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SHORT COMMUNICATION

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Photochromism of spirobenzopyran in the membrane of surfactant vesicle and in the cavity of cyclodextrins

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Abstract Photochromic reaction of water insoluble 1′,3′,3′-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2′-indoline] (SP) was studied in water with the aid of vesicles and γ-cyclodextrin (γ-CD). In both systems, the photochromic reaction of SP was observable in spite of the low solubility of SP in water. In order to examine the microenvironment around the SP and the reaction product, photomerocyanin (MC), in those systems, the spectrum of MC was measured in various organic solvent of various polarity. Decreasing the polarity of the solvent decreased the peak absorbance and shifted the peak wavelength to the long wavelengths. When the vesicles were used, the reactant, SP, and the product, MC, were solubilized in different regions of different polarity. The reaction substrate was then supposed to have moved from the hydrophobic region of the membrane to the hydrophilic one after the photoisomerization. The photochromic reaction of SP in the presence of γ-CD was slower than in the vesicles and faster than that in methanol. The polarity in the vesicular membrane and the limited rotation of the reactant in the cavity of γ-CD may have influenced the reaction rate. The prolonged light irradiation period resulted in a simultaneous photoreaction and polymerization, producing some unknown side reaction.

Key words Photochromism – spirobenzopyran – surfactant – vesicle – cyclodextrin

Introduction

Gels or polymer materials containing photochromic dyes are known to change their size or wettability by light irradiation [1–3]. The photochromism of dyes can be used to control the characteristics of various materials using light [4]. Among the many photochromic dyes, spirobenzopyran derivatives are most frequently used [5, 6]. Their photochromisms have been studied in organic solvents, or are being studied after they are incorporated in a polymer structure by a polymer reaction or copolymerization [7]. The drastic polarity change of the spirobenzopyran derivatives under light irradiation has been utilized in the photocontrol of affinity chromatography [8], photo-induced reversible wettability control of the surface of a polymer film [9, 10], and the photocontrol of the chain conformation of spiropyran-containing polymers [11, 12]. For example, the value of cos θ (θ: contact angle with pure water) of a polymeric film containing

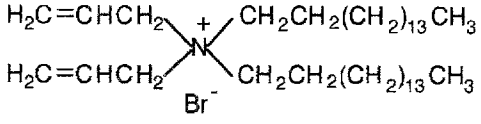
spiro[2H-chromen-2,2′-indoline] moiety increased from nearly zero to 0.19 on irradiation of UV light [10]. However, most of them are insoluble in water [13]. Therefore, little information about the photochromism of spirobenzopyran derivatives in water environment exists.

On the other hand, various surfactant assemblies, e.g., micelles [14] and vesicles [15], and cyclodextrins [16] are known to solubilize various water insoluble compounds in water. The surfactant assemblies can do this by entrapping the compounds in the hydrophobic region of the molecular assemblies, and the cyclodextrins can form an inclusion complex with hydrophobic guest compounds. The entrapped compounds are known to change their reactivities due to the change in the microenvironment [14–18]. Therefore, the surfactant assemblies and cyclodextrins have often been used as models of biomembranes or enzymes. Moreover, the polymerization of a surfactant in a vesicle is known not only to change the mechanical stability of the vesicle but also to change the nature of the membrane itself [17, 18]. Therefore, the polymerization of vesicles may change the microenvironment around the entrapped reactants.

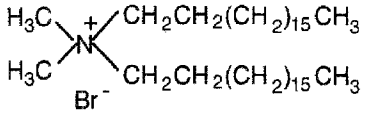
In this paper, we solubilized spirobenzopyran in water using polymerizable surfactants and cyclodextrins, and investigated their influences on the photochromism of a spirobenzopyran derivative. Moreover, the study of the influences of the polymerization of surfactants on the photochromism was also begun.

Experimental

The spirobenzopyran derivative used in this study was 1′,3′,3′-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2′-indoline] (SP). The SP was a commercially available guaranteed reagent (Tokyo Kasei Kogyo Co., Ltd.), and was used as received.



DCAB



DDAB

The surfactants used in this study were polymerizable dicetyldiallylammonium bromide (DCAB) and non-polymerizable dioctadecyldimethylammonium bromide (DDAB). DCAB was prepared according to the method of Tsuchida et al. [19]. DDAB was a commercially available reagent. Both of them have two long alkyl chains, while the DCAB also has two polymerizable allyl groups on the hydrophilic head. These surfactants formed vesicles (biomembrane-like closed molecular assembly) in water when they were sonicated. The SP was first dissolved in ethyl ether followed by evaporation of the solvent from the flask. The resulting thin film of SP was cosonicated with the surfactants in the water.

The cyclodextrins used were commercially available α-, β- and γ-cyclodextrins (Wako Pure Chemical Industries, Ltd.).

Water used for the preparation of solutions was purified before use by deionization and distillation.

Spectrophotometric measurements were conducted using a Shimadzu UV-3100 spectrophotometer equipped with electrically controlled thermostated cell holders and stirrers. The light path of the quartz cell was 1 cm. The light source for the photochromic reaction was a Toshiba 500 W Xe-lamp. A Toshiba filter, Type UV-D33S ($\lambda = 330 \pm 70$ nm) was used for UV irradiation, and Type Y-45 ($\lambda > 450$ nm) was used for visible light irradiation. The distance between the lamp and the center of the quartz test tube or quartz cell containing the photochromic compound was 30 cm. A thermostated cell holder was used to maintain or control the temperature of the solution in the quartz cell during the light irradiation. Dry nitrogen gas was bubbled in the solution during the photoreaction. Before the irradiation of UV light, the SP solution was irradiated by visible light in order to convert small amount of MC in the solution to SP completely.

The phase transition temperature of the surfactant vesicles was determined by differential scanning calorimetry (DSC). The DSC was measured using a MacScience DSC-3200.

Results and discussion

Ultraviolet light irradiation is known to change the SP colorless solution to red. This photochromism corresponds to the production of red photomerocyanin (MC) by the ring-opening reaction of SP. Because the SP reactant is a neutral substance and the produced MC has both negative and positive charges in its structure, the change in its polarity during the course of the reaction is large [8–12]. On the other hand, visible light irradiation of MC or the heating of MC results in the disappearance of the color due to the ring-closing backward reaction of MC.

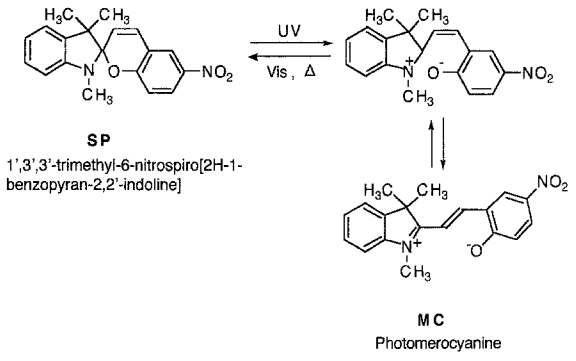


Figure 1 shows the spectrum change of SP in methanol as a function of UV irradiation time. The absorbance due to MC increased with the irradiation time. The absorbances at the peak wavelengths are plotted versus the irradiation time (Fig. 2). Upon irradiation with ultraviolet light, the absorbance of MC gradually increased and reached a plateau region, while by irradiation with visible light the absorbance of MC rapidly decreased. A similar reaction curve was observed in the vesicular system. The absorbance before UV irradiation was not zero due to certain turbidity, because the aqueous vesicular system is not the perfect solution. The difference between the absorbances of SP and MC in the vesicular system was smaller than that in methanol. However, the absorbances in methanol and that in the vesicles cannot be directly compared because the wavelengths at which the absorbances were measured were different (525 nm in methanol and 506 nm in DCAB vesicles). The response to the light irradiation in the vesicle system was much faster than that in methanol. This must be caused by the difference in the microenvironment around SP or MC. Fischer et al. found that the photoisomerization of stylbene and azobenzene derivatives is dependent on the polarity and the viscosity around the molecules and temperature [20]. The photochromic reaction of SP also contains the similar isomerization process. The vesicles enabled the photochromism of SP in water in spite of the low solubility of SP in pure water. Therefore, SP must have been solubilized in the vesicle membrane. In order to examine the microenvironment around the SP or MC in the vesicle membrane, the peak wavelength in the spectrum of MC was determined in various organic solvents (Fig. 3). With decrease in the solvent polarity, the peak wavelength of MC shifted to the long wavelengths and the peak absorbance decreased. In the figure (b), a polarity parameter, E_T, was plotted versus the peak wavelengths. The higher the values of E_T, the higher the polarity of the solvent. An almost linear relationship was obtained. It is apparent that MC in highly polar solvents showed a peak in the short wavelengths. Because MC in the vesicle system has a peak at 490–516 nm, the microenvironment around MC in the vesicular membrane is more polar than methanol. This means that MC is located near the ionic head groups of the surfactant membrane rather than in the hydrophobic region constructed from the alkyl groups of the surfactants. Because the hydrophobic SP is expected to be initially solubilized in the hydrophobic region of the membrane, the reactant is supposed to have moved from the hydrophobic region to the hydrophilic one after the photoisomerization.

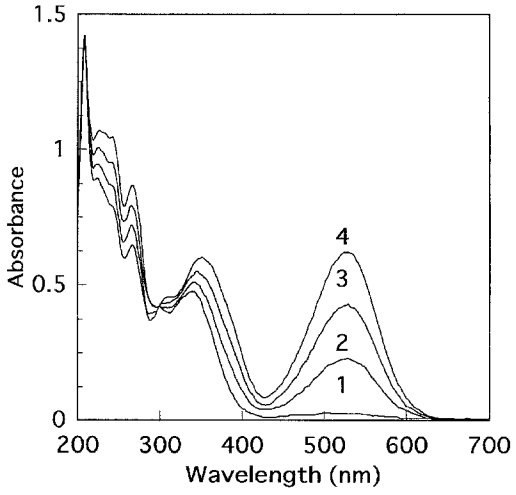


Fig. 1 Changes in absorption spectrum of SP in methanol with UV irradiation at 25 °C. [SP] = 5.00×10^{-5} M. UV irradiation time (**1**: 0, **2**: 2, **3**: 5, **4**: 10 min)

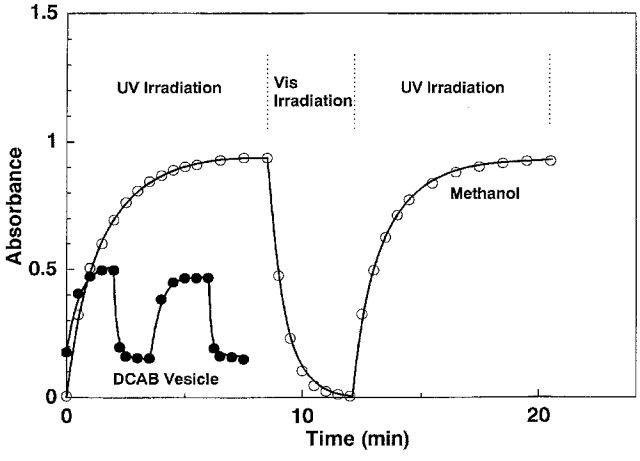


Fig. 2 Photochromism of SP in methanol and in the DCAB aqueous system. [SP] = 5.00×10^{-5} M, [DCAB] = 5.00×10^{-3} M. Wavelength: 525 nm (○), 506 nm (●)

Figure 4 shows the influence of the surfactant concentration on the absorbance change due to the photochromism of SP. Increasing the surfactant concentration increased the final absorbances, A, at the peak wavelengths. This result may be interpreted in terms of the

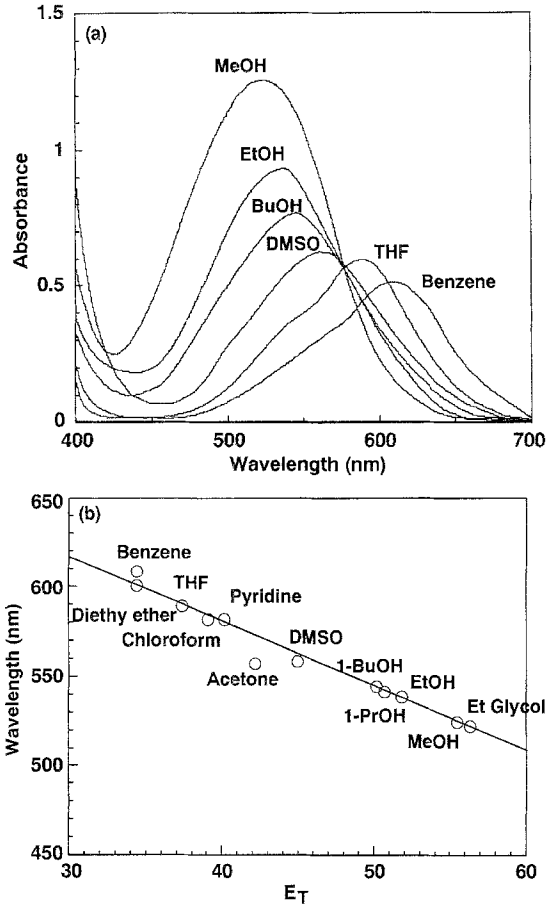


Fig. 3 Influence of solvent polarity, E_T, on (a) the absorption spectrum and (b) the peak wavelength of MC observed after 5 min UV irradiation. [SP] = 5.00×10^{-4} M

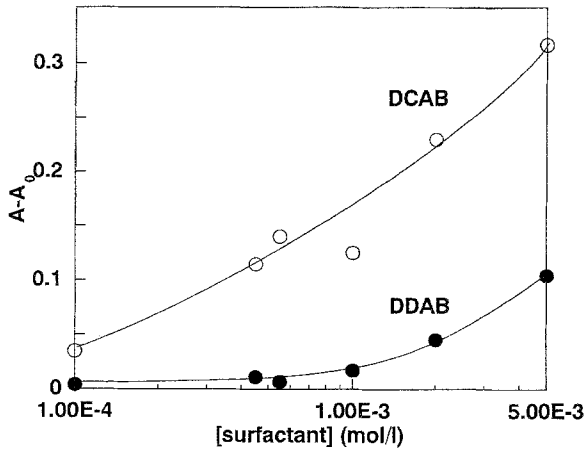


Fig. 4 Influence of surfactant concentration on the difference between the initial and the final absorbances (A_0 and A) at the peak wavelengths of the MC in the vesicular systems. The A_0 was measured before UV irradiation, and the A was measured after 15 min UV irradiation. Wavelength: 506 nm (○), 516.5 nm (●)

increased solubility of SP in the vesicles with the surfactant concentration. DDAB, which is nonpolymerizable and has longer alkyl chains than DCAB, showed a smaller concentration dependence than DCAB. This difference may be partly due to the difference in the polarity around MC in the two kinds of vesicles. As previously mentioned, SP solubilized in the hydrophobic domain of the membrane must move to the polar surface after the reaction. The partition of SP between the polar surface and the hydrophobic domain changes with the reaction. The ease of this migration of the reactant and the product is then supposed to be very important for the high apparent yield of the reaction. The longer the alkyl chain of the surfactant, the deeper the SP may be buried in the hydrophobic region of the vesicular membrane, and become harder to move toward the polar surface of the vesicles after the photoreaction. The difference in their peak wavelengths (DCAB 506.0 nm, DDAB 516.5 nm) of MC may confirm this interpretation. Another important difference between DCAB and DDAB is the allyl groups located at the polar head of DCAB. The allyl groups near the hydrophilic head may also provide a small solubilizing domain for the hydrophobic SP. The allyl groups of DCAB are supposed to solubilize more SP molecules than DDAB. This coincides with the observation that the turbidity of the SP solution in the presence of DDAB was higher than that of DCAB. Moreover, SP solubilized on the allyl groups near the polar head of DCAB can easily move to the hydrophilic head during the photoreaction. The difference in the phase transition temperature, T_C, may also be important. The T_C of DCAB was 30 °C and that of DDAB was 50 °C based on the DSC measurement. Because the temperature used for the photoisomerization from SP to MC was 25 °C, the reaction temperature was far below the T_C of DDAB. This means that the membrane of DDAB is sufficiently rigid at this temperature. All of these factors contributed to the low efficiency of the reaction in DDAB vesicles.

Next, in order to examine the influence of photopolymerization of the surfactant on the reaction curves of the photochromism, the long-term dependence of the absorbance at various wavelengths was measured (Fig. 5). In the DCAB vesicle system, the polymerization of surfactant and the photochromism of SP are supposed to be simultaneously occurring. The absorbance at 515 nm, where the MC has the peak absorbance, reached a maximum in 15 min and decreased with irradiation time. However, the absorbance at 400 nm increased with time. The color of the DCAB solution then changed from red to yellow with time. However, the reaction curves in the presence of the nonpolymerizable DDAB vesicles did not show such a

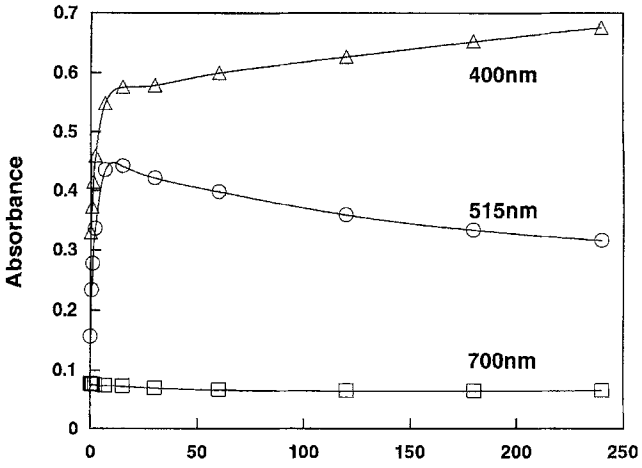


Fig. 5 Long-term dependence of the absorbance of SP in the DCAB vesicle on UV irradiation at various wavelengths at 25 °C. [SP] = 5.00×10^{-5} M, [DCAB] = 5.00×10^{-3} M

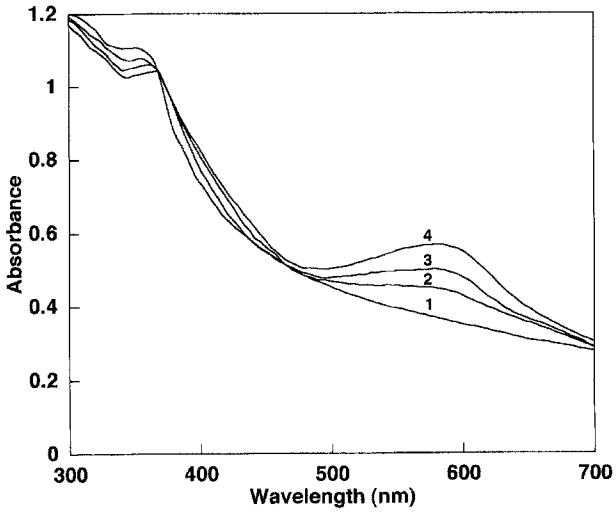


Fig. 6 Changes in absorption spectrum of SP in the γ-CD system at 25 °C. [SP] = 5.00×10^{-5} M, [γ-CD] = 5.00×10^{-3} M. UV irradiation time (**1**: 0, **2**: 2, **3**: 5, **4**: 10 min)

remarkable color change as that of DCAB. The polymerization of DCAB forms a polymer net on the surface of the vesicle and changes the packing of surfactant molecules in the vesicular membrane or changes the distance between the neighboring surfactant molecules. This might have changed the microenvironment or polarity around the photochromic compounds, and then the absorbance of MC. Another possibility is the formation of a side product from SP and the allyl groups of the surfactant. The solution, which had once turned yellow, did not show any backward reaction using visible light irradiation or by heat. This unknown side reaction was then certainly a part of the long time reaction curves of SP in the presence of DCAB. Therefore, the separation of the influence of polymerization on the photochromism from the reaction curves was unsuccessful. The characterization of the side product is now in progress.

Next, the influence of cyclodextrins on the photochromism of SP was studied. A continuous variation method was employed to determine the stoichiometry for the association of SP with cyclodextrins. SP and γ-CD formed a 1:1 inclusion complex because a maximum in the absorbance of the mixture appeared at the mole fraction of 0.5. α- or β-CD did not show any maximum, implying no inclusion complex formation between these cyclodextrins and SP. This is probably because the size of the cavity of these CDs did not fit with the molecular size of SP. Therefore, only the influence of γ-CD on photochromism of SP was investigated. In the presence of γ-CD, the peak absorbance of MC was observed at 583.5 nm. This result indicates that MC is solubilized in a relatively apolar environment like chloroform or THF. The polarity in the cavity of CD is then lower than methanol and the vesicles used in the above experiments. Figure 6 shows the change in the spectrum of MC in the presence of γ-CD versus light irradiation time. It is then apparent that we can observe the photochromic reaction of SP in aqueous solution if the reactant is solubilized using γ-cyclodextrin. The absorbance change due to the photochromic reaction was smaller than those in methanol and in the vesicles. Furthermore, the reaction was slower than that in the vesicles and faster than that in methanol.

This order may be partly due to the different characteristics of the vesicles from other mediums. Because the vesicles have both a hydrophobic region and a hydrophilic one in the same membrane, the vesicular membrane can serve as a solubilizing medium for both SP and MC. The restricted freedom of rotation of the molecule in the cavity of CD may have also influenced the reaction.

In conclusion: 1) The photochromic reaction of SP is observable in water when it is solubilized with the aid of vesicles and γ-CD. 2) The polarity of the microenvironment around MC formed by the photochromic reaction in the vesicles was higher than that in methanol, and the polarity in the γ-CD cavity was as low as in THF. 3) The polarity in the vesicular membrane and the limited rotation of the reactant in the cavity of γ-CD may have influenced the reaction. 4) The long light irradiation period resulted in a simultaneous photoreaction and polymerization, producing some unknown side product.

Identification of the side product and the study of the photochromism of spirobenzopyran derivatives, which have various long alkyl chains, are now in progress.

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