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Adsolubilization of Yellow OB and Parsol in Diocetadecyldimethylammonium Chloride Layer on Silica

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Abstract

When dioctadecyldimethylammonium chloride (DODAC) was adsorbed on silica from its vesicle in aqueous solution, a patchlike bilayer was formed due to the electrostatic attraction force between DODAC and silica. Yellow OB, a non-water-soluble dye, and Parsol, a UV absorber, were adsolubilized in the DODAC-adsorbed layer, resulted in hydrophobic surface; the incorporated amount of Parsol was larger than that of Yellow OB. Further, the Parsol adsolubilized in the DODAC-adsorbed layer showed a remarkable screening effect against UV light.

Key-words : *Adsolubilization, Silica, UV absorber*

1. Introduction

Adsorption of surfactants on particles has been studied to understand interactions at the solid/liquid interface¹⁾. The information obtained has been applied to many fields, such as paints, cosmetics, oil recovery, and so on. Physicochemical properties of surfactant-adsorbed layers on particles have been measured with fluorescence, ESR, and neutron scattering methods²⁻⁷⁾. Since micropolarity of surfactant-adsorbed layers shows a hydrophobic environment, similar to that of micelles, non-water-soluble compounds can be incorporated in the adsorbed layer, and that incorporation is called adsolubilization⁸⁾. Recently, some groups⁹⁻¹²⁾ have reported on partition coefficients of some alcohols and dyes between the bulk phase and an adsorbed surfactant layer. Furthermore, the polymerization of styrene in the surfactant-adsorbed layer has been performed¹³⁻¹⁵⁾ to prepare thin film on particles.

On the other hand, a variety of double-chain amphiphiles produce stable monolayer and bilayer membranes in dilute aqueous solution. Dioctadecyldimethylammonium chloride (DODAC), for example, is well known to provide unilamellar vesicles which are the simplest functioning membrane models. Properties of DODAC vesicles have been extensively studied¹⁶⁻¹⁹⁾. There are also a few reports about interaction of vesicles at solid/liquid interface²⁰⁻²³⁾. It is also expected that a DODAC-adsorbed layer on solids can adsolubilize non-water-soluble compounds, similar to the adsorbed layer of single-chain surfactants.

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In this work, we have studied adsolubilization of a dye and a UV absorber in a DODAC-adsorbed layer on silica. Further, a screening effect against UV light has been examined using the UV-absorber-adsolubilized silica.

2. Experimental

Materials Dioctadecyldimethylammonium chloride (DODAC) supplied by Tokyo Kasei Ltd. was used without further purification. 1-o-Tolyl-azo-2-naphthylamine (Yellow OB) was also supplied by Tokyo Kasei Ltd. 1-(4-Methoxyphenyl)-3-(4-tert-butylphenyl)-propan-1,3-dione (Parsol) was obtained from Givaudan Co. The chemical structures of Yellow OB and Parsol are given in **Figure 1**.

Silica was obtained from Japan Aerosol Co. The particle diameter and specific surface area (by nitrogen adsorption) were $1\ \mu\text{m}$ and $144.5\ \text{m}^2/\text{g}$, respectively.

The water used was purified by means of a Milli-Q Water Purification System.

Procedure Vesicles were prepared by the sonication of a DODAC-water mixture with a ultrasonic bath for 3 h at 25°C . The vesicle suspension was added to a known weight of silica in screw-capped vials, followed by stirring for 24 h. Then, after centrifuging the suspension, the supernatant solution was obtained. The concentration of DODAC in the supernatant solution was determined by the orange II-chloroform method²⁴. The adsorbed amount of DODAC was determined by the difference in the concentration of DODAC before and after adsorption.

The zeta potential of the suspension was measured with an electrophoretic apparatus (Pen Kem 500). The adsolubilization of Yellow OB and Parsol into the DODAC-adsorbed layer on silica was carried out as follows: Silica was placed in contact with DODAC vesicles for 24 h in which Yellow OB and Parsol had been solubilized for 2 h. Then, the concentrations of Yellow OB and Parsol in the supernatant solution obtained by centrifuging the suspension were determined by means of a UV-visible spectrophotometer (Hitachi, 200 A). The adsolubilized amounts of Yellow OB and Parsol were obtained by the difference in concentrations before and after adsolubilization.

Fig. 1 Chemical structures of Yellow OB and Parsol

Fig. 2 Adsorption isotherm of DODAC from its vesicle on silica

Using the samples of Parsol adsolubilized, a screen test of UV light was carried out as follows: After coating the samples with a constant thickness (40 μm) on quartz glass, the samples were dried. Then, absorptions (%) at 308 (UV-B) and 355 nm (UV-A) were measured, and a screening rate was evaluated.

All measurements were carried out at 25°C.

3. Results and discussion

Before studying adsolubilization of Yellow OB and Parsol into the DODAC-adsorbed layer on silica, we investigated adsorption behavior of DODAC on silica. **Figure 2** shows the adsorption isotherm of DODAC from its vesicle onto silica. At low DODAC concentrations, DODAC is completely adsorbed, or at least there is no measurable amount remaining in solution. The initial part of the isotherm is therefore vertical. At higher DODAC concentrations the adsorption graph is concave towards the equilibrium concentration until a saturation level of $1.6 \times 10^{-4} \text{ mol g}^{-1}$ is reached. The shape of this isotherm shows a strong affinity of DODAC on silica. Since DODAC and silica have opposite charges in water, it seems that the adsorption of DODAC occurs due to electrostatic attraction. It is important to consider whether the deposition of DODAC occurs by the interaction of intact vesicles with silica or via the adsorption of monomeric DODAC in equilibrium with the vesicles. By the facts that the vesicles contain ca. 7000 DODAC molecules¹⁹⁾ depending on their size and the concentration of monomeric DODAC²⁵⁾ is no greater than $10^{-6} \text{ mol dm}^{-3}$, the delivery of DODAC to the surface will be predominantly via vesicles rather than via monomer. From the surface area of silica ($144.5 \text{ m}^2 \text{ g}^{-1}$), the limiting value is obtained to be 1.50 nm^2 per molecule which is fairly large compared with the area of a DODAC molecule (0.68 nm^2)²⁶⁾. This result may indicate that at saturation the silica is covered with a patchlike DODAC bilayer. In a similar study, Horn²⁰⁾ reported that unilamellar phosphatidylcholine vesicles break open and adhere to a mica surface to form a bilayer coating. On the other hand, Jackson²²⁾ et al. reported that only a monolayer of phosphatidylcholine is formed onto glass beads. These studies are different from the present study since in each case both vesicle and solid surface have the same charge.

Fig. 3 Zeta potential of silica vs. equilibrium concentration of DODAC

Fig. 4 Adsolubilized amount of Yellow OB in DODAC-adsorbed layer on silica

The zeta potential of silica after the adsorption of DODAC is shown in **Figure 3**. Because of the adsorption of DODAC, the zeta potential of silica by adsorption of DODAC changes from negative to positive at above $8.4 \mu\text{mol dm}^{-3}$, then increases and reaches a saturated value, suggesting that the positively charged head group of DODAC is adsorbed on the negatively charged surface of silica at a low concentration of DODAC. This behavior in the zeta potential corresponds to that in the adsorption isotherm. Further, by the measurements of fluorescence and ESR spectroscopies, it has been reported²⁷⁾ that micropolarity and microviscosity in the adsorbed layer of DODAC on silica is lower and larger than those in the DODAC vesicle, probably due to an increase of packing for the DODAC layer. Thus the DODAC-adsorbed layers having a large hydrophobic capacity can be expected to adsorb non-water-soluble compounds.

The adsolubilization of alcohols and dyes has been studied by Harwell et al.¹²⁾ and Esumi et al.¹¹⁾ who reported that non-water-soluble compounds were partitioned between the bulk and an adsorbed layer and the microenvironmental properties of the adsorbed layer were altered by the adsolubilization. In this study, we carried out the adsolubilization of Yellow OB, a non-water-soluble dye, and Parsol, a UV absorber, in the adsorbed layer of DODAC (**Figure 4**). The feed concentration of DODAC was adjusted to 7 mmol dm^{-3} which corresponded to the saturation level. The adsolubilized amount of Yellow OB increased with an increase in the equilibrium concentration of Yellow OB, where the maximum ratio of Yellow OB to DODAC in the adsorbed layer is about 0.3. Since Yellow OB is not soluble in water at all, it is presumably incorporated into the hydrocarbon chains of the DODAC layer on silica. This value (0.3) is considerably greater than the value (0.04)¹⁰⁾ for lithium dodecyl sulfate bilayer on alumina. This difference can be easily understood, taking into consideration that the volume of hydrocarbon chains in the DODAC-adsorbed layer is greater than that in the lithium dodecyl sulfate.

The durability of the fixation of Yellow OB adsolubilized into the DODAC layer on silica against washing with distilled water was studied. Although the result is not given in the figure, the Yellow OB adsolubilized is almost completely retained even after several washings, suggesting that the interactions between DODAC and silica surface, and between DODAC and Yellow OB are so strong against the washing that the Yellow OB is irreversibly fixed.

Figure 5 shows the adsolubilized amount of Parsol in the DODAC layer on silica. The adsolubilized amount of Parsol increased with an increase in the equilibrium concentration of Parsol, similar to the result of Yellow OB except that the ratio of Parsol to DODAC in the adsorbed layer is about twice that of Yellow OB. This difference in the ratio may come from the molecular size of the adsolubilizes.

In the Parsol-DODAC-silica system, the screening rate was evaluated from UV spectra (**Table 1**), and the samples corresponding to the saturation level of Parsol were studied. In Table 1, the value of [(2)-(3)] shows a screening rate from the Parsol adsolubilized in the DODAC layer. In particular, a marked screening rate was observed against UV-A. At present the reason for this result is not understood, but the Parsol adsolu-

Fig. 5 Adsolubilized amount of Parsol in DODAC-adsorbed layer on silica

Table 1 Result of screening rate

	UV-A(%)	UV-B(%)
(1) D+P+H	5.3	13.6
(2) D+P+S+H	35.7	32.3
(3) S	13.3	18.6
(4) (2)-(3)	22.4	12.7

D, DODAC ; P, Parsol ; S, SiO₂ ; H, H₂O

bilized in the DODAC layer is found to be effective to shield UV irradiation.

The above results lead to the conclusion that the adsorption of DODAC from its vesicle occurs due to the electrostatic attraction force between positively charged DODAC and negatively charged silica, which results in a patchlike DODAC bilayer. Yellow OB and Parsol, both of which are not soluble in water, can be adsolubilized in the DODAC-adsorbed layer on silica. The Parsol adsolubilized in the DODAC layer showed a considerable screening rate against UV irradiation.

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