Adsorption Characteristics of Spiropyran-Modified Cationic Surfactants at the Silica/Aqueous Solution Interface

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We have characterized the adsorption of a spiropyran-modified cationic surfactant at the silica/aqueous solution interface and the subsequent photoresponsive nature of the adsorbed molecular assemblies. The surfactant used in this study was 1′(6-trimethylammoniohexyl)-3′,3′-dimethyl-6-nitrospiro-(2H-1-benzopyran-2,2′-indole) bromide (SP-Me-6). Visible light incident to the aqueous solution of SP-Me-6 results in the isomerization from the merocyanine (MC) form to the spiropyrone (SP) form, whereas the isomerized SP form reverts to the MC form when the surfactant solution is stored in the dark. The adsorption isotherms on colloidal silica particles reveal that the combination of electrostatic and intermolecular hydrophobic interactions drives the adsorption for both of the isomers, and the more hydrophobic SP form gives a greater adsorbed amount when compared with the zwitterionic MC form. In situ atomic force microscopy (AFM) has demonstrated that disklike or flattened spherical surface aggregates are formed in the adsorption plateau region on a flat silica plate, where the SP form gives larger surface aggregates as a result of its greater hydrophobic/associative character. Such a difference in the hydrophobic/associative nature between the two isomers induces reversible changes in the dispersion stability of silica suspensions as well as in the surface force, in response to the photoisomerization. By taking the in situ and ex situ color changes into consideration, it seems likely that the photoisomerization occurs reversibly even after surfactant adsorption on silica.

Introduction

Recent advances in synthesis methodology have allowed the design of a wide range of stimulus-responsive amphiphiles that undergo spontaneous self-assembly in aqueous solution in response to stimuli such as solution pH, temperature, electrical potential, and light irradiation. These materials are being developed for drug delivery applications, as nanoreactors for surfactants. The benefits of the photoresponsive nature as an additional controlling parameter for the viscoelasticity of worm-like micellar solutions as a result of the trans-cis photoisomerization of azobenzene-modified cationic surfactants. The benefits of the photoresponsive nature as an external stimulus over pH and thermal or electrical stimulation include scalable miniaturization, limited chemical contamination, and the potential performance of chemical reactions on a small scale without the need for channel confinement.

Spiropyran is also known to be a photoresponsive material: the energetically stable spiropyrone (SP) form changes to the zwitterionic merocyanine (MC) form as a result of UV-light irradiation in organic solvents (spiropyran itself is hardly soluble in water), whereas the MC form is isomerized to the original SP form in the dark (although the rate of this reverse isomerization is relatively slow and is accelerated by gentle heating). Since photochromic behavior was first reported in 1952, various kinds of water-insoluble spiropyran-modified amphiphiles have been synthesized with a view to developing photoresponsive Langmuir–Blodgett (LB) films formed at the air/water interface. The photoisomerization causes a dramatic change in the hydrophilic/hydrophobic nature of the substance (apparently, the zwitterionic MC form is more hydrophilic than the nonionic SP form). This has provided some opportunities in photoswitching (i) the interfacial tension at an oil/water interface and (ii) the wettability of solid (or membrane) surfaces coated with water-insoluble spiropyran derivatives. In addition, there are two interesting

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papers regarding colloidal particles modified with end-grafted polymer brushes containing spiropyran derivatives: the dispersion stability of these colloidal particles is observed to be photo-controllable in some organic solvents.25,26

Spiropyran-modified surfactants containing a hydrophobic hydrocarbon chain terminated with a permanently charged headgroup (e.g., quaternary ammonium group) have also been of great interest in anticipation of a controllable change in the physicochemical properties of their micellar solutions as a result of the photoisomerization.27 We have synthesized such cationic surfactants and have studied the aqueous surface tension of each form (i.e., before and after light irradiation):28 both the critical association concentration (cac) and the surface tension observed at the cac are found to be dependent on the isomerization form, as expected. A reversible change in surface tension is also observed for the photosomerization.29

In the current study, we have characterized the adsorption of a spiropyran-modified cationic surfactant on colloidal and flat silica and the subsequent photoresponsive behavior. As mentioned earlier, photoresponsive smart surface coatings have been developed in organic media by the use of spiropyran derivatives covalently bound to solid surfaces. From this point of view, our originality lies in the self-assembly of the photoresponsive surfactant when fabricating such photoresponsive surface coatings as well as in the use of aqueous solutions. On the basis of a similar concept, Zhang and co-workers have reported the adsorbed layer morphology of azobenzene-based cationic surfactants on flat substrates,30–33 however, this research topic still requires more detailed study not only from a qualitative standpoint (e.g., in situ morphological changes in the adsorbed layer, induced by photoisomerization) but also from a quantitative one (e.g., the adsorption isotherms for the two isomers). In our current work, systematic studies have been carried out as follows: (i) characterizing the aqueous solution properties of the spiropyran-modified surfactant, assessed by static surface tensiometry; (ii) determining the adsorption isotherms on colloidal silica particles; and (iii) measuring in situ morphologies of the surfactant layer adsorbed on a flat silica plate on the basis of soft-contact atomic force microscopy (AFM). These measurements were performed both before and after visible light irradiation to characterize the photoresponsive behavior.

Experimental Section

Materials. The surfactant employed in this study (1(6-trimethylammoniomethyl)-3’3’-dimethyl-6-nitrospirop(2H-1-benzopyran-2,2’-indoline) bromide, SP-Me-6) was synthesized according to the procedure reported previously.28 The chemical structure is given in Figure 1 for the two isomers. Hydrophilic silica particles (Aerosil 50) were kindly supplied by Japan Aerosil Co., Ltd., and given in Figure 1 for the two isomers. Hydrophilic silica particles (Aerosil 50) were kindly supplied by Japan Aerosil Co., Ltd., and "silicon wafers (Nilaco): a silicon wafer was immersed in a mixed solution of 5:1 H2O/NH3/H2O2 by volume for 15 min at 80 °C, followed by copious rinsing with deionized water to give a hydroxylated silica surface. A fresh piece of silica was used for each experiment and then discarded. NaBr, NaOH, and HBr (analytical grade) were purchased from Wako and used without further purification. The water used in this study was filtered with a Millipore membrane filter (0.22 μm in pore size) after deionization with a Barnstead NANO Pure Diamond UV system.

Methods. Aqueous surfactant solutions were prepared via direct dissolution of the powdered sample in the presence of 10 mmol dm−3 NaBr and were stored in the dark. Light irradiation was carried out using a San-ei Superence 2035 Hg–Xe lamp (200 W) equipped with a Kenko L-42 glass filter. This filter passes only λ > 420 nm light. The photoisomerization that occurs in bulk solution was monitored using a Hitachi U-3310 UV–vis spectrophotometer with quartz cuvette (1 cm path length). The surface tension of the aqueous surfactant solutions was measured using a Kyowa Wilhelmy CBVP-Z auto surface tensiometer with a platinum plate. The sample volume and effective surface area (for light irradiation) of the glass vessel used in this measurement were 10 cm3 and ∼12 cm2, respectively.

The adsorbed amount of the spiropyran-modified surfactant was determined by measuring the concentrations in solution before and after adsorption. Experiments were conducted in glass vials with caps. All suspensions (0.1 g of silica particles/10 cm3 in the presence of 10 mmol dm−3 NaBr) were equilibrated for 3 h at pH 6. During this equilibration, the sample suspensions were stirred either in the dark for the MC form or under visible light irradiation for the SP form. After this equilibration, the solids were separated by centrifugation and the surfactant concentration in the supernatant was measured using the Hitachi U-3310 UV–vis spectrophotometer at a fixed wavelength of 530 nm.

In situ imaging of the adsorbed surfactant layers on a flat silica plate was performed with a Seiko SPI3800 AFM. Cantilevers with an integral silicon nitride tip (Olympus OMCL-400PSA-1, nominal spring constant = 0.08 N m−1) were used for all AFM experiments. The chemically oxidized silicon wafer was assembled in the AFM instrument, and the surfactant solution prepared at the desirable concentration (∼1 cm3) was injected into the AFM fluid cell. After equilibration for 1 h (in the dark for the MC form and under visible light irradiation for the SP form), images were collected using the soft-contact method34 at a scan rate of 3 to 4 Hz; this uses the minimum force necessary to obtain an image, thereby minimizing scanning-induced deformations of the adsorbed layer. All images presented herein are deflection images. Interaction forces between the cantilever tip and the surfactant layer adsorbed on the silica/aqueous solution interface were also measured.

![Figure 1. Chemical structures of SP-Me-6 for both isomers. The MC form (left) is spontaneously formed in aqueous solution, and visible light irradiation results in photoisomerization to the SP form (right). The original MC form reappears when the isomerized SP solution is stored in the dark.](image-url)
Figure 2. Surface tension of an aqueous SP-Me-6 solution as a function of concentration. The surfactant solutions contain 10 mmol dm$^{-3}$ NaBr as a background electrolyte. These measurements were carried out both in the dark (the MC form, ♦) and under visible light ($\lambda > 420$ nm) irradiation (the SP form, △).

All measurements reported herein were performed at a constant temperature of 25 °C.

**Results and Discussion**

**Photoisomerization in Bulk Solution and at the Air/Aqueous Solution Interface.** Before presenting the adsorption characteristics of the spirocyan-modified cationic surfactant on silica, it is important to see the photoisomerization that occurs in bulk solution and at the air/aqueous solution interface. As mentioned in the Introduction, we have reported this topic in our previous solution and at the air/aqueous solution interface. As mentioned in the Introduction, we have reported this topic in our previous study, where the photoisomerization of the MC form to the SP form was observed at the air/aqueous solution interface (Supporting Information, Figure S1) and at the air/silica interface (Supporting Information, Figure S2). The photoisomerization of SP-Me-6 results in the isomerization from the MC form to the SP form (negative photochromism), and the isomerized SP form reverts to the MC form when the surfactant solution is stored in the dark. Indeed, the reverse isomerization rate is observed to be considerably slower than that seen for visible light irradiation ($\lambda > 420$ nm).

The static surface tension data of aqueous SP-Me-6 solutions are shown in Figure 2 for the two isomers. The physicochemical parameters including the cac, the surface tension measured at the cac ($\gamma_{\text{cac}}$), the surface excess concentration ($\Gamma_{\text{cac}}$), and the occupied area per surfactant molecule adsorbed at the air/silica interface ($A_{\text{cac}}$) are summarized in Table 1. Again, the observed trend is qualitatively similar to that observed for the SP-Me-12 system, where no significant difference in the adsorbed amount ($\Gamma_{\text{cac}}$) is observed between the two isomers but is not as large as that measured in bulk solution. We note that, in a similar manner to the SP-Me-12 system, a reversible change in surface tension is observed for the two isomers at a given SP-Me-6 concentration (i.e., before and after visible light irradiation, data not shown). This means that the photoisomerization of SP-Me-6 causes reversible changes in interfacial properties as well as in bulk solution properties. This allows us to develop photoresponsive smart surface coatings, as mentioned below.

**Adsorption and Photoisomerization on Silica Particles.** Figure 3 shows the adsorption isotherms of SP-Me-6 on silica particles in the presence of 10 mmol dm$^{-3}$ NaBr as a background electrolyte. These measurements were carried out both in the dark (the MC form, ♦) and under visible light ($\lambda > 420$ nm) irradiation (the SP form, △). The experimental errors in adsorbed amounts are estimated as ca. ±3% in the region of low surfactant concentration and ca. ±15% in the region of high surfactant concentration.

In bulk solution, we note that, in a similar manner to the SP-Me-12 system, a reversible change in surface tension is observed for the two isomers at a given SP-Me-6 concentration (i.e., before and after visible light irradiation, data not shown). This means that the photoisomerization of SP-Me-6 causes reversible changes in interfacial properties as well as in bulk solution properties. This allows us to develop photoresponsive smart surface coatings, as mentioned below.

**Table 1. Summary of the Physicochemical Properties of SP-Me-6 Adsorbed at the Air/Aqueous Solution Interface and at the Silica/Aqueous Solution Interface**

<table>
<thead>
<tr>
<th></th>
<th>cac (mmol dm$^{-3}$)</th>
<th>$\gamma_{\text{cac}}$ (mN m$^{-1}$)</th>
<th>$\Gamma_{\text{cac}}$ (m$^{-2}$)</th>
<th>$A_{\text{cac}}$ (μmol m$^{-2}$)</th>
<th>$\Gamma_{\text{silica}}$ (m$^{-2}$)</th>
<th>$A_{\text{silica}}$ (μmol m$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MC form</td>
<td>1.5</td>
<td>3.9</td>
<td>4.9</td>
<td>0.34</td>
<td>0.87</td>
<td>1.9</td>
</tr>
<tr>
<td>SP form</td>
<td>0.59</td>
<td>42</td>
<td>4.9</td>
<td>0.34</td>
<td>0.87</td>
<td>1.9</td>
</tr>
</tbody>
</table>

*a* Based on the static surface tension data shown in Figure 2. *b* Based on the surface tension data shown in Figure 2 and the Gibbs adsorption equation. *c* Based on the adsorption isotherm data shown in Figure 3.

observed for the MC form may result from the greater hydration of surfactant assemblies formed in the first adsorption region and their further buildup or growth in the region of high concentrations. We assume, therefore, that the observed difference in the adsorption isotherms primarily results from the difference in the hydrophobicity between the two isomers. This is supported by the greater adsorbed amount of the SP form compared to the MC form. (See also Table 1, where the adsorbed amount at the maximum adsorption point ($\Gamma_{\text{silica}}$) and the minimum occupied area per surfactant molecule adsorbed on silica particles ($A_{\text{silica}}$) are summarized.)

The dispersion stability of silica suspensions with the adsorption of SP-Me-6 has been visually assessed, as shown in Figure 4. These pictures were taken after adsorption equilibration and subsequent standing for 15 min. For both the isomers, the adsorption results in sedimentation of the silica suspensions. (Note that such sedimentation does not occur in the absence of SP-Me-6 on the standing timescale.) It seems likely that, on the basis of this visual assessment, the SP form (under visible light irradiation) induces the sedimentation more significantly than does the MC form (in the dark).

It is known that when ionic surfactants are adsorbed on oppositely charged solid surfaces a charge reversal occurs at least in the region of adsorption saturation. In our current case, the low dispersion stability of silica suspensions in the presence of SP-Me-6 led to a difficulty in measuring $\zeta$ potentials (based on electrophoretic mobility measurements), and hence it is not possible to correlate the dispersion stability with the $\zeta$-potential data. Instead of this, the adsorption isotherm data may provide a possible interpretation regarding the low dispersion stability. On the basis of the adsorption amount data shown in Table 1, the surface coverage at the maximum adsorption point is estimated to be 9% for the MC form and 28% for the SP form, respectively, under the assumptions that (i) 100% surface coverage corresponds to monolayer adsorption at the air/aqueous solution interface ($\Gamma_{\text{silica}}$) and (ii) a classical bilayer is formed on silica. Such low surface coverage will necessarily result in the low dispersion stability, as a result of the partial neutralization of negative charges on silica (i.e., decreased electrostatic repulsion between particles) as well as the hydrophobic interaction, overcoming stability factors such as additional positive charges and/or hydration by SP-Me-6 adsorption.

In our current work, we have observed that photoisomerization causes reversible changes in sample color and dispersion stability, even after surfactant adsorption on colloidal silica particles. The visible light incident on the MC system results in a dramatic change in the suspension color, and the original MC color reappears when the suspension is stored in the dark. Similarly, the dispersion stability of silica suspensions changes in response to the sample color and hence in response to the isomerization form, although the stability change is not as dramatic as the color change that we have observed here. Of course, the sample suspensions prepared under visible light irradiation (as the SP form) gradually change color to orange-red in the dark, and the original SP color is regained under visible light irradiation. These results suggest that photoisomerization occurs reversibly even after the surfactant adsorption on colloidal silica particles.

Interestingly, negative photoisomerization occurs for the SP-Me-6-coated silica particles even after drying. The silica particles coated with the surfactant were collected by centrifugation, rinsed with 10 mmol dm$^{-3}$ NaBr aqueous solutions, and then dried in a vacuum oven at room temperature. (b) Visible light absorption spectra (reflection mode) of the silica particles coated with SP-Me-6. The sample preparation method was the same as for part a. The sample was first stored in the dark, irradiated with visible light ($\lambda > 420$ nm) for 5 min, and then stored in the dark again. (c) Change in absorbance (at a fixed wavelength of 521 nm) of silica particles coated with SP-Me-6. The sample was first stored in the dark, irradiated with visible light ($\lambda > 420$ nm) for 5 min, and then stored in the dark for 90 min. This procedure was repeated three times.
the dried silica particles. The particle color is observed to be orange-red in the dark, whereas the particles discolor under visible light irradiation. The original orange-red color is regained when the particles are stored in the dark. This color change has been examined using visible light absorption spectroscopy (reflection mode), as shown in Figure 5b. The characteristic absorption peak of the MC form at a wavelength of 521 nm disappears under visible light irradiation, and the peak is gradually regained in the dark and attains the original level within 90 min. The negative photocromism observed here is rationalized by the fact that the surface silanol groups stabilize the thermodynamically unstable MC form in air.37 Figure 5c shows the changes in absorbance during the MC–SP–MC isomerization cycle, and one can see complete photoreversibility of the adsorbed surfactant layer on colloidal silica particles. On the basis of these experimental results, we conclude that it is possible to fabricate photoresponsive smart surface coatings in aqueous media as a result of spontaneous adsorption of the spiropyran-modified surfactant.

In Situ AFM Studies of Photoresponsive Surfactants Adsorbed on Flat Silica Plates. The purpose of our current study is to characterize the adsorption of the spiropyran-modified cationic surfactant on oppositely charged silica surfaces and the subsequent photoresponsive behavior of the adsorbed surfactant layer. To address this research purpose, we have performed in situ AFM measurements. On the basis of the adsorption isotherm data, we have selected two surfactant concentrations for AFM measurements: one is 0.1 mmol dm\(^{-3}\) (low-surfactant-concentration region) and the other is 0.8 mmol dm\(^{-3}\) (high-surfactant-concentration region corresponding to the adsorption saturation region for the two isomers). We shall present the soft-contact AFM deflection images and surface force data in the following discussion.

Figure 6a shows the force curves measured at 0.1 mmol dm\(^{-3}\) SP-Me-6 aqueous solution in the presence of 10 mmol dm\(^{-3}\) NaBr. In the first adsorption stage, the surfactant solution was introduced into the AFM system in the dark and hence the surfactant molecules exist as the MC form at the silica/aqueous solution interface. Then, incident visible light induces the photoisomerization to the SP form, and again the system was equilibrated in the dark to induce the reverse isomerization to the MC form. Clearly, an attractive interaction is observed for both isomers. Importantly, the attractive interaction observed for the SP form (under visible light irradiation) is significantly greater than that observed for the MC form (in the dark), and the attractive interactions observed here are reversibly photochangeable. We assume that these attractive interactions originate from the hydrophobic interaction between the adsorbed surfactant layers formed on the AFM cantilever tip and the silica surface,38 and the greater attractive interaction observed for the SP form reflects the more hydrophobic nature of the isomer.

The corresponding soft-contact AFM images are shown in Figure 6b (MC–SP–MC isomerization cycle at 0.1 mmol dm\(^{-3}\) SP-Me-6). Although no significant surface features are present in these AFM images (because of the hydrophobic attractive interaction), the adsorbed layer morphology is reversibly changed in response to the photoisomerization. The greater hydrophobic attraction observed for the SP form results in a fainter image when compared with the AFM images obtained for the MC form.

An increased surfactant concentration (to 0.8 mmol dm\(^{-3}\)) results in significant changes in surface force data and AFM images for both isomers. Figure 7a shows the force curves measured during the MC–SP–MC photosomization cycle. A repulsive interaction is detected for both isomers. These repulsive interactions are seen from ca. 12 nm in apparent separation. Unfortunately, it is not possible to determine an accurate decay length for these repulsions because of their poor signal-to-noise ratio. However, the weak repulsions observed here are deemed to be

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(38) Bremmel, K. E.; Jameson, G. J.; Biggs, S. Colloids Surf., A 1999, 146, 75.
electrostatic in nature, taking the adsorption mechanism into consideration, and are consistent with the low dispersion stability of colloidal silica suspensions at these surfactant concentrations. Then, the force curves experience a jump to contact at 2.5–5 nm. (The push-through distance provides a measure of the adsorbed layer thickness under an applied normal pressure;\(^3^9\) the cantilever tip senses the forces from the adsorbed layer and then experiences adhesive contact with the substrate at a specific separation.) It seems that the general shapes of these force curve data resemble each other, but the jump-to-contact distance depends on the isomerization cycle (i.e., the apparent separation shifts to the left side when the adsorbed layer experiences the MC–SP–MC isomerization cycle). This suggests that the adsorbed layer is gradually flattened during the isomerization cycle, probably because of the normal pressure (compression) that will be more significant during repeated AFM scanning.

The corresponding soft-contact AFM images obtained at 0.8 mmol dm\(^{-3}\) (MC–SP–MC cycle) are shown in Figure 7b. These AFM images were obtained at scanning forces in the weak electrostatic repulsion region. One can see small circular dots (ca. 10 nm in diameter) in these images. On the basis of their jump-to-contact distance data shown in Figure 7a (corresponding to the \(z\) heights of these aggregates), we suggest the presence of disklike (or flattened spherical) surface aggregates for both isomers. One may notice that, when the adsorbed layer undergoes the MC–SP–MC isomerization cycle, the diameter of these aggregates increases and the image resolution becomes poor. Again, we assume for this reason that the adsorbed layer is gradually flattened as a result of the normal pressure being applied during repeated AFM scanning, which is consistent with the force curve data shown in Figure 7a. The combination of Figure 7a,b leads to the conclusion that, during the MC–SP–MC isomerization cycle at 0.8 mmol dm\(^{-3}\) (in the high-surfactant-concentration region), the adsorbed layer morphologies and the corresponding force curve data are not dramatically changed in response to the photoisomerization, as we have observed at 0.1 mmol dm\(^{-3}\) (in the low-surfactant-concentration region).

In spite of this, we can suggest differences in surface morphologies between the two isomers when the SP form is initially adsorbed on silica under visible light irradiation (in other words, no isomerization cycle). Figure 7c is the soft-contact AFM image of the SP form adsorbed directly onto the silica surface, observed in the adsorption saturation region. One can see spherical aggregates in this image. Importantly, the diameter (ca. 20 nm) is much larger than the diameter of surface aggregates observed in Figure 7b. This is again consistent with the experimental result that the adsorbed amount of the SP form is greater than that of the MC form as a result of the greater hydrophobic nature of the SP form. The combination of Figure 7b,c suggests that the initial isomerization form is a crucial factor determining the adsorbed layer morphology (and hence the surface force) in the adsorption saturation region, although the photoisomerization does take place on silica even at such high surfactant concentrations.

**Conclusions**

We have characterized the adsorption of the spiropyran-modified cationic surfactant (SP-Me-6) on colloidal and flat silica and the subsequent photoresponsive behavior. The adsorption isotherm data reveal that the combination of electrostatic and intermolecular hydrophobic interactions drives the adsorption for both isomers. Hence, the more hydrophobic SP form gives a greater adsorbed amount when compared with the zwitterionic MC form. In situ AFM measurements have demonstrated that dislikelike or flattened spherical surface aggregates are formed in the adsorption plateau region on a flat silica plate, where the SP form gives larger surface aggregates as a result of its greater hydrophobic/associative character. Such a difference in the hydrophobic/associative nature between the two isomers induces reversible changes in the dispersion stability of silica suspensions as well as in the surface force (this is obvious at low SP-Me-6 concentrations), in response to the photoisomerization. Taking the in situ and ex situ color changes into consideration, it seems likely that the photoisomerization occurs reversibly even after surfactant adsorption on silica. We conclude, therefore, that it is possible to fabricate photoresponsive smart surface coatings in aqueous media as a result of the spontaneous adsorption of SP-Me-6. The photoresponsive surface coatings developed here are expected to be useful as a capture/release reaction field of hydrophobic substances.

**Supporting Information Available:** UV–vis absorption spectra of SP-Me-6 before and after visible light irradiation. This material is available free of charge via the Internet at http://pubs.acs.org.

\(^3^9\) Wanless, E. J.; Ducker, W. A. \emph{J. Phys. Chem.} \textbf{1996}, \emph{100}, 3207.
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