Solubilization and Photoreaction of Thiazine Dyes in Reversed Micelles

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Thiazine dyes were solubilized very slowly in dodecylammonium propionate reversed micellar cyclohexanic solutions containing 0.5 M H2O. Light accelerated highly the solubilization of the dyes. The dye monomer band blue- or red-shifted by the solubilization dependent on the dye species. Thiazine dyes solubilized in the reversed micelles containing 0.1 M H2O exhibited a new absorption band at about 500 nm.

The photoreduction of thiazine dyes by allylthiourea was enhanced drastically by solubilizing the dyes in the reversed micellar solutions containing 0.5 M H2O, and the singlet oxygen production was also effectively photosensitized by the solubilized thiazine dyes. The relative quantum yields for the photoreduction of the dyes by allylthiourea and the furan oxidation by singlet oxygen produced by the photosensitization of the dyes were obtained in the reversed micellar solutions. Results obtained were discussed in connection with the solubilization.

Abbreviations: AB: azure B; AC: azure C; MB: methylene blue; TH: thionine; DAP: dodecylammonium propionate; ATU: allylthiourea; DF: 1,3-diphenylisobenzofuran.

Introduction

In the previous paper [1], we have investigated the solubilization behaviour and solubilized state of MB in DAP reversed micellar cyclohexanic solutions. The solubilization of MB in the micellar solutions depended strongly on the water content.

In the present paper, the solubilization of four thiazine dyes (MB, AB, AC and TH) in DAP reversed micelles is spectroscopically investigated and the difference in the solubilization behaviour among the dyes is made clear up. Further, the chemical reactivities of solubilized thiazine dyes such as photoreduction by allylthiourea and photosensitization for singlet oxygen production are also studied. Results obtained are discussed in connection with the dye solubilization in DAP micelles.

Materials and Methods

AB from Tokyo-kasei Industrial Ltd. and AC from Chroma Chemical Co. were guaranteed reagents. TH from Takeda Chemical Ltd. and ATU from Katayama Chemical Co. were of special grade.

The reaction mixture (0.5 M H2O DAP micellar solution) for the photoreduction of thiazine dyes was prepared by 20 min dark-standing after the mixing of aqueous ATU (0.4 M H2O) and 0.1 M H2O DAP micellar cyclohexanic solutions. The reaction mixture was N2-bubbled during the dark-standing. The other chemicals, the experimental methods and the micellar preparation have been stated in the previous papers [1–2].

Results and Discussion

When aqueous thiazine dye (MB, AB, AC or TH) and DAP cyclohexanic solutions were mixed in the dark under stirring at 30 °C, the dye absorption spectrum underwent various changes with time. Such spectral changes strongly depended on the H2O content solubilized in the DAP micelles.

Fig. 1 shows the absorption spectra of MB and TH in aqueous and DAP reversed micellar cyclohexanic solutions. The 0.1 M H2O DAP micellar solution prepared by the mixing of aqueous MB or TH (0.1 M H2O) and DAP cyclohexanic solutions had a new absorption band at about 500 nm, and the monomer band blue-shifted in MB and red-shifted in TH, compared with the respective bands in aqueous solutions. (The concentration ratio of the monomer, dimer and 500 nm species changed to...
Fig. 1. Absorption spectra of MB and TH in aqueous and DAP reversed micellar cyclohexanic solutions. Concentrations of MB or TH, and DAP, $3.6 \times 10^{-6}$ and $8.0 \times 10^{-2}$ M, respectively; bulk pH of aqueous MB or TH solutions used, 10.0; temperature, 30 °C.

[A]: Absorption spectra of MB. Curve a, aqueous solution; Curve b, 0.1 M H$_2$O DAP micellar solution; Curve 1, 0.5 M H$_2$O DAP micellar solution just after mixing of aqueous MB (0.5 M H$_2$O) and DAP cyclohexanic solutions; Curve c, 20 min after 3 min-irradiation of the Curve 1 solution or 5 h dark-standing of the Curve 1 solution. Inserted figure: Changes of the band peak from Curve 1 to c after 3 min-irradiation of the Curve 1 solution; Curves 2 and 3, 1 and 3 min after the 3 min-irradiation, respectively; light, 652 nm light isolated from a 500 W xenon lamp through an interference filter (half-width, 12 nm); light intensity, 25 W · m$^{-2}$.

[B]: Absorption spectra of TH. Curve a, aqueous solution; Curve b, 0.1 M H$_2$O DAP micellar solution; Curve 1, just after mixing of aqueous TH and DAP cyclohexanic solutions; Curve c, 30 min after 3 min-irradiation of the Curve 1 solution or 10 h dark-standing of the Curve 1 solution. Inserted figure: Changes of the band peak from Curve 1 to c after 3 min-irradiation of the Curve 1 solution; Curves 2 and 3, 1 and 3 min after the 3 min-irradiation, respectively; light, 621 nm light isolated from a 500 W xenon lamp through an interference filter (half-width, 14 nm); light intensity, 25 W · m$^{-2}$.

(A shoulder at 650 nm)

some extent in sample to sample because of a slight difference in micellar size distribution.) In the 0.5 M H$_2$O DAP micellar solution prepared by the mixing of aqueous MB or TH (0.5 M H$_2$O) and DAP cyclohexanic solutions, the 500 nm band diminished remarkably, and the monomer band gradually blue-shifted in MB and red-shifted in TH with time in the dark after the mixing. The stable solubilization state (Curve c) was attained in 5~10 h. This solubilization of MB or TH was highly accelerated by light. The changes of the monomer band by the 3 min irradiation and dark-standing are shown in the inserted figures (Curves 1 $\rightarrow$ 2 $\rightarrow$ 3 $\rightarrow$ c). Curve c in Fig. 1 was also obtained by merely 20 min dark-standing after adding 0.4 M H$_2$O to the micellar solution prepared by the mixing of aqueous dye (0.1 M H$_2$O) and DAP cyclohexanic solutions. The similar behaviour to the MB or TH solubilization was observed in the solubilization of AB and AC (appearance of the 500 nm band; blue-shift of the monomer band in AB; red-shift of the monomer band in AC) as seen in Fig. 2. (A shoulder at 650 nm)

Fig. 2. Absorption spectra of AB and AC in aqueous and DAP reversed micellar cyclohexanic solutions. The spectra of AC are shifted by 0.06 upward. Concentrations of AB or AC and DAP, $3.6 \cdot 10^{-6}$ and $8.0 \cdot 10^{-2}$ M, respectively; Curves a and a', aqueous solutions of AB and AC, respectively; Curves b and b', 0.1 M H$_2$O DAP micellar solutions solubilizing AB and AC, respectively; Curves 1 and 1', just after mixing of aqueous AB or AC and DAP cyclohexanic solutions, respectively; Curves c and c', 20 min after 3 min-irradiation of the Curve 1 and 1' solutions or 5 h dark-standing of the Curve 1 and 1' solutions, respectively; light, light isolated from the xenon lamp through interference filters (649 nm for AB and 621 nm for AC); light intensity, 24.5 W · m$^{-2}$; bulk pH of aqueous AB or AC solutions used, 10.0; temperature, 30 °C.
Fig. 3. Dependence of the MB monomer band position on light intensity. Concentrations of MB and DAP, 3.6 \times 10^{-6} and 8.0 \times 10^{-2} M, respectively; bulk pH of aqueous MB solutions used, 10.0; temperature, 30 °C; measured just after 3 min-irradiation of the 0.5 M H_2O DAP micellar solutions solubilizing MB (prepared by mixing of aqueous MB and DAP cyclohexanic solutions); light, 652 nm light isolated from a 500 W xenon lamp through an interference filter (half-width, 12 nm); light intensity, 25 W \cdot m^{-2}; dark-standing indicated by arrows, 10~30 min; --- ---, final solubilization state.

in Curve a' might be due to a head-to-tail type dimer.

Fig. 3 shows the dependence of the MB monomer band position on the light intensity. The blue-shift of the MB monomer band by irradiation increased with the increase of light intensity, but the stable solubilization state (652 nm) was obtained by the dark-standing within 30 min at any light intensity as shown in Fig. 3. These phenomena were also observed with other thiazine dyes. The band positions of the thiazine dye monomers in aqueous and 0.5 M H_2O DAP micellar solutions were given in Table I.

Table I. Monomer band positions of thiazine dyes in aqueous and 0.5 M H_2O DAP micellar solutions. Concentrations of thiazine dyes and DAP, 3.6 \times 10^{-6} and 8.0 \times 10^{-2} M, respectively; bulk pH of aqueous dye solutions used, 10.0; temperature, 30 °C.

<table>
<thead>
<tr>
<th>Dyes</th>
<th>H_2O solutions</th>
<th>DAP micellar solutions</th>
<th>Stable solubilization state*</th>
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<tbody>
<tr>
<td></td>
<td>Monomer band positions [nm]</td>
<td>Just after preparation</td>
<td></td>
</tr>
<tr>
<td>MB</td>
<td>661</td>
<td>659</td>
<td>652</td>
</tr>
<tr>
<td>AB</td>
<td>645</td>
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<td>AC</td>
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<td>615</td>
<td>611</td>
</tr>
<tr>
<td>TH</td>
<td>597</td>
<td>609</td>
<td>613</td>
</tr>
</tbody>
</table>

* Dark-standing for several ten min after irradiation (3 min) of 0.5 M H_2O DAP micellar solution or by merely dark-standing (≥ 5 h).

Next, the initial rate of the MB photoreduction by ATU was measured as shown in Fig. 4. The reduction of MB was monitored by the absorbance decrease of the MB monomer. The photoreduction proceeded very slightly in aqueous MB solution under the present experimental conditions, but it was highly enhanced in the 0.5 M H_2O DAP micellar solution. The 0.5 M H_2O DAP micellar solution, prepared by 20 min dark-standing after the mixing of aqueous ATU (0.4 M H_2O) and 0.1 M H_2O DAP micellar cyclohexanic solutions, was employed for the simplicity of sample preparation. The large difference between the slopes (proportional to the reaction constant for the photoreduction) of two curves in Fig. 4 indicates that the MB photoreduction was remarkably catalyzed by the micelles. The reaction constant was about 100 times larger than that in aqueous solutions. Such micellar catalysis was reported by Fendler et al. [3, 4]. The 500 nm band species of thiazine dyes were not photoreduced by ATU in the 0.1 M H_2O DAP reversed micellar solutions, but the monomer species showing the absorption band above 600 nm were photoreduced.

Furthermore, we examined the photosensitizing activity of solubilized thiazine dyes for singlet oxygen production, using DF as scavenger for singlet oxygen. Fig. 5 shows changes in DF concentration with the irradiation time in 0.1 and 0.5 M H_2O DAP reversed micellar solutions solubilizing MB. The 500 nm species of MB solubilized in 0.1 M H_2O DAP micelles had no photosensitizing activity.
for singlet oxygen production, but the monomer having the absorption band at 650 nm photosensitized singlet oxygen production. This was also valid for AB, AC and TH. The MB monomer in the 0.5 M H$_2$O DAP micelles was an effective photosensitizer, and the DF concentration decreased rapidly with the irradiation of the monomer band. The DF oxidation by singlet oxygen was inhibited by ATU. The monomer species of AB, AC and TH solubilized in 0.5 M H$_2$O DAP micelles were also effective for the photosensitization of singlet oxygen production.

The relative quantum yields for the photoreduction of thiazine dyes by ATU and the DF oxidation by singlet oxygen produced by the photosensitization of these dyes are given in Table II. Both quantum yields increased in the order of MB, AB, AC, TH. Under the present experimental conditions, the $\Phi_{DF}$ values given in Table II can be regarded as the relative quantum yield for singlet oxygen production. By the procedure described in the previous paper [2], we obtained the quantum yield for singlet oxygen production in 0.5 M H$_2$O DAP micellar solutions of 0.70 for MB, which is much larger than the values (0.52 in H$_2$O, MeOH and EtOH) in non-micellar solutions. For this reason, it is considered that TH has the quantum yield near unity for singlet oxygen production in DAP micelles.

It is known that the aggregation number of DAP micelle in cyclohexane is strongly water-dependent and increases with increasing the solubilized H$_2$O content [5]. At 0.1 M H$_2$O, all the solubilized H$_2$O is present as bound water, but some head groups in the micelle are un-hydrated. The binding of dye to the open head group, possibly through hydrogen bonding and Coulomb interactions, may be responsible for the appearance of the 500 nm band as described in the previous paper [1]. This solubilized state of thiazine dyes was photochemically stable and inactive for the photoreduction by ATU and the photosensitization of singlet oxygen production. The solubilization of dyes in 0.5 M H$_2$O DAP micelles containing free water occurred very slowly in the dark, but it was highly accelerated by light. This light effect is still open to be elucidated. The absorption band of dye monomer in the solubilized state appeared at the short (MB and AB) or long (AC and TH) wavelength side of that in aqueous solution. The red- or blue-shift of the monomer absorption band on solubilization may be caused by the difference in the orientation of dye molecule in the micro-field inside the micelle depending on the number and position of methyl group in dye molecule. The solubilized monomer dyes were highly active for the photoreduction and photosensitization. The photoreduction of thiazine dyes by ATU and the photosensitization for singlet oxygen production are thought to be caused through the dye triplet state. For this reason, the solubilization of thiazine dyes in 0.5 M H$_2$O DAP micelles may enhance the population and/or stabilization of the dye triplet state. A highly viscous micro-environment may be provided inside the micelle. Further, reactants, ATU and O$_2$ may be concentrated in the interior of the micelle. This factor is also indispensable for the catalytic action of DAP reversed micelles.

### Table II. Relative quantum yields for photoreduction ($\Phi_{Red}$) of thiazine dyes by ATU and DF oxidation ($\Phi_{DF}$) by singlet oxygen produced by photosensitization of thiazine dyes; normalized $\Phi_{DF}$ and $\Phi_{Red}$ values of TH to unity.

<table>
<thead>
<tr>
<th>Dyes</th>
<th>$\Phi_{Red}$</th>
<th>$\Phi_{DF}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MB</td>
<td>0.30</td>
<td>0.77</td>
</tr>
<tr>
<td>AB</td>
<td>0.49</td>
<td>0.83</td>
</tr>
<tr>
<td>AC</td>
<td>0.87</td>
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</tr>
<tr>
<td>TH</td>
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