Surface Potential of Mixed Micelles Composed of Prostaglandin B_2 and Heptaethylene Glycol Dodecyl Ether by the Fluorescence Method

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The surface state of negatively charged mixed micelles prepared by addition of prostaglandin B_2 (PGB_2) to nonionic heptaethylene glycol dodecyl ether (HED) has been investigated and the surface potential ($\Delta\psi$) of the micelles has been estimated by measuring the fluorescence intensity of ammonium 8-anilino-1-naphthalenesulfonate (ANS) as a fluorescent probe. Since the binding constant of ANS, *k*, is dependent on the surface potential of the micelle, the value of $\Delta\psi$ was determined according to the equation $\Delta\psi=-59.16 \log(k_0/k)$ at 25°C, where k_0 is the *k* of HED micelle. The value of $|-\Delta\psi|$ increases with increasing mole fraction of PGB_2 (X_{PGB_2}) and decreases with increasing ionic strength (*J*). These changes are due to the effects of the negative charge of PGB_2 and of ionic atmosphere of Na^+, respectively. Surface charge density (σ) was, therefore, determined from $\Delta\psi$ according to the Gouy-Chapman theory, with a result that σ is nearly independent of *J* and proportional to X_{PGB_2}. These results have led to a conclusion that the state of the diffuse layer surrounding the Stern layer on the micelle surface is represented well by the Gouy-Chapman theory as well as a previous result for the system of sodium dodecyl sulfate (SDS) and HED. The value of $|-\sigma|$ for PGB_2 micelle is less than that for SDS micelle, which suggests that PGB_2 forms a loosely packed micelle.

Regarding physicochemical properties of prostaglandins, critical micelle concentration, tilting angle, the area occupied by a molecule at air-water interface, solubility behavior, and ionization constant have been studied.[1-3] No surface potential of prostaglandin micelle has been determined, except a value[2] of −41 mV for prostaglandin $F_{2\alpha}$ as the maximum surface potential of micelle.

We have been studying the degradation of prostaglandins under such a condition that prostaglandins may form mixed micelles with a nonionic surfactant, heptaethylene glycol dodecyl ether. For accurate analysis of data in relation to catalysis in micellar systems, it is absolutely necessary to know the surface potential of mixed micelles composed of prostaglandins and heptaethylene glycol dodecyl ether.

From these points of view, we have studied the surface potential of mixed micelles composed of prostaglandin B_2 and heptaethylene glycol dodecyl ether, and compared with previous results[4] obtained for mixed micelles composed of sodium dodecyl sulfate and heptaethylene glycol dodecyl ether.

Experimental

Materials. Prostaglandin B_2 (PGB_2) of 99% purity was purchased from Sigma Chemical Company. Heptaethylene glycol dodecyl ether (HED) as a nonionic surfactant and ammonium 8-anilino-1-naphthalenesulfonate (ANS) as a fluorescent probe were the same as those used for a previous study.[4] Mixed micelles composed of PGB_2 and HED were prepared as previously described,[4] and dissolved in a phosphate buffer containing NaH_2PO_4 and Na_2HPO_4 (pH 7.0 with ionic strength 0.02 mol dm^{-3}) when fluorescence intensity was measured. All PGB_2 molecules were considered form mixed micelles with HED, on the basis of a previous result[4] that all sodium dodecyl sulfate (SDS) molecules formed mixed micelles with HED and of the less solubility of PGB_2 than that of SDS in phosphate buffer.

The degradation of PGB_2 at pH 7.0 and 25 °C in course of measurement was considered to be negligible because of its stability described in a previous paper.[1]

Measurement of Fluorescence Intensity. Mixed micelles were dissolved in a phosphate buffer (pH 7.0 with ionic strength 0.02 mol dm^{-3}). The total concentration of PGB_2 and HED was kept constant at 1 mmol dm^{-3}. A solution of ANS as a fluorescent probe was added to solutions of PGB_2 and HED up to 5×10^{-5} mol dm^{-3}. The fluorescence intensity was measured by use of a Hitachi F-4000 spectrofluorometer equipped with a pump-circulating water at a constant temperature through an outer tube. The temperature of the thermostat was maintained at 25±0.2 °C. The wavelength of excitation and emission are 360 and 480 nm, respectively. The measured fluorescence intensity was corrected as described in a previous paper.[4] Sodium chloride was used to control the ionic strength of buffer solution.

Results

Fluorescence Intensity. The relationship between the corrected fluorescence intensity, *F*, and the concentration of ANS, *D*, is shown in Fig. 1. As can be seen in Fig. 1, the plot of *F* vs. *D* is linear.

Adsorption of ANS on Micelle Surface. It is considered that fluorescence intensity is proportional to the amount of ANS adsorbed on micelle surface, because ANS fluoresces when adsorbed on micelle surface. The Langmuir adsorption isotherm can, therefore, be applied. The equation may be written as

$$\Gamma = \frac{D_m}{C} = \frac{\Gamma_s k D_f}{1+kD_f}, \qquad (1)$$

where Γ is the adsorbed amount of ANS per mole of micelle, Γ_s is the saturated adsorbed amount, *k* is the association constant related to the strength of adsorption, *C* is the total concentration of PGB_2 and HED which are in the form of micelle, D_m is the concentration of bound ANS, and D_f is the concentration of free

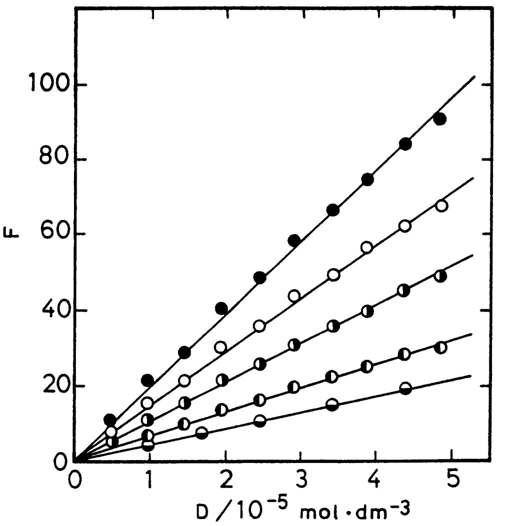

Fig. 1. Relationship between fluorescence intensity with correction and concentration of ANS. Mole fraction of PGB_2: ●; 0 (HED only), ○; 0.2, ◑; 0.4, ◐; 0.6, ⊖; 0.8. Total concentration of PGB_2 and HED: 1 mmol dm^{-3}. Ionic strength: 0.02 mol dm^{-3}.

ANS; $D = D_m + D_f$. Fluorescence intensity F is related to D_m by

$$F = fD_m, \quad (2)$$

where f is the fluorescence coefficient of ANS.

F_∞ is defined by

$$F_\infty = \lim_{D \to \infty} F = Cf\Gamma_s. \quad (3)$$

Equation 4 is, therefore, derived from Eqs. 1—3:

$$\frac{1}{F_\infty - F} = k\left(\frac{D}{F} - \frac{1}{f}\right). \quad (4)$$

Under our experimental conditions, D is sufficiently large. Therefore, Eq. 4 is reduced to

$$\frac{F}{D} = k(F_\infty - F). \quad (5)$$

Plots of F/D against F are presented in Fig. 2, which show a good linear relationship in accord with Eq. 5. From the values of slope and intercept, k and F_∞ are evaluated.

Values of F_∞ and k. The values of F_∞ are 439, 400, 351, 306, and 270 for the samples whose mole fractions of PGB_2 are 0 (HED alone), 0.2, 0.4, 0.6, and 0.8, respectively. The value of F_∞ decreased with increasing mole fraction of PGB_2. This is because the value of F_∞ depends on the concentration of HED, as described in a previous paper.[4)]

Values of k are shown in Fig. 3 against the mole fraction of PGB_2. The value of k decreased with increasing mole fraction of PGB_2. This is due to the electrostatic repulsion between PGB_2 and ANS on the micelle surface. The value of k for HED obtained in this paper is consistent well with the value for HED obtained in a previous paper[4)] at the same ionic strength, so that the results obtained in this paper may be taken to be reasonable.

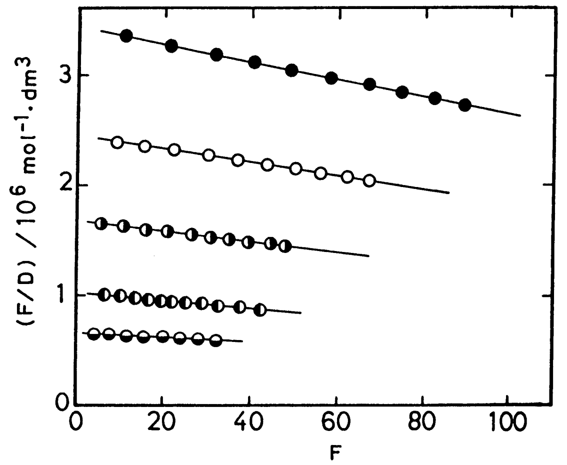

Fig. 2. Langmuir plots of F/D vs. F. Mole fraction of PGB_2: ●; 0 (HED only), ○; 0.2, ◑; 0.4, ◐; 0.6, ⊖; 0.8. Total concentration of PGB_2 and HED: 1 mmol dm^{-3}. Ionic strength: 0.02 mol dm^{-3}.

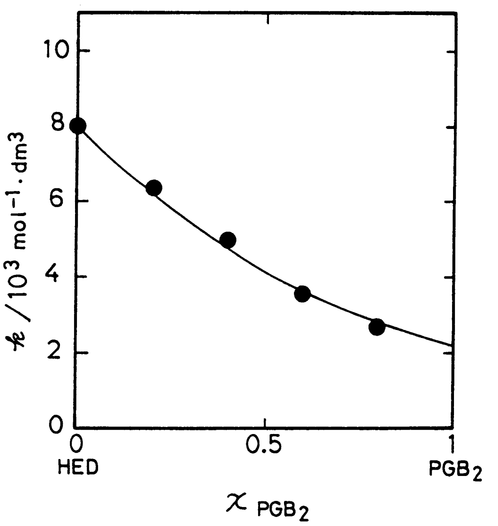

Fig. 3. Relationship between k and mole fraction of PGB_2. Total concentration of PGB_2 and HED: 1 mmol dm^{-3}. Ionic strength: 0.02 mol dm^{-3}.

Discussion

Surface Potential of Micelles. On the assumption described in a previous paper,[4)] the binding constant of ANS to HED-PGB_2 mixed micelles, k, depends on the surface potential of the micelle, $\Delta\psi$. The relation is, therefore, written as

$$k = k_0 \exp(-z\boldsymbol{F}_A\Delta\psi/\boldsymbol{R}T), \quad (6)$$

where z is the valency of ANS, $\boldsymbol{F}_A$ is the Faraday constant, $\boldsymbol{R}$ is the gas constant, and k_0 is the k for nonionic HED micelle. By substituting $z = -1$, $\boldsymbol{F}_A = e \cdot \boldsymbol{N}_A = 9.648 \times 10^4$ (C mol^{-1}), $\boldsymbol{R} = k_B\boldsymbol{N}_A = 8.314$ (J mol^{-1} K^{-1}), and $T = 298.15$ K at 25 °C, we obtain

$$\Delta\psi = -59.16 \cdot \log \frac{k_0}{k} \quad (7)$$

The surface potential of the micelle, $\Delta\psi$, as calculated from the values of k shown in Fig. 3 by using Eq. 7, is plotted with closed circles against the mole fraction of PGB_2 in Fig. 4. To investigate the effect of ionic strength on the surface potential of the micelle, experiments were carried out with buffer solutions containing sodium chloride so that their ionic strengths are 0.06 and 0.20 mol dm^{-3} as well as 0.02 mol dm^{-3}, plots of $\Delta\psi$ against the mole fraction of PGB_2 being shown by symbols ◑ and ○ in Fig. 4.

No micelles composed of PGB_2 molecules alone are formed under these experimental conditions that the total concentration of PGB_2 and HED is 1 mmol dm^{-3}. The critical micelle concentration of PGB_2 is about 6 mmol dm^{-3}.[1] The surface potential of PGB_2 micelle is, therefore, obtained by extrapolation of the theoretical curve based on the Gouy-Chapman equation, which will be described in a later section. The surface potential of PGB_2 micelle thus obtained at ionic strength 0.02 mol dm^{-3} is −33 mV. This value |−33 mV| for PGB_2 micelle is less than the value[4] |−73 mV| for SDS micelle at the same ionic strength, which suggests that PGB_2 forms a loosely packed micelle.

The surface potential of the micelle becomes more negative with increasing mole fraction of PGB_2. On the other hand, the surface potential of the micelle, $|-\Delta\psi|$, becomes smaller as the ionic strength is increased by adding sodium chloride. These changes may be considered due to the effects of the negative charge of PGB_2 and of ionic atmosphere of Na^+, respectively.

Surface Charge Density of Micelles. According to the Gouy-Chapman theory, the relation between surface potential, $\Delta\psi$, and surface charge density, σ, is expressed as

$$\frac{\sigma}{\mathrm{C \cdot cm^{-2}}} = -5.8673 \times 10^{-6} \sqrt{\sum_i \left[\left(\frac{C_i}{\mathrm{mol \cdot dm^{-3}}} \right) \left\{ \exp\left(-0.03892\, z_i \frac{\Delta\psi}{\mathrm{mV}} \right) - 1 \right\} \right]}, \quad (8)$$

where 78.54[5] is used as the value for the relative dielectric constant of water at 25 °C. The relationship between surface charge density and the mole fraction of PGB_2 is shown in Fig. 5, The value of σ was found proportional to X_{PGB_2}, and thus the relation can be written as

$$\sigma = -1.044 \times 10^{-6} \cdot X_{PGB_2}. \quad (9)$$

By using this relation and Eqs. 7 and 8, theoretical values of the surface potential of the micelles and the binding constant were calculated, the results being shown in Figs. 3 and 4 by solid lines, respectively.

On the other hand, the surface charge density, σ, was found nearly independent of ionic strength.

These results indicate that the state of the diffuse layer surrounding the Stern layer on the micelle surface is represented well by the Gouy-Chapman theory as well as a previous result[4] obtained for the system of sodium dodecyl sulfate and HED.

Dissociation Degree of Micelles. The relationship

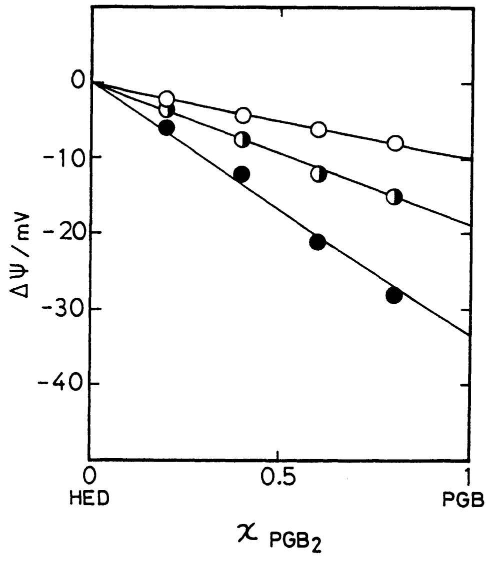

Fig. 4. Effect of ionic strength on the plots of surface potential of micelle, $\Delta\psi$, vs. mole fraction of PGB_2. Ionic strength: ●; 0.02, ◑; 0.06, ○; 0.20 mol dm^{-3}. Total concentration of PGB_2 and HED: 1 mmol dm^{-3}. Solid lines: theoretical curves by the Gouy-Chapman equation for $\sigma = -1.044 \times 10^{-6} \cdot X_{PGB_2}$ C cm^{-2}.

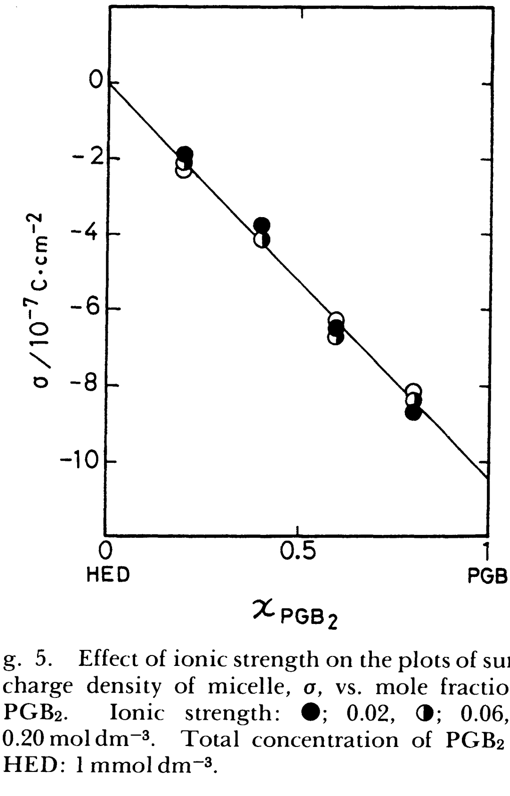

Fig. 5. Effect of ionic strength on the plots of surface charge density of micelle, σ, vs. mole fraction of PGB_2. Ionic strength: ●; 0.02, ◑; 0.06, ○; 0.20 mol dm^{-3}. Total concentration of PGB_2 and HED: 1 mmol dm^{-3}.

between surface charge density, $|\sigma|$, and dissociation degree, α, of micelles can be expressed by

$$\alpha = \frac{|\sigma| \cdot \mathrm{A}}{X_{\mathrm{PGB_2}} \cdot e}, \tag{10}$$

where A is the area occupied by a $\mathrm{PGB_2}$ molecule, and e=1.6021×10^{-19} C. The area occupied by a $\mathrm{PGB_2}$ molecule has been reported to be 54 Å^2 [1] as a value for maximum compression. A value of 80 Å^2 has been derived from a 3-dimensional model of prostaglandin molecule.[2,3] If a calculation is developed for the system of $\mathrm{PGB_2}$ and HED in terms of these values (54—80 Å^2), the dissociation degree of $\mathrm{PGB_2}$ in HED micelle is approximately 4—5%. The value of dissociation degree is found nearly independent of the mole fraction of $\mathrm{PGB_2}$. This value ($\alpha \fallingdotseq 4.5\%$) is a bit smaller than those obtained for sodium dodecyl sulfate in HED micelle (α=10%,[4] 8%[6]), so that the results obtained in this paper may be taken to be quite reasonable.

Effect of Electrolyte on the Surface Potential of Micelles. To investigate the effect of electrolyte on the surface potential of the micelle in a little more detail, experiments at various ionic strengths were carried out for a mixed micelle composed of $\mathrm{PGB_2}$ and HED at $X_{\mathrm{PGB_2}}$=0.6, the results being shown in Fig. 6. As shown in Fig. 6, the surface potential of the micelle, $|-\Delta\psi|$, becomes smaller as the ionic strength is increased by adding sodium chloride. By using the value of σ defined by Eq. 9 and the equation of Gouy-Chapman, theoretical values of the micellar surface potential are calculated, and represented by the solid line in Fig. 6. Thus, the relationship between ionic strength and micellar surface potential was found to be represented well by the Gouy-Chapman theory.

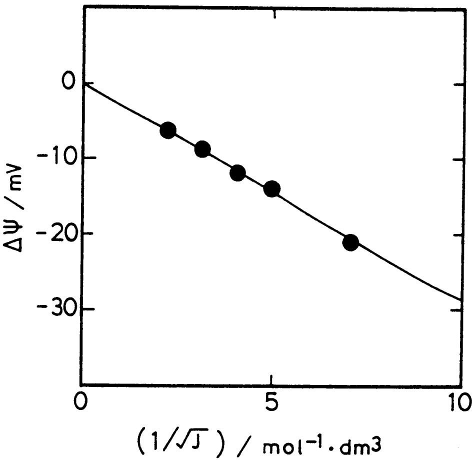

Fig. 6. Effect of ionic strength on surface potential of micelle composed of $\mathrm{PGB_2}$ and HED at $X_{\mathrm{PGB_2}}$= 0.6. Total concentration of $\mathrm{PGB_2}$ and HED: 1 mmol dm^{-3}. Solid line: theoretical curve by the Gouy-Chapman equation for σ=−6.263×10^{-7} C cm^{-2}.

Conclusion

The surface potential of mixed micelles composed of $\mathrm{PGB_2}$ and HED has been determined by the fluorescence method.

The surface potential of the micelle, $|-\Delta\psi|$, increases with increasing mole fraction of $\mathrm{PGB_2}$ ($X_{\mathrm{PGB_2}}$), and decreases with increasing ionic strength. The surface state of the micelles is, therefore, represented well by the Gouy-Chapman theory. The value of $|-\Delta\psi|$ for $\mathrm{PGB_2}$ micelle is less than that for sodium dodecyl sulfate micelle at the same ionic strength, which suggests that $\mathrm{PGB_2}$ forms a loosely packed micelle.

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