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SHORT COMMUNICATION

Microscopic location of photosensitive Malachite Green surfactant in mixed micelle and its photoinduced enhancement of solubilizing power

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Abstract A Malachite Green derivative carrying a long alkyl chain affords photogenerated amphiphilicity by UV irradiation. The behavior of the photoresponsive Malachite Green surfactant was studied in mixed micelle solutions containing cetyltrimethylammonium chloride. We found that the Malachite Green surfactant increases the solubility of oily substance by UV irradiation. The role of the Malachite Green surfactant has been investigated by dynamic light scattering and spectroscopic analysis. The Malachite Green surfactant causes an increase in the micelle size, and its hydrophilic head group lies at the micellar interface. The mechanism of the photoinduced uptake of oily substances is discussed at the viewpoint of the microscopic location of the Malachite Green surfactant in the micelle.

Keywords Photoresponsive surfactant · Mixed micelle · Microscopic location · Photoinduced uptake

Introduction

Surfactants, which contain both hydrophilic and hydrophobic moieties, are likely to undergo molecular aggregation in aqueous media. The molecular aggregation can be controlled by shifting the balance of hydrophobicity and hydrophilicity. If a surfactant contains a photochromic moiety, photoirradiation can be an external trigger to control the hydrophobic/hydrophilic balance without any temperature change or any addition of electrolyte. Molecular design of photochromic surfactants has attracted considerable attention, which may realize a controlled release of entrapped reagents in various applications.

The mostly studied photochromic surfactants contain an isomerizable group, such as azobenzene or stilbene, in the hydrophobic chain or the hydrophilic head group [1–11]. Malachite Green leuconitrile undergoes ionization by UV irradiation [12, 13] and thereby may afford another class of photochromic surfactant which can cause a change in the head group polarity. We have thus designed a Malachite Green derivative carrying a long alkyl chain **1** [14, 15] (Scheme 1).

Under dark conditions, compound **1** behaves only as a lipophilic compound. Compound **1**, when ionized photochemically, exhibits both hydrophilicity and hydrophobicity by its triphenylmethyl cation and its long alkyl chain, respectively, resulting in photogenerated amphiphilicity. The photogenerated electrical charge on the head group is expected to provide a drastic effect on the molecular aggregation. Actually, we have observed significant changes induced by compound **1** in the critical micelle concentration (cmc) [14] and the solubility of oily substance into the micelle solution [15]. The photoinduced effect of compound **1** is remarkable, but it is not fully understood how the photoresponsive surfactant contributes to the micelle aggregation. For the photochemical control of micelle aggregation, several works have been reported on photochromic surfactants containing azobenzene or stilbene moiety, which were dispersed in aqueous media to form

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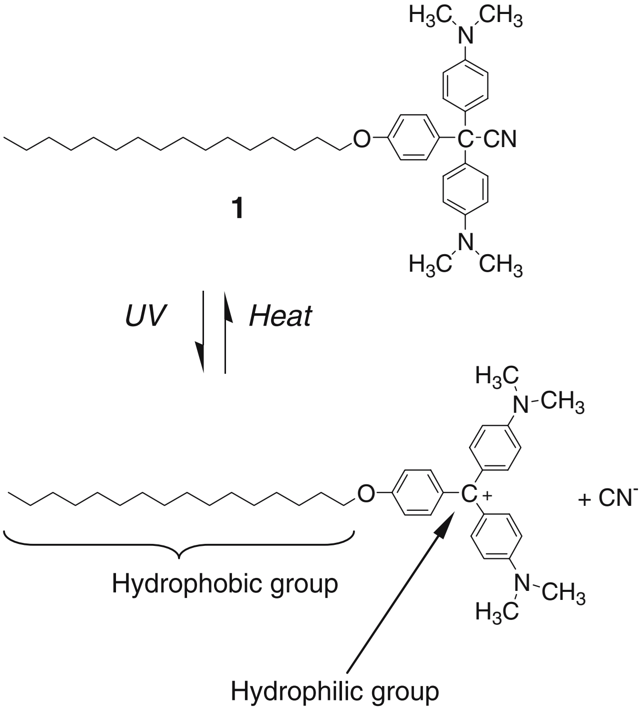


Scheme 1 Photogenerated amphiphilicity on compound **1**

micelles [10, 11]. In these systems, only photochromic surfactant constituted micelles, and the role of photochromic surfactant was apparent. In contrast, the photocontrolled micelle aggregation in the present system of compound **1** has been attained when the functionalized surfactant **1** is mixed with a conventional surfactant. Therefore, there are some interactions between the photochromic surfactant **1** and the conventional surfactant. With respect to mixed layer assemblies, such as LB membrane or vesicle, several investigations have been conducted on the aggregation phenomena induced by photochromic surfactants, the environment around photochromic surfactants, and the structures of assemblies [1–8]. These studies elucidated the mechanism of the photoresponsive leakage, membrane mobility, and layer packing [1–8].

In this work, we report the contribution of compound **1** to the increased solubility of oily substance into micelle solutions by means of light scattering and spectroscopic methods. The light scattering analysis can offer some insight into the solubilizing volume of micelles. Because triphenylmethyl cation is known to be useful to study hydrophilic environment [16–18], the microscopic environment around compound **1** can be informed without any additional probe molecule. And then we discuss the relationship of the micelle size and microscopic environment of compound **1** to reveal how functionalized surfactant **1** increases the solubility of oily substance by photoirradiation.

Material and methods

Materials

The synthesis of compound **1** was previously described [14, 15]. Cetyltrimethylammonium chloride (CTAC) was recrystallized from tetrahydrofuran (THF). Deuterium oxide had a purity of 99.9%. Water was deionized. Methanol, ethanol, octanol, acetonitrile, acetone, and THF were of spectroscopy grade for absorption spectra. Other materials were of analytical grade and were used without further purification.

Preparation of solutions

CTAC micelle solutions with and without a Malachite Green derivative were prepared using 0.1 mol·dm^{-3} acetate buffer (pH 4.8). Even without photoirradiation, the ionization of compound **1** was strongly promoted in solutions more acidic than pH 4.0, exhibiting an absorption peak in the visible light region which was assigned to ionized **1**. When the pH of the sample solution was above 5.0, no absorption peak was observed in the visible light region. This indicates that the photoionized **1** was immediately hydroxylated with the disappearance of the positive charge on the Malachite Green moiety. Therefore, an appropriate buffer solution was required for any samples in this work except Malachite Green oxalate solutions. Photoirradiation was continued for 15 min on the solutions containing compound **1**. UV light source (<330 nm) was a xenon lamp (500 W) equipped with a photoguide tube and a Toshiba UV-D33S filter. The concentration of Malachite Green derivatives was 1.0×10^{-5} mol·dm^{-3} for the ^{1}H NMR and dynamic light scattering measurements. For the spectroscopic measurements, a Malachite Green derivative concentration of 1.0×10^{-6} mol·dm^{-3} was required to obtain the appropriate absorbance.

^{1}H NMR

The sample solutions for NMR measurements were prepared in D_2O containing 1,4-dioxane (1 vol.%) as the internal reference. Benzene was added in excess (approximately 0.1 cm^3) to a 1-cm^3 sample solution, which was then stirred for saturation. The excess benzene caused neither reversed micelle nor emulsion in the prepared solutions. The sample was withdrawn by a syringe just before the measurement so as not to include the excess benzene. The experiment temperature was 25 °C. NMR measurements were carried out on a JOEL JNM-270 instrument operating at 270 MHz. The experimental uncertainties associated with the NMR measurements were ±1%.

Dynamic light scattering

Dynamic light scattering measurements were made using an Ohtsuka DLS700 instrument equipped with a helium–neon laser. The solutions were filtered first by a 0.45-μm Millipore filter and then by a 0.1-μm Millipore filter. Measurements were performed at 45° and 25 °C. The experimental values of diameter were in errors within 4%.

Results and disccusion

Photoinduced solubilization of benzene in micelle solution

We have previously reported the simple relationship between the solubility of benzene and the NMR chemical shift of benzene in micelle solutions [15]. Based on the relationship [15], the benzene solubility in sample solutions was determined, and it was plotted against CTAC concentration as shown in Fig. 1.

The CTAC concentrations in Fig. 1 are higher than its cmc. Because the higher concentration of surfactant results in the higher concentration of micelle, the benzene solubility increases with the CTAC concentration (Fig. 1, empty squares). The CTAC solution containing 1.0×10^{-5} mol·dm^{-3} of compound **1** (Fig. 1, filled circles) afforded similar solubility to the CTAC solutions without compound **1** (Fig. 1, empty squares) over the whole concentration range of CTAC. The obvious change in the solubility was obtained by UV irradiation on the solution containing compound **1** and CTAC in the concentration range from 4 to 20 mmol·dm^{-3} (Fig. 1, empty circles). Though photoionized **1** causes the remarkable increase in the solubility, it is not well understood how the photogenerated amphiphilicity contributes to the enhanced solubility. Thus, we focused on Malachite Green oxalate (MG+) (Scheme 2) as a model compound which is completely ionized and considered to be the hydrophilic head group of surfactant **1**.

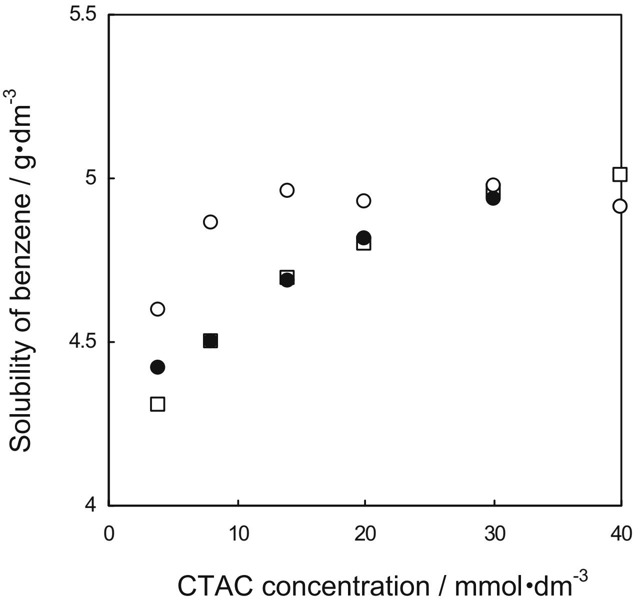


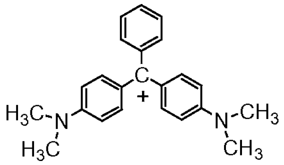
Fig. 1 Solubility of benzene in CTAC solution under dark conditions (*filled circles*, *empty squares*) and after UV irradiation (*empty circles*). Concentration of **1**: 0 mol·dm^{-3} (*empty squares*), 1.0×10^{-5} mol·dm^{-3} (*filled circles*, *empty circles*)

Figure 2 shows the benzene solubility in CTAC solutions containing 1.0×10^{-5} mol·dm^{-3} of MG+ (Fig. 2, filled squares) in comparison with the benzene solubility in CTAC solutions without MG+ (Fig. 2, empty squares). There is no distinct difference in the solubility between the CTAC solutions with and without MG+. This indicates that MG+ hardly induces any change in the benzene solubility. The solubility in micelle solution is related to the micelle concentration and the micelle aggregation number [19, 20]. Because the concentrations of compound **1** and MG+ are considerably lower than that of CTAC, the micelle concentration is hardly affected by the addition of compound **1** and MG+. Booth et al. [21] reported the solubilization of a drug with a poor water solubility into the micelle solutions of a copolymer which has hydrophilic and hydrophobic blocks with various lengths. They showed that the solubility per the hydrophobic weight of the copolymer depends on the micelle aggregation number and concluded that the micelles with large hydrophobic cores are advantageous for the solubilization of oily substance. Hence, in our system, the benzene solubility is considered to be attributed primarily to the hydrophobic core of the micelle in Figs. 1 and 2.

Micelle size

To obtain information about the micelle size, dynamic light scattering experiments were carried out. The diameter of micelle is shown in Table 1. The micelles formed by CTAC afforded a diameter of 4.3 nm which is consistent with the value estimated by Tanford [22]. The diameter of micelle in the system of CTAC with MG+ (1.0×10^{-5} mol·dm^{-3}) is 7.2 nm. Since micellar growth based on the solubilization was reported by several groups [23–25], the increased size with a diameter of 7.2 nm in the system of CTAC with MG+ is explained by the MG+ solubilization into the micelle. The bulkiness of compound **1** provides the greater effect on

Scheme 2 Chemical structure of MG+



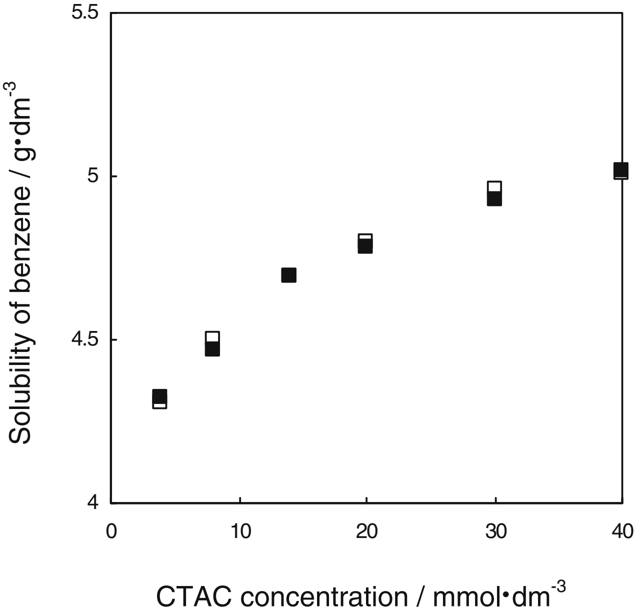


Fig. 2 Solubility of benzene in CTAC solution containing MG+. Concentration of MG+: 0 mol·dm^{-3} (*empty squares*), 1.0×10^{-5} mol·dm^{-3} (*filled squares*)

the micelle size than MG+ does. The diameter is 8.1 nm under dark conditions and 8.5 nm after UV irradiation in the system of CTAC and compound 1.

Though the micelle in the system of CTAC with compound **1** under dark conditions has bigger size than that in the system of CTAC without compound **1**, the benzene solubility remains unchanged (Fig. 1). Under dark conditions, compound **1**, which showed no absorption peak in the visible light region and thereby was not ionized, is simply a lipophilic compound. Therefore, compound **1** occupies the hydrophobic core of the micelle. Consequently, there is no space to allow the higher benzene solubilization than that for the system of CTAC without compound **1**. Therefore, in spite of the bigger size, the solubilizing power of the micelle was not changed by the addition of compound **1**. On the contrary, after UV irradiation, the benzene solubility was increased. This means that the diameter of 8.5 nm is responsible for the larger core of micelle than that for the system of CTAC without compound **1**. Thus, photoionized **1** is not considered to occupy the micelle core.

Table 1 Dynamic light scattering measurements for micellar size determination

Solution	Under dark conditions Diameter (nm)	After UV irradiation
CTAC[a]	4.3	–
CTAC[a] and MG+[b]	7.2	–
CTAC[a] and **1**[b]	8.1	8.5

[a] Concentration is 40 mmol·dm^{-3}.
[b] Concentration is 1.0×10^{-5} mol·dm^{-3}.

Spectroscopic analysis

Several probe molecules are applied to investigate microscopic environment of ordered assemblies. Triphenylmethane dyes act as the indicator [16–18, 26, 27], with a significant absorption peak in the visible light region, which is sensitive to the solvent employed [16, 18]. We examined the spectral dependence of MG+ in solvents with varying dielectric constant (Fig. 3). The peak was red-shifted in the solvent with a low dielectric constant, and, particularly, the solvents of similar chemical structure, such as the primary alcohols, give a clear dependence of the absorption wavelength on dielectric constant. This phenomenon resembles that of Brilliant Green reported by Karukstis et al. [18].

Because compound **1** has a triphenylmethyl cationic moiety after UV irradiation, some information about the microscopic environment around photoionized **1** can be obtained. We therefore compared the wavelength at maximum absorbance (λ_{max}) of photoionized **1** with that of MG+ in CTAC micelle solution. Figure 4 shows the λ_{max} of MG+ in the solutions of various CTAC concentrations. When the CTAC concentration is lower than 4 mmol·dm^{-3}, the λ_{max} of MG+ is constant at 617 nm. This reflects a polar environment similar to water (Fig. 3 affords 616 nm for the λ_{max} in water). In CTAC concentrations higher than 7 mmol·dm^{-3}, the peak of MG+ shifted to the longer

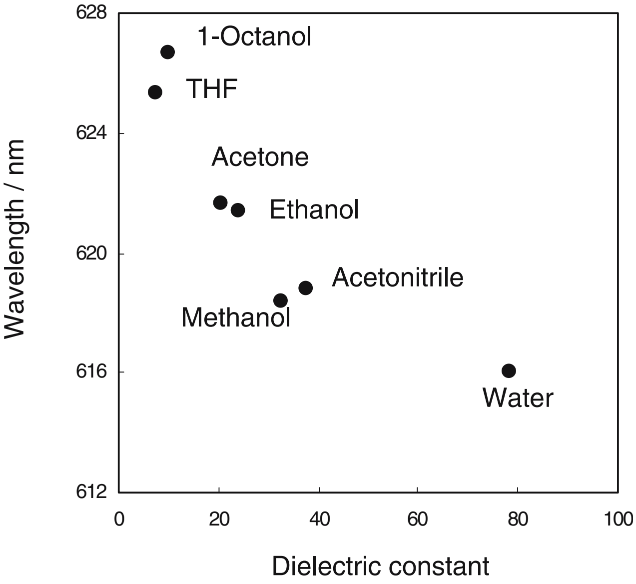


Fig. 3 Solvent dielectric constant dependence of wavelength at absorption maximum of MG+. The values of dielectric constants are taken from Lide [28]

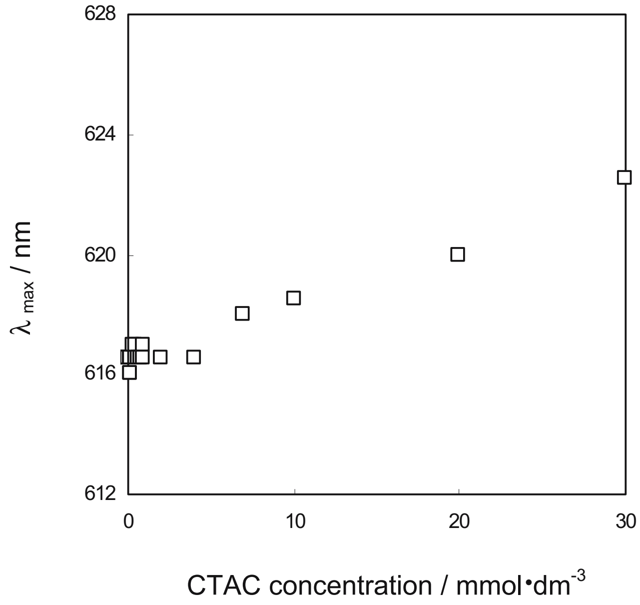


Fig. 4 Wavelength at absorption maximum of MG+ in solutions with varying CTAC concentration

wavelength with increasing CTAC concentration, indicating that MG+ is in a low polar environment. Thus, Fig. 4 tells that MG+ is dissolved in the buffer solution at the micelle concentration lower than 4 mmol·dm^{-3} of CTAC. The MG+ then goes into the core of micelle at the higher micelle concentration than 7 mmol·dm^{-3} of CTAC. It is interesting to note that compound **1** afforded a different result from MG+, i.e., photoionized **1** did not exhibit such red shifts as seen in the MG+ system (Fig. 5). The λ_{max} of ionized **1** is almost constant (617 nm) at the CTAC concentrations higher than 4 mmol·dm^{-3}. The constant wavelength (617 nm) indicates that ionized **1** is in a polar environment, not in the micelle core. Comparing 617 nm of photoionized **1** with 622.5 nm of MG+ at 30 mmol·dm^{-3} of CTAC, there is a decisive difference between the locations of MG+ and photoionized **1**. Photoionized **1** is located at the interface of the micelle and water, a polar environment, and its long alkyl chain is expected to be in the lipophilic micelle core. The difference between MG+ and photoionized **1** is illustrated in Fig. 6.

Compound **1** is in the lipophilic micelle core under dark conditions. Irradiated by UV light, compound **1** has amphiphilicity and moves to the micellar interface. Consequently, the inner lipophilic volume of micelle is increased to enhance the benzene solubilization. In contrast, MG+ occupies the micelle core and therefore the solubilizing power of the micelle is not increased.

At the concentration of CTAC lower than the cmc (0.1 mmol·dm^{-3}), photoionized **1** provides a peak at the

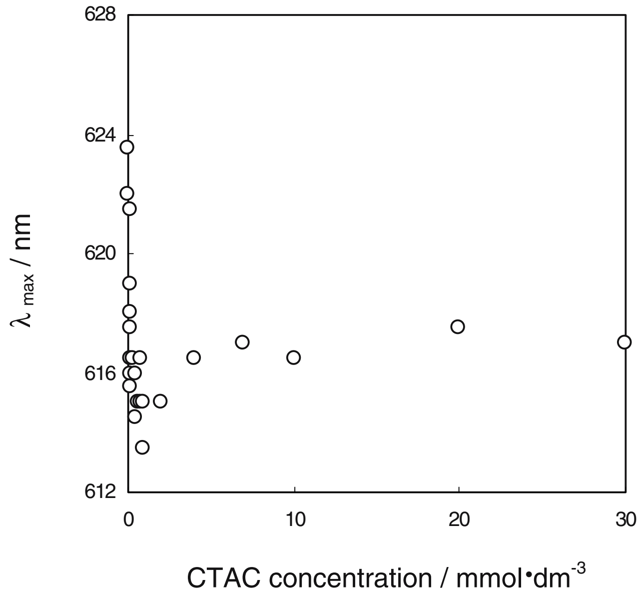


Fig. 5 Wavelength at absorption maximum of photoionized **1** in solutions with varying CTAC concentration. The UV irradiation was carried out for 15 min

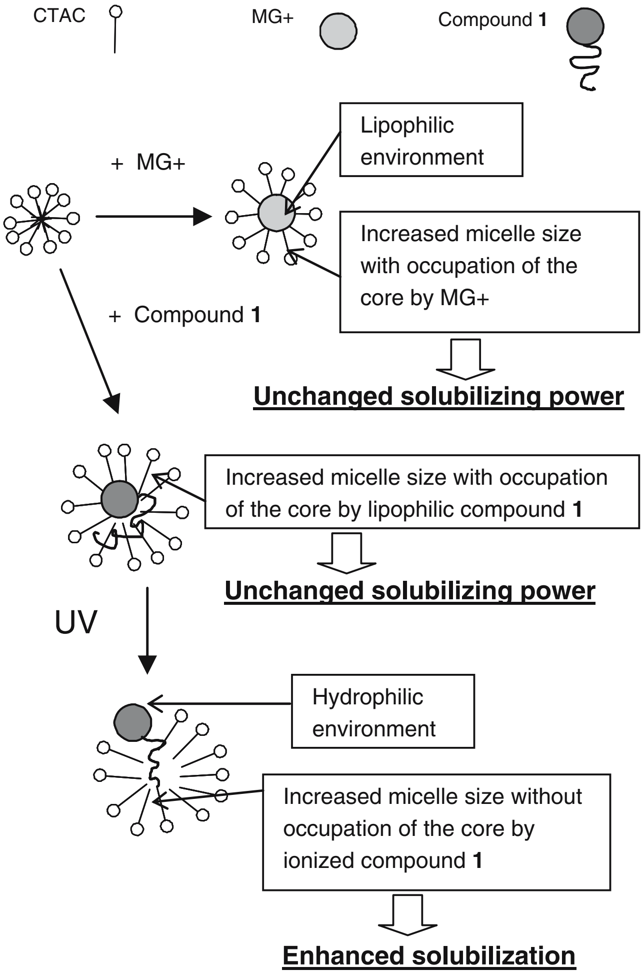


Fig. 6 Conceptual representation of the difference between MG+ and compound **1** of the location in micelle and their resulted solubilizing power

wavelength longer than 617 nm, reflecting a low polar environment. Because electrically neutral compound **1** is hardly dissolved in aqueous solution without micelle, the photoionized reaction of **1** is prevented at the CTAC concentration lower than the cmc. We have reported that the photoionization ratio of **1** is less than 0.05 at the CTAC concentrations lower than 1 mmol·dm^{-3}, increasing to 0.5 at a CTAC concentration of 30 mmol·dm^{-3} [15]. Photoionized **1** is considered to be surrounded by electrically neutral compound **1**, which does not undergo photoionization. Thus, a slight amount of photoionized **1** is affected by a number of electrically neutral (lipophilic) compound **1**, therefore resulting in the peak shift to the longer wavelength at the low CTAC concentrations as seen in Fig. 5.

Conclusions

The mechanism for the photoinduced solubilization of benzene into the mixed micelle solutions containing photochromic compound **1** was investigated. We have shown that photoionized **1** is located at the interface of the micelle which affords a greater diameter of 8.5 nm than that of the micelle without compound **1**, and thereby the mixed micelle with photoionized **1** has a large hydrophobic core for the solubilization. To apply the photocontrol of micelle formation in various fields including those of cosmetics, perfumes, and foods, it is desirable to use the mixed micelle system of commercially available surfactants and functionalized surfactants. Therefore, this study is important for understanding the role of functionalized surfactant in the mixed micelle and for designing the photoresponsive system.

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