Absorption Spectra of Rhodamine 6G by Slab Optical Waveguide Spectroscopy

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Slab optical waveguide (SOWG) was employed for obtaining absorption spectra of rhodamine 6G (Rh6G) with the concentration of 1 μmol/dm^3. It was found that Rh6G existed as a monomer and dimer on SOWG surfaces. On the SOWG surfaces treated with octadecylsilane only the band assigned to a monomer of Rh6G was observed.

Recently measurement of fluorescent emission from coloring matters adsorbed on interfaces was attempted for single molecule detection.[1] Because there is a possibility that the photochemical property of materials is affected by the adsorption, it is of much importance to study adsorbed states of these compounds. A slab optical waveguide (SOWG) spectroscopy has been known as a powerful tool to obtain detailed information about species adsorbed on interfaces.[2-6] Tsunoda et al. studied the adsorption behavior of Methylene Blue on SOWG surfaces from the change of absorbance at fixed wavelengths.[7] However, it is necessary for study of surface phenomena to obtain absorption spectra because there are possibilities of the existence of multiple bands and spectral change due to adsorption. We have reported the sensitive SOWG system which can obtain absorption spectra of submonolayer of Cu-porphyrin complex in LB films.[8] In this report, we describe the absorption spectra of dilute solution of rhodamine 6G (Rh6G) (1 μmol/dm^3) using the SOWG system and discussed its adsorbed species. In addition, the absorption spectra obtained by the SOWG treated with octadecylsilane (ODS-SOWG) was compared with those obtained by non-treated SOWG.

The SOWG system used in this study was similar to that described previously,[8] except the CCD camera (S-2300, Soma Optics Ltd.) was used for detection. SOWGs were fabricated by an ion-exchange process from non-fluorescent slide glasses (S-3314, Matsunami, 24 mm×76 mm×1 mm) in molten potassium nitrate at 400 ℃ for 30 min. The SOWG cell was made up of a SOWG and a poly(tetrafluoroethylene) (PTFE) block. The block was set on the SOWG, and was 10 mm thick and had a 16.7 mm× 30 mm hall. A silicon rubber spacer was set between the block and the SOWG. Therefore, the cell length was 3 cm and the surface area of SOWG covered with sample solution was about 5 cm^2. The sample volume was about 4 ml. Absorption spectrum in liquid phase was measured by Shimadzu UV-2100PC spectrophotometer with a 1 cm cell. All the chemicals were reagent grade, which were purchased from Tokyo Kasei Co. Ltd. and used as received. The sample solution was prepared with distilled water. The sample concentration was 1 μmol/dm^3. ODS was introduced onto the SOWG surface by the method of Thompson et al.[9] Transmission spectra of both the water and sample solution in the SOWG cell were measured separately by the SOWG system. Absorption spectra of Rh6G were obtained from the ratio between these transmission spectra.

Figure 1(a) shows the absorption spectrum of Rh6G in liquid phase measured with a 1 cm cell. An absorption band at around 526 nm is assigned to a monomer of Rh6G in solution.[10]

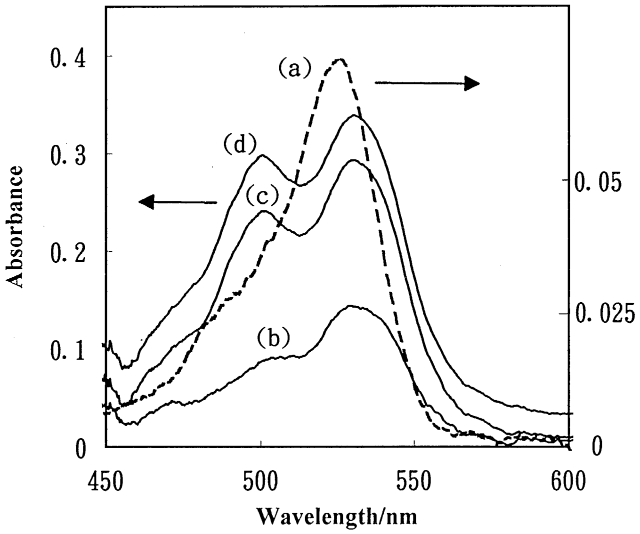

Figure 1. Absorption spectra of rhodamine 6G (Rh6G) with the concentration of 1 μmol/dm^3. (a) : absorption spectrum of liquid phase obtained with a 1 cm cell; (b)-(d) : absorption spectra obtained with SOWG spectroscopy. (b) was obtained soon after the addition of Rh6G solution to the cell, and (c) and (d) were obtained after 2 and 10 min from the addition, respectively.

Figure 1(b)-(d) shows the absorption spectra of Rh6G obtained by SOWG spectroscopy. Figure 1(b) shows the spectra measured soon after the addition of sample solution to the cell. In Figure 1(b), a peak at 530 nm and a shoulder peak at 500 nm are observed. This spectra almost corresponded to those of dense Rh6G solution (100 μmol/dm^3) obtained by Arbeloa[10] and it suggests that Rh6G existed both as monomer and dimer on the SOWG surface. With a time passed, it is seen that the absorbance of these peaks increased. After 10 min the absorbance reached to an equilibrium and there are two peaks at 500 and 530 nm as shown in Figure 1(d). Figure 1(d) almost corresponds to the estimated absorption spectrum of dimer in solution.[10]

Rh6G solution was transferred from the SOWG cell to a 1 cm cell after 10 min and the absorbance was measured. The concentration decrease of Rh6G was less than 1%. This suggests that the surface concentration of Rh6G was much less than a monolayer coverage.

Figure 2 shows the absorption spectra of Rh6G measured with ODS-SOWG. In this case only a peak at 526 nm is observed as shown in Figure 2. With a time passed, absorbance of this peak increased and it needed about 20 min to reach to an equilibrium. Figure 2(c) is the absorption spectra obtained after 20 min. In the case of ODS-SOWG, only the peak assigned to monomer of Rh6G was observed.

Though the peak position of the two absorption bands are almost the same as shown in Figure 1(b)-(d), the ratio of the two

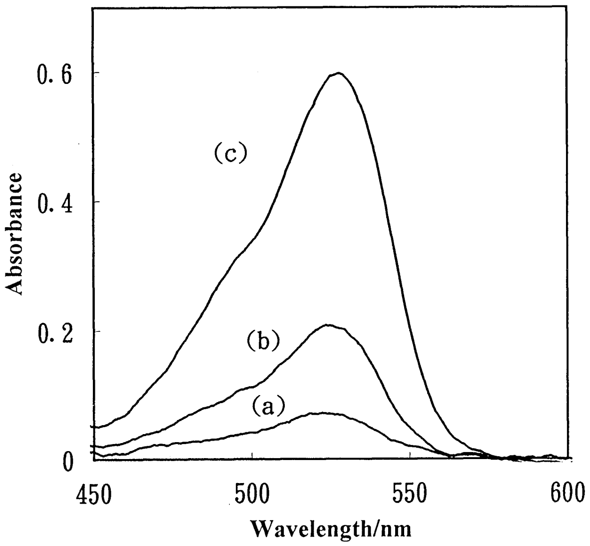

Figure 2. Absorption spectra of rhodamine 6G (Rh6G) adsorbed on SOWG treated with octadecylsilane (ODS-SOWG). The concentration of Rh6G is 1 μmol/dm^3. (a) was obtained soon after the addition of Rh6G solution to the cell, and (b) and (c) were obtained after 2 and 20 min from the addition, respectively.

bands in the absorbance changed with a time passed. Further consideration on the absorption spectra qualitatively elucidated the change in the ratio of monomer to the dimer. That is, the monomer fraction was inversely proportional to the ratio of absorbances, R, which is given by $R=A_{500}/A_{526}$ where A_{500} and A_{526} are the absorbances of two peaks assigned to dimer and monomer at 500 and 526 nm, respectively.[10] In this approximation, the larger the value of R is, the less the ratio of monomer is. In Figure 1(b)-(d) the values of R were 0.63, 0.80 and 0.91, respectively. These results also clearly shows that the ratio of the dimer increased with a time passed. On the contrary in Figure 2(a)-(c), the values of R were 0.54, 0.55 and 0.57, respectively. These results suggests that there is no change in absorption band assigned to dimer (at 500 nm) and that adsorbed species was almost the same through adsorption process in the case of ODS-SOWG. These results mentioned above also coincide with adsorption behavior of Methylene Blue on SOWG surfaces measured at fixed wavelengths by Tsunoda et al.[7]

As a result, absorption spectra of Rh6G with the concentration of 1 μmon/dm^3 were successfully observed. It was shown that adsorbed species of Rh6G were different on untreated SOWG and ODS-SOWG. The difference of the surface nature between these two SOWGs might cause the change in the states of adsorbed species. The results mentioned above show that the SOWG system is a sensitive technique to adsorbed species on solid/liquid interfaces. Additionally it was clearly shown that this promising technique can give us more detailed information about adsorption behavior than conventional absorption method. Since it is evident that the wavelength fixed by the laser used does not always coincide with the peak position, it is effective to obtain absorption spectra of adsorbed species. Further investigation about the adsorption phenomena of Rh6G on SOWG surfaces is now in progress.

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