

Review Commentary

Photochemical micelle control by long-alkyl-chain Malachite Green

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ABSTRACT: We have designed a Malachite Green leuconitrile carrying a long-alkyl-chain which controls micelle formation photochemically. The Malachite Green derivative, when ionized photochemically, exhibits some hydrophilicity by its triphenylmethyl cation and some hydrophobicity by its long alkyl chain. The behavior of the photoresponsive Malachite Green surfactant was studied in mixed micelle solutions containing cetyltrimethylammonium chloride (CTAC) and a small quantity of the Malachite Green. We found that UV irradiation drastically decreased the critical micelle concentration (cmc) of the mixed micelle solutions and that the Malachite Green derivative realized photoinduced uptake of oily substances based on its photogenerated amphiphilicity. The mechanism of the photoinduced enhancement of solubilizing oily substances is discussed at the viewpoint of the microscopic location of the Malachite Green surfactant in the micelle. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: micelle; photocontrol; photoresponsive compound; Malachite Green

INTRODUCTION

Surfactants, which contain hydrophilic and hydrophobic moieties, spontaneously form assemblies, such as micelle, mono- and multi-layers, liposomes, and reversed micelle. In an aqueous environment, control of the assemblies can be achieved by shifting the hydrophilic and hydrophobic balance. For instance, the control can be done by adding electrolytes, switching pH, and changing temperature. Alternatively, if surfactants contain a suitable chromophore, then photoirradiation can be used as an external trigger, eliminating the need for the composition or temperature changes. Therefore, several classes of photoreactions which can cause a shift in the hydrophilic/hydrophobic balance have been reported. Typical photosensitive surfactants, which contain an isomerizing group, such as azobenzene and stilbene, in the hydrophobic chain or the headgroup, undergo *cis/trans* isomerization and lead to a change in the packing of the assemblies and the resulting disruption.^{1–10} Figure 1 shows the photochemical reaction of the surfactant containing azobenzene moiety, which is synthesized by Kunitake *et al.* The steric change in the hydrophilic chain

is provided by photoirradiation.⁷ The *cis/trans* isomerization also has been applied to the so-called ‘gemini-surfactants’ which caused the photoinduced change in assemblies.^{11–13} The second type of photoreaction leading to destabilization of the assemblies is photolysis. Cleavage reactions between hydrophobic and hydrophilic moieties should result in the spontaneous destabilization of assemblies. Photolysis of benzylammonium lipid, as shown in Fig. 2, has been found to induce headgroup cleavage.¹⁴ The third type of photoreaction, which we focus on in this review, involves a change in the hydrophilicity of the head group. The reaction may involve photoionization of head group as illustrated in Fig. 3, or may represent more modest changes in polarity. Triphenylmethanenitriles and spiropyrans afford the third type of compounds which generate electric charges on photoirradiation. Long-alkyl-chain spiropyrans have been synthesized by several groups and investigated in mixed mono-layers on water and glass substrates.^{15–18} In contrast, few studies have been carried out on the surfactant containing triphenylmethanenitrile moiety. Triphenylmethanenitrile undergoes photoionization by dissociating cyanide ion with a high quantum efficiency,^{19,20} thus affording a positive charge generation on the molecule by UV irradiation. Fukunishi *et al.*²¹ have reported that a long-alkyl-chain Malachite Green which does not carry cyanide group is not a photoresponsive

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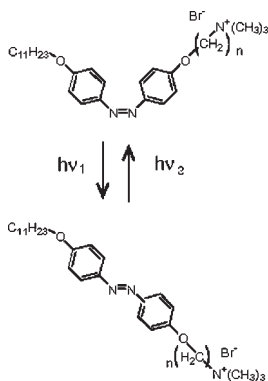


Figure 1. Photochemical reaction of surfactant containing azobenzene moiety⁷

surfactant. We have designed a Malachite Green leuconitrile possessing a bis(monoaza-15-crown-5) structure, which shows a drastic change, so-called ‘all-or-none’ type switching, in the cation binding upon photoionization (Fig. 4).^{22–24} The electrostatic repulsion between the photogenerated positive charge and a crown-complexed metal ion results in an effective release of the metal ion. The photocontrol of complexation indicates that the generated positive charge is an efficient trigger to control the properties. This prompted us to apply Malachite Green leuconitrile to an amphiphilic compound and we have recently reported that a long-alkyl-chain Malachite Green leuconitrile (LMG) undergoes photoionization and that it exhibits hydrophilicity by its triphenylmethyl cation and hydrophobicity by its long-alkyl-chain (Fig. 5).^{25,26} Consequently, the Malachite Green generates an amphiphilicity on the lipophilic compound by photoirradiation. A typical absorption-spectral change of a LMG solution before and after photoirradiation is shown in Fig. 6. An absorption peak around 270 nm, which was decreased by UV irradiation, can be assigned to the electrically neutral leuconitrile form of LMG. Its ionized form was confirmed by the appearance of a peak at 610 nm after UV irradiation, indicating the photoinduced ionization of LMG.

Since the third reaction, that is, photoionization at the head group, is expected to cause a drastic change in the hydrophilic and hydrophobic balance, it can be an effective approach to alter the character of assemblies. Accordingly, the photoresponsive surfactant can trigger to change the property of the whole assemblies, being so-called ‘command compound’ which affords more sophisticated systems. The idea was proposed by

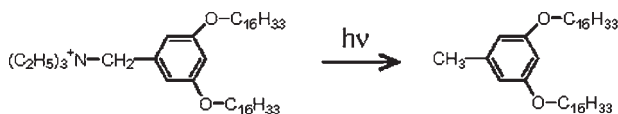


Figure 2. Photochemical reaction of benzylammonium lipid¹⁴

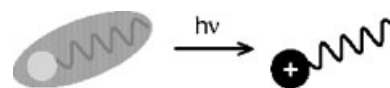


Figure 3. Photoresponsive surfactant which undergoes changes in head group polarity

Ichimura *et al.*^{27,28} and they represented ‘command surface system’ by liquid crystal aligned by azobenzene mono-layer. By *cis/trans* isomerization of an azobenzene compound on the substrate, alignment changes of the bulk liquid crystals took place. In such a system, there was no need of photosensitive liquid crystals and then conventional liquid-crystalline molecules can be applied for changing the property.

This review is concerned with the photoresponsive ‘command compound’ in micelle aggregation. We discuss the possibility of LMG to command micelle formation as compared with the other system. We also mention the mechanism for triggered micelle aggregation by LMG.

PHOTOCHEMICAL CHANGE IN CRITICAL MICELLE CONCENTRATION

Critical micelle concentration (cmc) is minimum surfactant concentration to form micelle and then indicates the property of the micelle aggregation. The cmc determination is often performed by measuring the electric conductivity of sample solution. The specific conductivity increased linearly with surfactant concentration and the

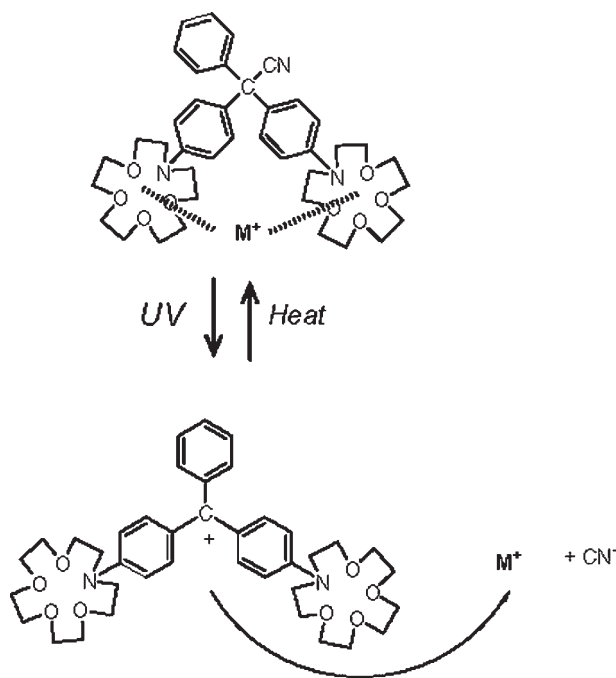


Figure 4. Photochemical control of cation binding by bis-crowned Malachite Green leuconitrile

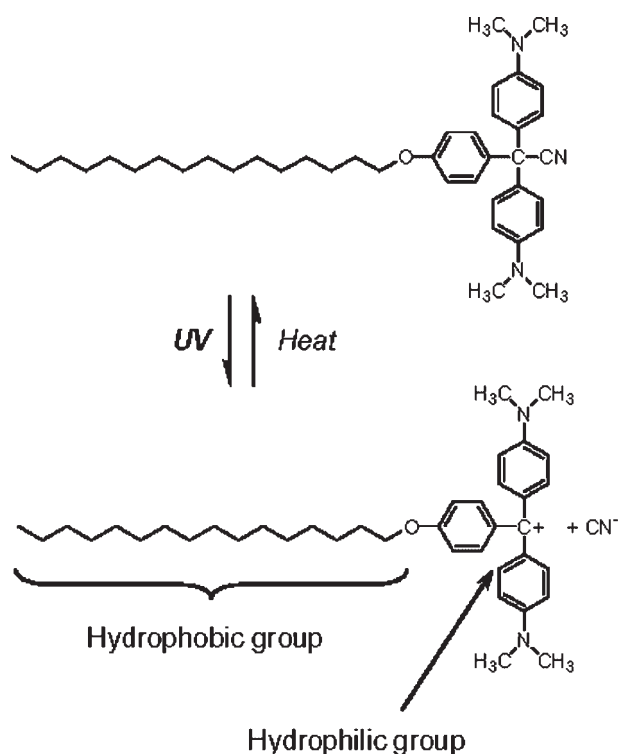


Figure 5. Photochemical reaction of long-alkyl-chain Malachite Green (LMG)

slope of the conductivity curve changes abruptly at a certain concentration. The cmc values correspond to the bending point on the conductivity curve.²⁹ Figure 7 shows the dependence of specific conductivity of a mixed micelle solution containing LMG and cetyltrimethylammonium chloride (CTAC) prepared by 0.1 mol dm⁻³ acetate buffer on CTAC concentration. LMG is a

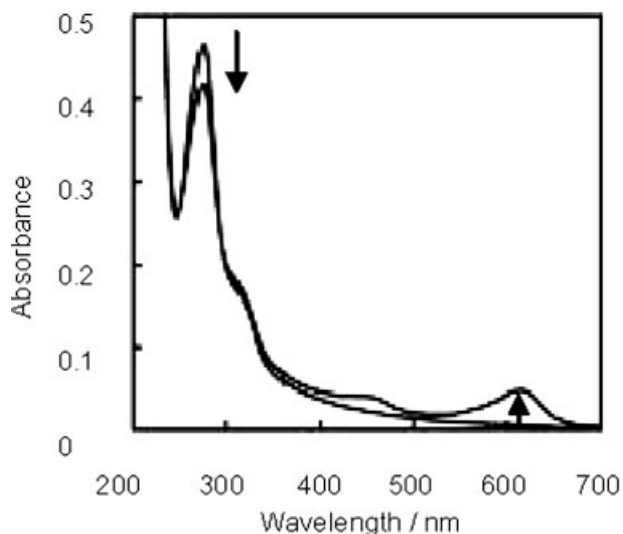


Figure 6. Absorption-spectral changes of 0.1 mol dm⁻³ acetate buffer solution containing 4.0 mmol dm⁻³ CTAC and 1.0 × 10⁻⁵ mol dm⁻³ LMG under dark conditions and after UV irradiation for 15 min. The arrows denote changes by photoirradiation. (Taken from Ref. 26)

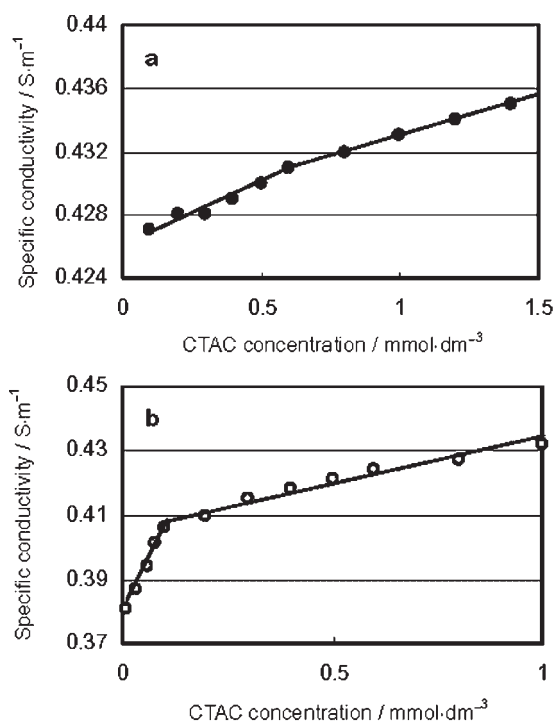


Figure 7. Specific conductivity of 0.1 mol dm⁻³ acetate buffer solution containing CTAC and 1 × 10⁻⁵ mol dm⁻³ LMG as a function of CTAC concentration under dark conditions (a) and after UV irradiation (b). (Taken from Ref. 25)

functionalized compound and CTAC is a conventional surfactant.

Under dark conditions, the cmc was found to be 0.6 mmol dm⁻³ (Fig. 7a), which is smaller than a reported value (1.3 mmol dm⁻³) for CTAC.³⁰ Since addition of electrolytes such as NaCl generally diminishes cmc values of surfactants,^{30,31} the smaller cmc value was caused by acetate ion in buffered sample solutions. The effect of acetate ion on the cmc explains the increased cmc in the samples prepared by 0.01 mol dm⁻³ acetate buffer solution (Fig. 8a). In the diluted buffer solution, the cmc was found to be 0.8 mmol dm⁻³ which is closer to the reported value of 1.3 mmol dm⁻³. UV irradiation causes obvious changes in the cmc (Fig. 7b). The cmc was shifted from 0.6 to 0.1 mmol dm⁻³ by photoirradiation and the cmc change was caused by 1.0 × 10⁻⁵ mol dm⁻³ LMG. The photoinduced change in the cmc was not very significant in 0.01 mol dm⁻³ acetate buffer solution, where the cmc was 0.8 mmol dm⁻³ under dark conditions and 0.6 mmol dm⁻³ under UV-irradiated conditions (Fig. 8). In order to investigate whether the photoinduced change of the cmc is remarkable and therefore whether LMG can be the 'command compound', let us compare it with other types of photoresponsive surfactants. Sakai *et al.*¹⁰ reported a cmc change of 4-butylazobenzene-4'-(oxyethyl) trimethylammonium bromide which undergoes *cis/trans* isomerization and the cmc was found to be 2.7 mmol dm⁻³ for *trans* isomer and 8.2 mmol dm⁻³ for

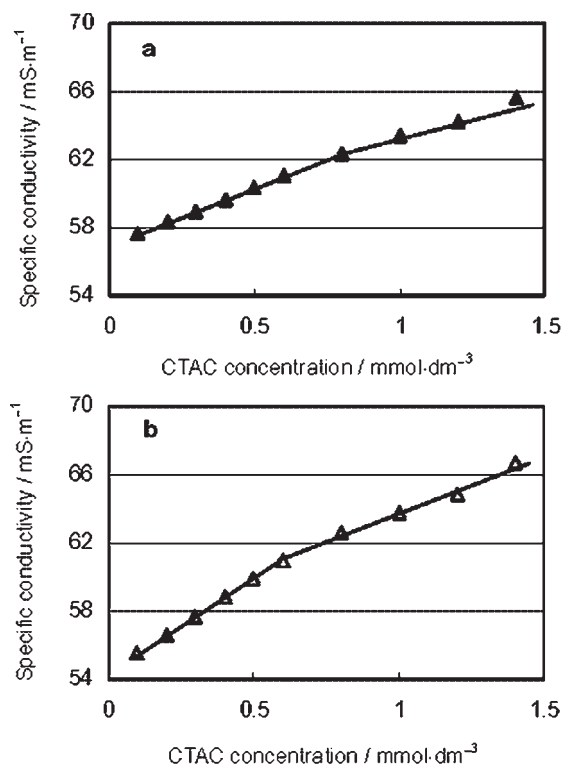


Figure 8. Specific conductivity of 0.01 mol dm^{-3} acetate buffer solution containing CTAC and $1 \times 10^{-5} \text{ mol dm}^{-3}$ LMG as a function of CTAC concentration under dark conditions (a) and after UV irradiation (b)

the *cis* isomer. Tazuke *et al.*³² have measured the surface tension of the surfactants containing a spiropyran moiety at head group. Though the exact value of the cmc for the spiropyran surfactant was not given, the data of surface tension indicate a difference of less than 0.1 mmol dm^{-3} in the cmc change induced by the photoisomerization from the zwitterionic form to the neutral form. It should be considered that the photoresponsive surfactant forms micelles by itself in the azobenzene and spiropyran systems, which are completely different from our mixed micelle system of LMG and CTAC. Table 1 summarizes the difference in the photoinduced cmc change and the concentration of the photoresponsive surfactants to cause the difference. To induce the cmc change in our system, $1.0 \times 10^{-5} \text{ mol dm}^{-3}$ of LMG is required. On the other hand, a much greater amount of the photoresponsive surfactants is required for the azobenzene and spiropyran systems, that is, the photocontrol of micelle formation was carried out by photoirradiation on the azobenzene

surfactant solution at the concentration higher than 2.7 mmol dm^{-3} and the spiropyran surfactant solution at the concentration higher than $6.0 \times 10^{-5} \text{ mol dm}^{-3}$. Therefore, Table 1 indicates that a small quantity of LMG triggers the cmc changes of the micelle assembly.

PHOTOINDUCED UPTAKE OF OILY SUBSTANCE IN MICELLE SOLUTIONS

One of the desired functionality for micelle is to solubilize a poorly water-soluble substance in the micelle interior, since the solubilization is applied in various fields. Nuclear magnetic resonance (NMR) is a powerful tool for investigation of various properties of substances and has been applied to the elucidation of colloid-chemical behaviors in aqueous solutions.³³ We have reported a simple relationship between the solubility of benzene and NMR chemical shift of benzene in micelle solutions.²⁶ When a slightly water-soluble compound, for example, benzene, is solubilized into an aqueous solution of a surfactant, some of the benzene molecules are in surfactant micelles and others in the bulk water phase. They are constantly exchanged between these two environments, thus maintaining an equilibrium. The chemical shift of the benzene proton is generally different in these two environments and only one signal will appear at an appropriately averaged position if the exchange is rapid. Therefore, the observed chemical shift of benzene is the weighted average of the chemical shifts in the aqueous phase and in the micellar phase. Thus, we have obtained the relationship between observed chemical shift and the solubility of benzene in the solution. The detailed study has been reported in the Ref. 26. Based on the relationship, the benzene solubility in micelle solutions was determined and was plotted against CTAC concentration as shown in Fig. 9. Photoirradiation increased the solubility of benzene for mixed micelle solutions containing CTAC and LMG. A significant change by photoirradiation was attained with 8 mmol dm^{-3} CTAC containing $1.0 \times 10^{-5} \text{ mol dm}^{-3}$ LMG, the benzene solubility changing from 4.55 g dm^{-3} under dark conditions to 4.81 g dm^{-3} by photoirradiation (Fig. 9). It should be noted that a small amount of LMG ($1.0 \times 10^{-5} \text{ mol dm}^{-3}$) induces a significant increase (0.26 g dm^{-3}) in the solubility of benzene. The uptake of ethylbenzene in the micelle of 4-butylazobenzene-4'-(oxyethyl) trimethylammonium bromide was reported and $1.0 \times$

Table 1. Cmc change caused by photoresponsive surfactants

Photoresponsive moiety	Difference in the photoinduced cmc change (mM)	Concentration of photoresponsive surfactant
Malachite Green	0.5	$1.0 \times 10^{-5} \text{ M}$
Azobenzene	5.5^{a}	$>2.7 \text{ mM}^{\text{a}}$
Spiropyran	$<0.1^{\text{b}}$	$>6.0 \times 10^{-5} \text{ M}^{\text{b}}$

^a From Ref. 10.

^b From Ref. 32.

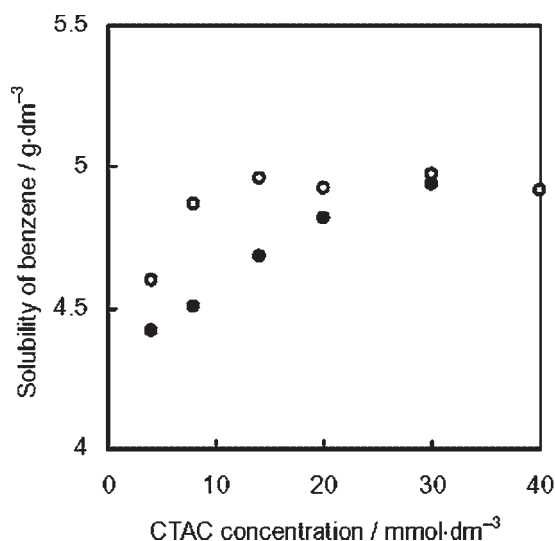


Figure 9. Solubility of benzene in CTAC solution under dark conditions (closed symbols) and after UV irradiation (opened symbols) (270 MHz). Concentration of LMG: 10^{-5} mmol dm⁻³. (Taken from Ref. 26)

10^{-2} mol dm⁻³ of the azobenzene surfactant was required to obtain 0.26 g dm⁻³ of the photoinduced gain in ethylbenzene solubility.¹⁰ As a consequence, the difference between 1.0×10^{-5} mol dm⁻³ of LMG and 1.0×10^{-2} mol dm⁻³ of the azobenzene surfactant suggests that LMG behaves as a command compound for the photoinduced uptake of oily substance in micelles.

As shown in Fig. 9, the photoinduced uptake was enhanced in the solution with more than 4 mmol dm⁻³ of CTAC and for the samples with less than 4 mmol dm⁻³ of CTAC, any distinct change of solubility of benzene was not obtained by UV irradiation. We consider that the solubilizing ability under UV-irradiated conditions is concerned with the amount of ionized LMG. The photoionization ratio of LMG in the solution is plotted against CTAC concentration in Fig. 10. The ratio does not

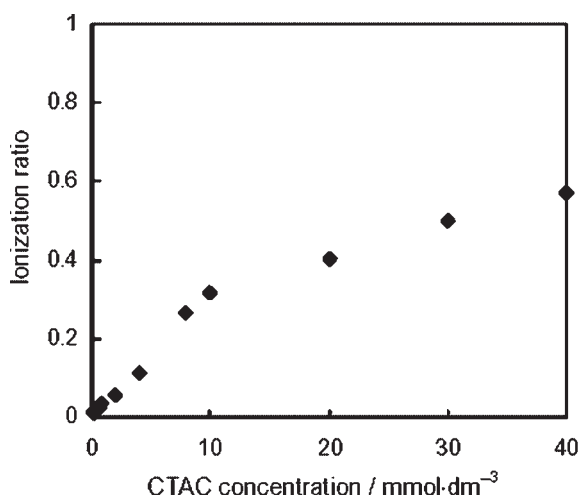


Figure 10. Dependence of photoionization ratio of LMG on CTAC concentration. (Taken from Ref. 26)

show any significant increase up to 4 mmol dm⁻³, above which it increases abruptly. These results coincide with Fig. 9, indicating that the photoionization of LMG contributes to increasing the photoinduced uptake of benzene into micelle solution. The reason for the increasing photoionization ratio with the CTAC concentration is that the electrically neutral LMG is difficult to dissolve in water under dark conditions and that an appropriate concentration of micelle is required to dissolve it. Photoirradiation promotes the ionization of LMG in the CTAC micelle, resulting in the abrupt increase in the photoionization ratio. Besides, a gradual increase of ionization ratio was observed above 20 mmol dm⁻³ of CTAC and this is in good agreement with the data for Fig. 9, that is, the benzene solubility is not highly enhanced by UV irradiation above 20 mmol dm⁻³.

ROLE OF LONG-ALKYL-CHAIN MALACHITE GREEN IN PHOTOINDUCED UPTAKE

For the photochemical control of micelle aggregation, several works have been reported on photochromic surfactants containing azobenzene or stilbene moiety, which were dissolved in aqueous media to form micelles.^{10,32} In these systems, the photochromic surfactant formed micelles by themselves. In contrast, our system of LMG affords the photocontrolled micelle aggregation based on a 'command compound'. Only a small quantity of functional surfactant controls the whole of the micelle aggregates and the photoionized LMG causes the remarkable change in the benzene solubility (Fig. 9). Nevertheless, it is not well understood how the 'command compound' contributes to the enhanced solubility. In order to understand the mechanism of LMG system, we focused on Malachite Green oxalate (MG⁺) (Fig. 11) as a model compound which is completely ionized to yield a hydrophilic head group of LMG. The cmc and the benzene solubility were examined for CTAC solutions containing 1.0×10^{-5} mol dm⁻³ of MG⁺. The bending point in Fig. 12 shows the cmc of CTAC with MG⁺ to be 0.8 mmol dm⁻³ which is higher than 0.1 mmol dm⁻³ for the system of CTAC with photoionized LMG. Thus, MG⁺ does not contribute to decrease the cmc of the mixed micelle solution. Figure 13a shows the benzene

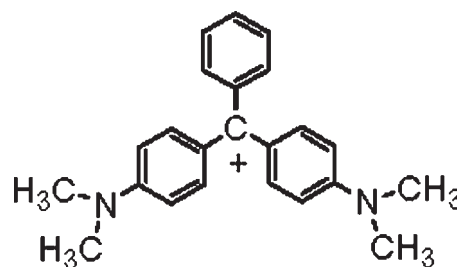


Figure 11. Chemical structure of Malachite Green oxalate (MG⁺)

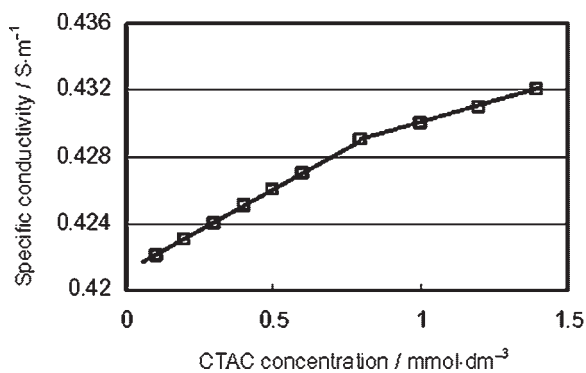


Figure 12. Specific conductivity of 0.1 mol dm⁻³ acetate buffer solution containing CTAC and 1 × 10⁻⁵ mol dm⁻³ MG+ as a function of CTAC concentration

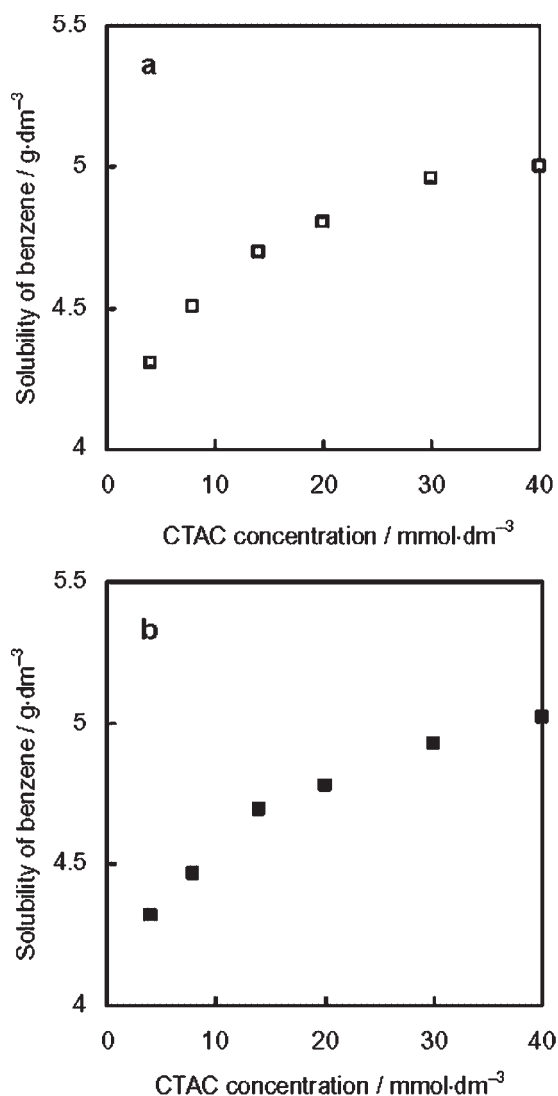


Figure 13. Solubility of benzene in CTAC solution containing 1.0 × 10⁻⁵ mol dm⁻³ of MG+(a) and without MG+(b)

solubility in CTAC solutions containing MG+, in comparison with the solubility in CTAC solutions without MG+ (Fig. 13b). 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 microscopic location of LMG in the mixed micelles is important for understanding the mechanism of the photoinduced enhancement in the solubilizing power. Triphenylmethane dye is a probe molecule with an absorption maximum that depends on the environment for the molecule location. For example, crystal violet affords a wavelength of 590 nm at maximum absorbance (λ_{\max}) in a polar solvent such as water and that of 605 nm in a nonpolar solvent such as benzene.³⁴ For brilliant green, the λ_{\max} is 624 nm in water and 630 nm in 1-hexanol.³⁵ We examined the spectral dependence of MG+ in solvents with varying dielectric constant (Table 2). The peak was red-shifted in solvents with a low dielectric constant. Since LMG has a triphenylmethyl cationic moiety after UV irradiation, some information about the microscopic environment around the photoionized LMG can be obtained. We therefore compared λ_{\max} of photoionized LMG with that of MG+ in CTAC micelle solutions. Figure 14 shows the λ_{\max} of MG+ in the solutions with 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, because Table 2 shows 616 nm for the λ_{\max} in water. In the CTAC concentrations of higher than 7 mmol dm⁻³, the peak of MG+ was shifted to a longer wavelength with increasing CTAC concentration. This indicates that MG+ is in a low polar environment, that is, the core of the micelle. Interestingly, Fig. 15 gives a different result for LMG from that for MG+, that is, the photoionized LMG did not exhibit such red shifts as seen in the MG+ system. The λ_{\max} of ionized LMG is almost constant (617 nm) at the CTAC concentrations higher than 4 mmol dm⁻³. The constant wavelength at 617 nm indicates that ionized LMG is in a polar environment, not in the micelle core. Comparing 617 nm of photoionized LMG with 622.5 nm of MG+ at 30 mmol dm⁻³ CTAC, there is a decisive difference in the location between MG+ and the photoionized LMG.

Table 2. Wavelength at absorption maximum of MG+ in various solvents

Solvent	ϵ^a	λ_{\max}/nm
Water	78.54	616.0
Acetonitrile	37.5	618.8
Methanol	32.63	618.4
Ethanol	24.3	621.4
Acetone	20.7	621.6
1-Octanol	10.3	626.7
Tetrahydrofuran	7.6	625.3

^aFrom Ref. 36.

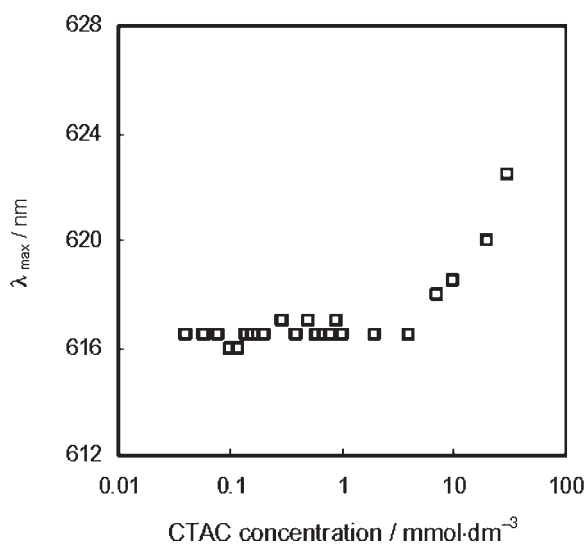


Figure 14. Wavelength at absorption maximum of MG+ in solutions with varying CTAC concentration

The microscopic location of LMG in the micelle is represented in Fig. 16, in comparison with that of MG+. LMG is in the lipophilic micelle core under dark conditions. LMG, when irradiated by UV light, has an amphiphilicity and moves to the interface between the micelle and water, a more polar environment, and its alkyl chain is expected to be in the lipophilic micelle core. 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 remains unchanged. The size of micelle obtained by dynamic light scattering experiments supports the mechanism in Fig. 16. The

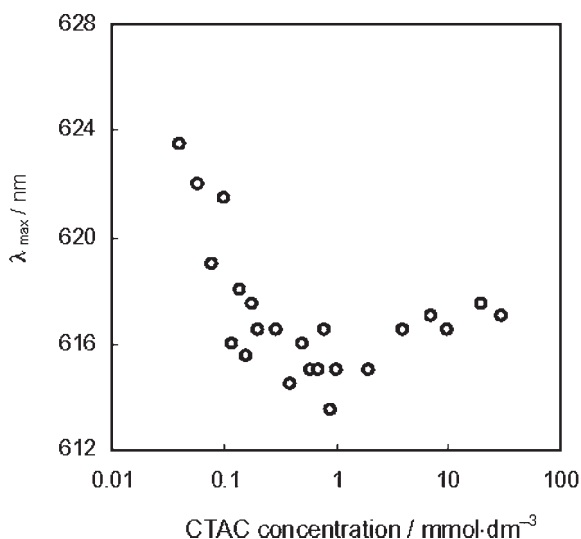


Figure 15. Wavelength at absorption maximum of photoionized LMG in solutions with varying CTAC concentration. The UV irradiation was carried out for 15 min

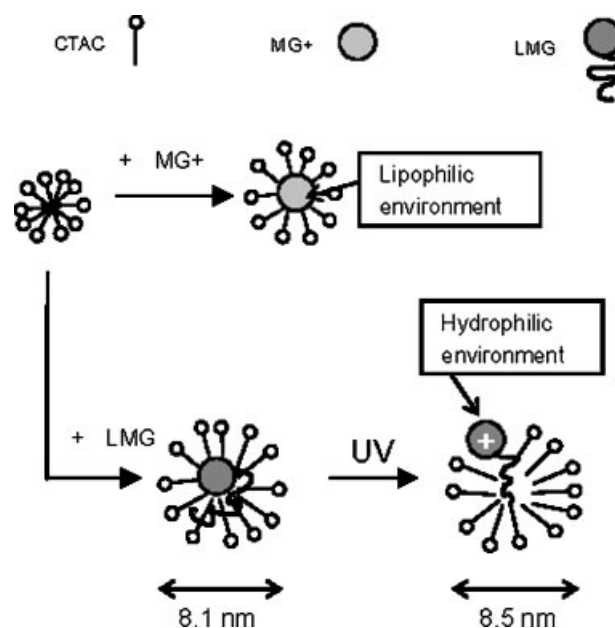


Figure 16. Difference between MG+ and LMG of the microscopic location in CTAC micelle

diameter of the mixed micelle solution containing CTAC and LMG is 8.1 nm under dark conditions and 8.5 nm after UV irradiation. The photoionized LMG is located at the micellar interface and the diameter of 8.5 nm is responsible for the bigger inner volume of the micelle than that under dark conditions.

CONCLUSION

We have shown that photoirradiation on the mixed micelle concentration containing CTAC and a small quantity of LMG results in the significant decrease of the cmc and the enhancement of the solubility of oily compound in the micelle solution. This indicates that the photoionized reaction at the surfactant head group controls the aggregation of the whole mixed micelles. It was thus found that LMG works as a 'command compound' in the mixed micelle system. The microscopic location of LMG in the micelle was elucidated and the role of LMG in the control of micelle aggregation was also discussed.

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