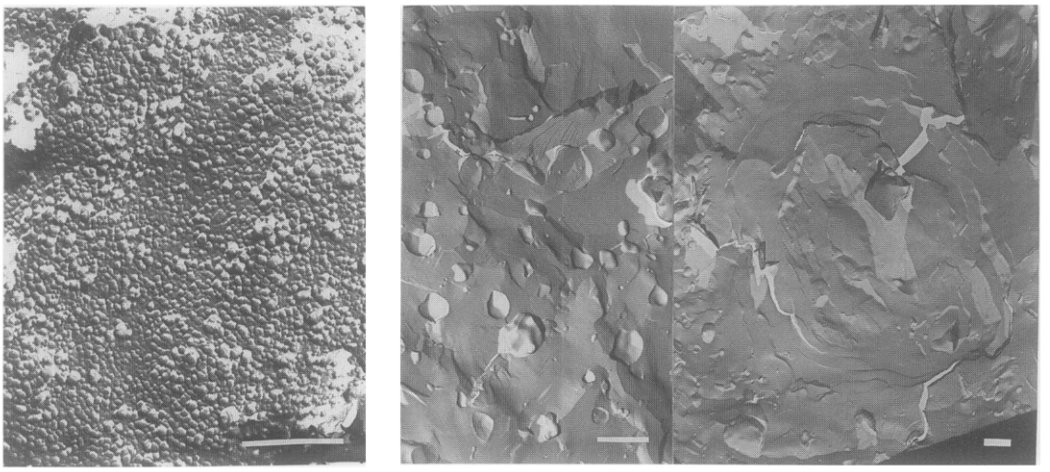

FIG. 2. TEM photographs of an aqueous solution of 30 mM C_{14}DAO mixed with 60 mM hexanol and 60 mM decane (b) and its 1/3 dilution (a). The bars represent 1 μm.

struction is schematically illustrated for each surfactant solution in Fig. 3. While plate-like assemblies, unilamellar vesicles, or globular microemulsions are formed in dilute surfactant solutions without iridescence, multilamellar layers, multilamellar vesicles, or multilamellar microemulsions are observed in iridescent solutions of C_{18}DAO, C_{18}DGE, or C_{14}DAO/hexanol/decane, respectively. On the other hand, lamellar liquid crystal is constructed in

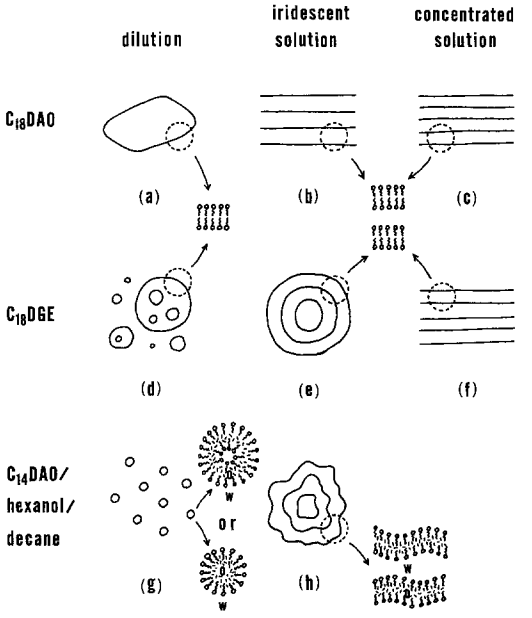

FIG. 3. Schematic representation of the assemblies formed in aqueous solutions of C_{18}DAO, C_{18}DGE, and C_{14}DAO/hexanol/decane at different concentrations. (a) Plate-like assemblies; (b) multilamellar layers; (c) lamellar liquid crystal; (d) unilamellar vesicles; (e) multilamellar vesicles; (f) lamellar liquid crystal; (g) globular microemulsions or unilamellar vesicles; and (h) multilamellar microemulsions.

birefringent concentrated solutions of C_{18}DAO and C_{18}DGE. This aspect is consistent with that estimated from VEM (8). Moreover, it should be noted that the assembly construction of C_{18}DGE depending on surfactant concentration is similar to that of C_{16}SA at 60 ~ 70°C (8).

It is evident that the iridescence is induced by the formation of multilamellar layers, and the iridescence phenomenon can be explained as a result of the interference of light arising from the Bragg reflection between layers. Then the separation distance between lamellar layers must be 200 ~ 400 nm. The distances between layers in iridescent solutions of C_{18}DAO, C_{18}DGE, and C_{14}DAO/hexanol/decane satisfy this condition and are consistent with the iridescent colors green, blue, and red, respectively.

REFERENCES

1. Nagai, M., and Onishi, M., *J. Soc. Cosmet. Chem. Jpn.* **18,** 19 (1984).
2. Suzuki, Y., and Tsutsumi, H., *Yukagaku* **33,** 786 (1984).
3. Satoh, N., and Tsujii, K., *J. Phys. Chem.* **91,** 6629 (1987).
4. Imae, T., Sasaki, M., and Ikeda, S., *J. Colloid Interface Sci.* **131,** 601 (1989).
5. Thunig, C., Hoffmann, H., and Platz, G., *Prog. Colloid Polym. Sci.* **79,** 297 (1989).
6. Platz, G., Thunig, L., and Hoffmann, H., *Prog. Colloid Polym. Sci.* **83,** 167 (1990).
7. Baumann, J., Kalus, J., Hoffmann, H., Thunig, C., and Lindner, P., *Ber. Bunsenges. Phys. Chem.* **95,** 795 (1991).
8. Imae, T ., and Trend, B., *J. Colloid Interface Sci.* **145,** 207 (1991).
9. Deamer, D. W., *Methods Enzymol.* **32,** 45 (1974).

TOYOKO IMAE*,[1]
TOHRU IWAMOTO†

* *Department of Chemistry, Faculty of Science*
† *Equipment Center for Education and Research School of Medicine*
Nagoya University
Nagoya 464, Japan

Received January 17, 1992; accepted May 6, 1992

[1] To whom correspondence should be addressed.