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Micellar Aggregation Behavior of 11-Ferrocenylundecyl Polyoxyethylene Ether Surfactant in Water

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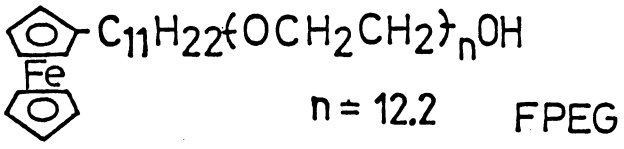
Micellar aggregate formed by 11-ferrocenylundecyl polyoxyethylene ether is investigated using four complementary techniques. The measurements show that the micelle is a spherical particle with the radius of 3.8 ± 0.3 nm and with the aggregation number of 62 on the average.

In recent years, a novel film-formation method, micellar disruption method (MD method), has been presented.[1] This method utilizes surfactants with a ferrocenyl moiety. Upon electrochemical oxidation of this moiety, the micelle incorporating a film-forming material is broken up into monomeric surfactants, and then the material is released from the micelle and deposits on the electrode surface, leading to the formation of the film. Thin films of azo-dye, viologen, and polymer compounds have been prepared using (11-ferrocenylundecyl)trimethylammonium bromide (FTMA) as the surfactant.[1] More recently, this finding has been extended to preparation of phthalocyanine thin films using (11-ferrocenylundecyl)polyoxyethylene ether (FPEG).[2] The latter surfactant is promising for preparing devices such as color filter, photoreceptor, etc.



Although there have been a few papers on electrochemical properties of the FPEG solution and its application to film-forming technology,[2,3] no study on its aggregation behaviors such as the aggregation number, the size, and the shape of the FPEG micelle has been reported, in spite of its technological importance. In the present study, dynamic and static modes of light scattering (DLS and SLS, respectively), small-angle X-ray scattering (SAXS), and transmission electron microscopic observation (TEM) were applied to the aqueous FPEG solution. The micellar size was obtained from light-scattering experiments[4] and

from a small-angle X-ray scattering experiment.[5] Direct observation of the FPEG micelle was carried out by the TEM method. On the basis of the results obtained by DLS, SLS, SAXS, and TEM measurements, the structure of the FPEG micelle is discussed.

The FPEG surfactant was purchased from Dojin Chemical Co. and used as received. The commercially available FPEG was composed of a series of homologous compounds when checked by a gas chromatography-mass spectrometry. The average number of the oxyethylene unit was found to be 12.2. The FPEG surfactant solution (2 mM - 40 mM) was prepared by dissolving FPEG in triply-distilled deionized water, and the solution was filtered through a 0.05 μm membrane filter five times. The radius of the micelle was determined by SAXS, DLS, and the TEM method. The shape and the aggregation number of the micelle were determined by SLS method. The light source for light scattering measurements was an Ohtsuka Denshi Model DLS-700 He-Ne laser operating at 633 nm where FPEG does not absorb light at all. The specimen for TEM measurement was prepared as follows: To 5 ml of FPEG surfactant solution (10 mM, 1 M = 1 mol dm^{-3}) a few drops of an aqueous OsO_4 solution (1 wt%) was added with stirring, and a drop of the solution was left on a Pt mesh, followed by drying to give a micelle with its hydrophilic group labeled with OsO_4. In order to obtain small angle scattering intensities from solutions, a position-sensitive proportional counter was adopted. The beam path between the X-ray source and the counter was evacuated to reduce scattering by air. The wavelength of X-ray used was 1.54 Å (CuK_α radiation).

The critical micelle concentration (cmc) of the FPEG surfactant was determined to be 13 μM from the surface tension-concentration profile,[6] in good agreement with that determined by the dye solubilization method,[6] 15 μM.

Table 1 shows the dependence of the radius of the micelle, r_H, measured by the DLS method on the FPEG concentration, [FPEG]. The micellar radius depended little on the concentration of FPEG and was almost constant at 3.8 ± 0.3 nm. The constancy of the r_H value suggests that there is little change in the micellar size and/or in the micellar shape with increasing the surfactant concentration.

Table 1. The effect of the FPEG concentration, [FPEG], on the radius of the FPEG micelle, r_H, determined by dynamic light scattering

[FPEG]/mM	r_H/nm
10	3.8
20	4.0
30	3.7
40	3.8
50	3.5

The mean radius of gyration of the FPEG micelle, r_G, was measured by the SAXS technique.[5] Figure 1 shows a logarithm of scattering intensity, I, of the FPEG micellar solution against the square of the scattering parameter, S, (Guinier's plot) where $S = 4\pi\sin\theta/\lambda$; 2θ is the scattering angle and λ is the wavelength. The unit for I is given by the number of X-ray induced electrons. The concentration of the FPEG surfactant was 40 mM. The micellar radius was determined from the slope, $-S^2 r_G/3$, of the line

(solid line in Fig. 1) fitted to experimental points. This Ln I - S profile suggests that there exists micelles with $r_G \approx$ 3.7 nm in the FPEG surfactant solution. This value compares well with the hydrodynamic radius, r_H, obtained by the DLS measurements.

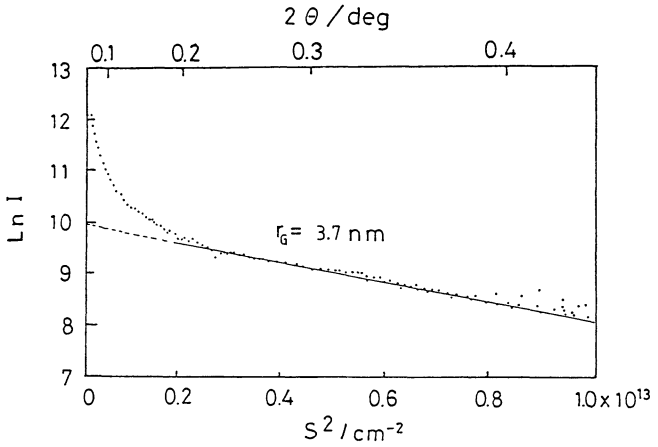


Fig. 1. Guinier plot of Ln I versus S^2 for the FPEG micellar solution.

The shape and the aggregation number of the FPEG micelle were investigated by the SLS technique. The weight average micellar weight, M_W, and the shape of the FPEG micelle were determined by measuring the angular and the concentration dependence of the light scattered by the micellar solutions. The procedure is to plot Kc/R_θ against $\sin^2(\theta/2) + Bc$ (Zimm plot),[4] where R_θ is the reduced intensity at the angle θ and c the concentration of the FPEG surfactant, B an arbitrary constant chosen for convenience. $K = 2\pi^2 n_0^2 (dn/dc)^2 / N\lambda^4$, where n_0 is the solvent refractive index, dn/dc the refractive index increment, N Avogadro's number, and λ the wavelength of light in vacuum. The data for the FPEG surfactant fall on the pattern illustrated in Fig. 2, showing both the $\theta = 0$ line and the $c = 0$ line. A double extrapolation of the quantity Kc/R_θ to $\theta = 0$ and $c = 0$ gave the weight of the FPEG micelle, 58500, corresponding to the aggregation number of 62. As can be seen from this figure, the dependence of Kc/R_θ on c did not give curvature to the lines. This result indicates that the micellar weight remains constant over the concentration range employed (2 - 50 mM), because theory predicts that the curvature should increase as the weight of pareticles goes up. The plot of Kc/R_θ vs. θ also gave a linear dependence, indicating that the FPEG micelle is spherical.

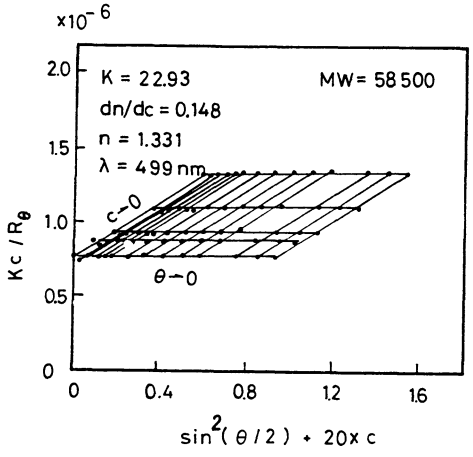


Fig. 2. A typical Zimm plot for the FPEG micelle in water.

Direct observation of the FPEG micelle was performed using the TEM technique. Figure 3 shows the TEM image of FPEG micellar particles labeled with OsO_4. The white regions of the image correspond to micellar cores packed with the alkyl chains of the surfactants, because such hydrophobic part of the micelle is unlikely to be labeled with OsO_4. This result indicates that the micellar core is roughly regarded as a sphere with the average radius of 2 nm.

Figure 4 depicts the structure of the FPEG micelle derived from the results of DLS, SLS, SAXS, and TEM measurements. The FPEG micelle is a spherical particle with a total radius of 3.8 nm and with a core radius of 2 nm.

The present authors have revealed the structure of a micelle formed by the functionalized surfactant, FPEG. The results described in this letter will be promisingly useful for elucidating a film-formation mechanism of the micellar disruption method and its modified method developed recently.[7)]

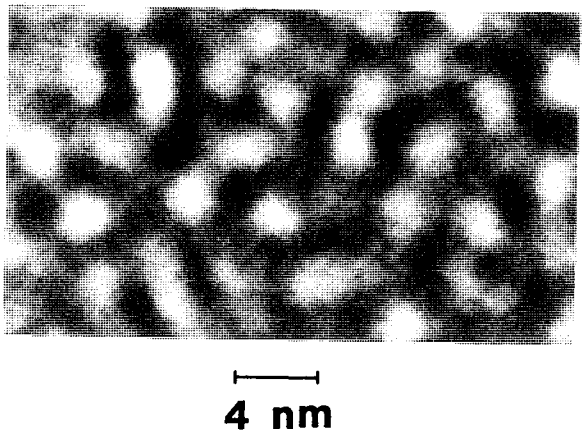


Fig. 3. TEM image of the FPEG micelle.

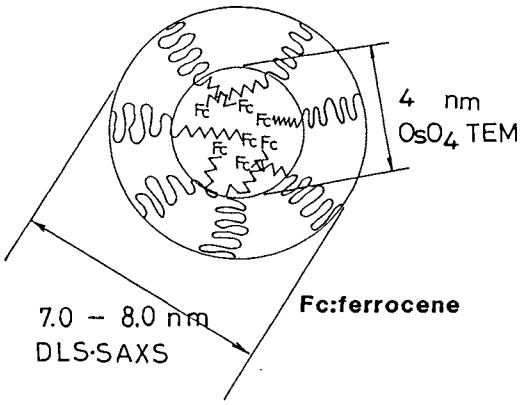


Fig. 4. The structural model for the FPEG surfactant micelle.

References

1) K. Hoshino and T. Saji., J. Am. Chem. Soc., 109, 5881 (1987); Chem. Lett., 1987, 1439; 1988, 547.
2) T. Saji, Chem. Lett., 1988, 693.
3) Y. Harima, K. Yamashita, and T. Saji, Appl. Phys. Lett., 52, 1542 (1988); Y. Harima and K. Yamashita, J. Phys. Chem., 93, 4184 (1989).
4) B. H. Zimm, J. Chem. Phys., 16, 1093, 1099 (1948); A. M. Holtzer, H. Benoit, and P. Doty, J. Am. Chem. Soc., 58, 624 (1954); H. Boedtker and P. Doty, ibid., 58, 968 (1954).
5) A. Guinier and G. Fournet, "Small Angle Scattering of X-Ray," Wiley & Son, New York (1955); J. C. Grosskreutz, "Handbook of X-Rays," ed by E. F. Kaelble, McGraw-Hill, New York (1967), Chap. 16, pp. 16-1 - 16-20.
6) K. Shinoda, T. Nagakawa, B. Tamamushi, T. Isemura, "Colloidal Surfactant," Academic Press, New York and London (1963).
7) K. Hoshino, S. Yokoyama, T. Saji, and H. Kokado, Chem. Lett., 1989, 1137.

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