Study on Photochromism of Amphiphilic Spiropyran Monolayers by Surface Reflection

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Photoreactions and aggregation of spiropyran with a long alkyl chain (SP98) were studied by surface reflection spectroscopy at the air-water interface. SP98 in mixtures with arachidic acid formed stable monolayers on pure water or on a subphase containing Cd\(^{2+}\). Colored photomerocyanine (PMC98) was formed at the air-water interface by UV-irradiation. The reflection peak of PMC98 shifted from 545 nm to 618 nm with increasing surface pressure on a subphase containing Cd\(^{2+}\). The latter corresponded to the peak of aggregates observed in non-polar solutions. PMC98 formed J-like aggregates at surface pressures above 10 - 20 mN m\(^{-1}\) on the subphase containing Cd\(^{2+}\), but hardly formed them on pure water. The back reaction from PMC98 to SP98 upon visible irradiation depended on the surface pressure and the subphase. About 36% of aggregated PMC98 remained even after 90 min at 30 mN m\(^{-1}\), while at 10 and 1.5 mN m\(^{-1}\) PMC98 converted completely to SP98 within 20 and 10 min, respectively.

Keyword: spiropyran, aggregation, photochromic, air-water interface

1. Introduction

Photochromic materials such as fulgide, azobenzene, spiropyran or diarylethene are expected as promising candidates for high density optical memories and switching devices. Many efforts have been made to synthesize photochromic compounds with superior chemical and photochemical properties, to elucidate both photophysical and thermal-reactions, and to apply them in optical devices.[1] More functions and applications can be expected if orientation and interaction of photochromic molecules will be controlled. There have been some interests especially in long-chain spirobas (SP) in surface monolayers or in the monolayer assemblies prepared by the Langmuir-Blodgett (LB) technique.[2-10] The LB technique is well known as a useful method for organizing, controlling and modifying various photochemical and photophysical properties including photochromism by organizing molecules in well-ordered structures.[11] Several groups have reported photoreactions in monolayer on water surface and LB films.[2-10] We have recently reported novel ultra-fast all optical parallel switching based on complex refractive index changes in a guided wave geometry composed of a silver thin film and a polymer thin film containing SP.[12, 13]

Only a few studies have been reported on photoreactions of SP at the air-water interface.[3, 6, 10] But, no spectroscopic works have been made, to our best knowledge, on photochromic reactions of long-chain SP at the air-water interface. In the present work, we studied photochromic reactions upon UV and visible light irradiation together with aggregation properties of long-chain SP at the air-water interface by reflection spectroscopy.
2. Experimental

3',3'-Dimethyl-1'-octadecyl-6-nitrospiro[2H-1-benzopyran-2,2'-indoline] (abbreviated to SP98, Hayashibara Kankoh-Shikiso Kenkyusho) was used without further purification. The structures and abbreviations are shown in Scheme 1. SP98 was dissolved in acetone and n-hexane for absorption measurement. Mixtures of SP98 with arachidic acid (AA) in benzene were employed for π-A isotherm and reflection measurements. The absorption spectra of solutions were measured with a Hitachi U-3500 spectrophotometer. A Hamamatsu 150W Hg-Xe lamp was used to irradiate surface monolayers through a U340 filter (Hoya Optics) for UV-irradiation and a G550 filter for visible-irradiation. An IR-cut filter was also used to prevent possible thermal effects in both photoreactions. The π-A isotherms were measured with a KSV minitrough (KSV Instruments) in the dark. Purified and deionized water was prepared by a Milli-Q Organex system. Both pure water and 0.25 mM CdCl₂ aqueous solution at pH = 6.3 were used as a subphase. The subphase temperature was controlled at 18 °C by using a Lauda RMS-6 circulating bath. The reflection spectra were measured with a reflection spectrometer system composed of a Jobin-Yvon CP200 polychromator and Hamamatsu S3904-1024Q photodiode array as shown in Fig. 1.[14]

3. Results and Discussion

3.1. Photochromic reactions in solutions

Photochromic reactions for SP98 upon UV irradiation were first studied in solutions. The absorption spectra for PMC98 depended on polarity of solvents as shown in Fig. 2. In n-hexane (ε=1.88), PMC98 showed two peaks at 578 and 616 nm in the visible region, whereas a single peak was observed at 566 nm in acetone (ε=20.70). The peaks at 566 and 578 nm were assigned to monomeric PMC98 whereas the peak at 616 nm was assigned to aggregates of PMC98. These results corresponded well with those reported by Ando et al. for SP with one or two long alkyl chains.[7]

3.2. π-A isotherms

The π-A isotherms were measured for mixtures with molar ratios (SP98: AA) of 1:0, 1:1, 1:2, 1:4, and 1:8. The results for mixtures on the subphase containing 0.25 mM Cd²⁺ are shown in Fig. 3, together with that for a 1:1 mixture on pure water. SP98 alone could not form a stable condensed monolayer (not shown). All π-A isotherms of mixtures with AA on the subphase containing Cd²⁺ A black quartz plate was set at the bottom of the trough to exclude the contribution of reflection. The surface pressure dependence of reflection spectra for PMC98 were measured under UV-irradiation. All reflection spectra were obtained by log(Rdy/Rref), where Rdy and Rref are wavelength-dependent reflection intensities from subphase surface with and without monolayers, respectively.
showed a solid condensed phase with plateau at about 5 mN m⁻¹ as shown in Fig. 3. The limiting molecular area were obtained by using following equation.

\[ A_{\text{av}} = f_1 A_1 + f_2 A_2 \]

where \( A_{\text{av}} \) is the average molecular area in the mixed film, \( f_i \) are the molar fraction of the components, and \( A_i \) are the molecular areas in the pure component films at the same surface pressure. The limiting molecular areas of SP98 in the 1:1 mixture were estimated as 0.0 and 0.44 nm² at 30 and 1.5 mN m⁻¹, respectively. Polymeropoulos and Möbius estimated the surface area of the spiropyran ring system to lie between 0.4 and 0.5 nm².[2] The limiting molecular area at low pressure agrees with their result so that it is expected SP98 lying flat at a pressure lower than 5 mN m⁻¹ and squeezed out with increasing surface pressure. On the other hand the \( \pi-A \) isotherm on pure water showed the solid condensed phase with a limiting area of about 0.20 nm², but did not show plateau as on the subphase containing 0.25 mM Cd²⁺. The limiting area of 0.20 nm² is equivalent to that of AA and an alkyl chain of SP98. These results strongly suggests that SP98 which is in head-on configuration makes a mixed monolayer with AA at a whole surface pressure range.

3.3. Reflection spectra of PMC98 at the air-water interface

No PMC98 was formed on the subphase containing Cd²⁺ in the dark even after 60 min for the 1:1 mixtures at 30 mN m⁻¹. It is contrary to the mixed LB films of stearic acid and SP containing a long alkyl chain and a methoxy group which spontaneously formed J-PMC in the dark.[9] Surface pressure dependence of reflection spectra were then measured at surface pressure 1.5, 3, 10, 20 and 30 mN m⁻¹ with compression under UV irradiation. The observed spectra for the 1:1 mixture on subphase containing Cd²⁺ are shown in Fig. 4. The reflection intensity increased and red-shifted from about 545 nm to about 618 nm with increasing surface pressure. At 10-20 mN m⁻¹ both peaks at 545 and 618 nm were observed, whereas at 30-40 mN m⁻¹ the 618 nm peak was predominant. Similar results were observed for mixtures with molar ratios 1:2, 1:4 and 1:8 as shown in Fig. 5 for the 1:4 mixture as an example. These results clearly indicated that spectral shift did not depend on the concentration of SP98 in mixed monolayers, but on the surface pressure. The reflection spectra below 10 mN m⁻¹ were assigned to the monomeric PMC98 from the result of absorption spectra in acetone. Those observed predominantly above 30-40 mN m⁻¹ were assigned to the aggregated PMC98 because this peak corresponds well with the absorption spectrum assigned to the aggregated PMC in n-hexane as shown in Fig. 2. The longer wavelength (618 nm) peak at 30-40 mN m⁻¹ was sharper and much stronger as compared with that in n-hexane solution.

![Fig. 3 π-A isotherms for the mixture of SP98 and AA with molar ratio (a) 1:1, (b) 1:2, (c) 1:4, (d) 1:8 on the subphase containing Cd²⁺ and (e) 1:1 on pure water at 18 °C.](image)

![Fig. 4 The surface pressure dependence of reflection spectra for PMC98 and AA at molar ratio 1:1 on the subphase containing Cd²⁺ at (a) 1.5, (b) 3, (c) 10, (d) 20, (e) 30 and (f) 40 mN m⁻¹.](image)
The peak wavelength agrees with that of J-PMC with two long alkyl-chains observed in LB films.[7] But it was not so sharp as that of J-PMC in LB films. From these results it was found that PMC98 formed J-like aggregates by compression to 30-40 mN m\(^{-1}\) on the subphase containing Cd\(^{2+}\).

In contrast, the reflection spectra of PMC98 on pure water were broader than those on the subphase containing Cd\(^{2+}\) and showed much smaller spectral shift from about 575 nm to 588 nm with increasing surface pressure at any molar ratio as shown in Fig. 6 for 1:1 mixture. These results can be explained in the following way. Since PMC98 is zwitterionic, Coulombic attraction will be made between anionic ends of two PMC98 molecules and one Cd\(^{2+}\) ion. At surface pressures higher than about 5 mN m\(^{-1}\), such PMC98 molecules are squeezed out onto the monolayer of AA as mentioned above. Therefore PMC98 will easily form J-like aggregates even at lower molar fractions as in the 1:8 mixture. On the other hand on pure water, zwitterionic PMC98 will form a mixed monolayer with AA at the whole surface pressure range as mentioned above due most probably to increased hydrophilicity of PMC98. It will explain much smaller contribution of aggregated PMC98 on pure water, which will be formed by phase separation in mixed monolayers.

### 3.4. Photochromic reactions upon UV and visible irradiation at the air-water interface

Surface pressure dependence of photochromic reactions were measured upon UV and visible irradiation at several molar ratios. Surface monolayers were compressed to a given surface pressure such as 30, 10 and 1.5 mN m\(^{-1}\) in the dark, then was kept constant during UV and visible irradiation. UV-irradiation for 5 min was enough to change SP98 to PMC98 in all cases. Contrary to this, changes from PMC98 to SP98 by visible irradiation took more time and showed surface pressure dependence. Photochromic reactions at three surface pressures for the 1:1 mixture are shown in Figs. 7-9. At 30 mN m\(^{-1}\) the reflection spectra of aggregated PMC98 slowly decreased during visible irradiation as shown in Fig. 7.
After 90 min the shoulder at 550 nm disappeared, but the aggregation peak at 618 nm did not disappear completely corresponding to about 35% PMC98 remained. By the second UV-irradiation, SP98 changed to PMC98 again in a similar manner as in the first irradiation.

At 10 mN m⁻¹, the reflection spectra after 5 min of UV irradiation was not so sharp and the peak intensity was slightly weak as compared with that of 30 mN m⁻¹ as shown in Fig. 8. The reflection spectra of PMC98 decreased during visible light irradiation and disappeared completely after 20-30 min due to changes to SP98. It was found that at 10 mN m⁻¹, PMC98 changed back to the original SP98 at shorter irradiation times of visible light. At 1.5 mN m⁻¹ where SP98 will not be squeezed out, the reflection spectra showed only monomeric PMC98 at 550 nm as shown in Fig. 9. PMC98 changed to SP98 within 5-10 min upon visible light irradiation. From these results the rate of photochromic reaction from PMC98 to SP98 showed clear surface pressure dependence. In both acetone and n-hexane solutions the reaction from PMC98 to SP98 was very fast and completed within 2 min at the same irradiation condition. Although the molecular volume decreases by the reaction from PMC98 to SP98, it will become slower in surface monolayers and at higher surface pressures most probably due to restriction of molecular motions during photoreactions. Similar measurement were made on pure water. The reflection spectra during photochromic reactions on pure water are shown in Fig. 10 for the 1:1 mixture at 30 mN m⁻¹. Upon UV irradiation a small fraction of aggregated PMC98 were formed in addition to the main monomeric PMC98 as mentioned above. The peak at 567 nm seemed to shift to the longer wavelength during visible light irradiation. At longer irradiation time, absorption with a peak at about 600 nm due to the aggregated PMC98 became clear. Similar results were obtained at 10 mN m⁻¹ as those at 30 mN m⁻¹. These results indicated that monomeric PMC98 converted to SP98 faster than aggregated PMC98 upon visible light irradiation due probably to the smaller restriction of molecular motions in monomeric PMC98.

Thermal reactions from PMC98 to SP98 after 5 min of UV irradiation were also studied on pure water and the subphase containing Cd²⁺ at 18 °C. After 90 min in the dark, about 22% and 60% of PMC98 survived on pure water and on the subphase containing Cd²⁺, respectively. The half-life of PMC98 on pure water is similar to the one of PMC98 on water at pH=7. Cd²⁺ ions were again found to be effective to considerably stabilize the colored PMC form, due to Coulombic interactions.

4. Conclusion

Photochromic reactions were first studied by reflection spectra for SP98 (PMC98) on pure water and on the subphase containing Cd²⁺. The reflection spectra on the subphase containing Cd²⁺ clearly indicated the formation of aggregated PMC98 with increasing surface pressure during
UV irradiation. In contrast, only a weak aggregation peak was observed on pure water. The reaction from PMC98 to SP98 upon visible light irradiation was also observed at the air-water interface depending on the surface pressure and the subphase. Higher surface pressure slowed down the rate of the photo-reaction from PMC98 to SP98. Thermal back reaction from PMC98 was also controlled by the subphase. In conclusion, photochromic reactions and aggregation of long-chain spiropyran can be controlled by the subphase and the surface pressure.

References