

Fluorescence of Rhodamine 6G on Hydrotalcite —Possibility of Alcohol Sensing—

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The fluorescence intensity of Rhodamine 6G (R6G) introduced on hydrotalcite by the rehydration method was determined to depend strongly on the alcohol vapor pressure, whereas that of R6G simply adsorbed on hydrotalcite had low dependence on the vapor pressure. The intensity decreased with an increase in pressure, and the change in intensity was reversible. The degree of change differed according to the alcohol used and seemed to be related to the saturated vapor pressure of the alcohols.

Hybrid organic–inorganic materials containing Rhodamines have been investigated for their fundamental characteristics^{1–6} and for use as novel multifunctional materials.^{7–14} The fluorescence of Rhodamines has received much attention for a number of different applications. Solid-state dye-lasing^{7,9,10} and temperature sensor systems¹⁴ have been investigated from this viewpoint. The efficiency of emission and photostability of the dyes are important, especially in the former case. In addition, the method of sample preparation including the selection of inorganic materials and the relationship between the fluorescence intensity and orientation of dye molecules in the hybrid organic–inorganic materials have been studied as the foundation for applications of these materials. We investigated the fluorescent properties of a Rhodamine 6G–clay hybrid material in an effort to determine if this material would be a useful organic solvent vapor sensor. Clay materials capable of cation exchange are typically incorporated with Rhodamines as an inorganic component, because Rhodamines are cationic dyes. In the current work, we used hydrotalcite, a clay capable of anion exchange and obtained attractive results using this system.

Hydrotalcite (Kyowado-500, Kyowa Chemical Industry Co., white powder, 0.30 g) (Ht) was calcined at 773 K for 3 h. The calcined clay (0.18 g) was introduced into an aqueous solution (1.66×10^{-4} mol dm⁻³, 60 mL) of R6G (Sigma-Aldrich Co.), which was warmed to 353 K in order to minimize the effect of carbon dioxide in the reconstruction procedure. The dispersion solution was stirred for 30 min and filtered using a membrane filter. The amount of dye in the solution was 1% of Ht's AEC (3.3 meq g⁻¹).¹⁵ 95% of the dye in the solution was introduced on Ht. The filtered sample (R6G/Ht, dull pink powder) was dried in vacuo at 333 K until a constant weight was obtained. Although R6G/Ht showed a strong diffraction at $2\theta = 11.3^\circ$, which is characteristic of the original hydrotalcite in XRD measurements (Rigaku, RINT-2000, Cu K α radiation), a weak diffraction appeared at $2\theta = 6.5^\circ$ that indicates an elongation of the interlayer spacing in R6G/Ht. The peak at $2\theta = 6.5^\circ$ suggests the possibility of intercalation of R6G. The peak at $2\theta = 11.3^\circ$ for R6G/Ht shows that the original structure containing carbonate anion was reconstructed during the hydration to prepare R6G/Ht. The sample for spectral measurement was prepared by smearing 0.03 g of R6G/Ht on a quartz glass

plate in an area of 9 mm \times 30 mm using 100 μ L of water and by drying in vacuo at 333 K for 2 h after air-drying at room temperature. Fluorescence of R6G/Ht was measured (Hitachi F-4200, $\lambda_{\text{ex}} = 510$ nm) under air, in vacuo and under exposure to alcohol vapor (298 K, at saturated vapor pressure). Evacuation, exposure to alcohol and vapor pressure control were carried out using an apparatus shown in Figure 1.

The shape and intensity of the fluorescence of R6G/Ht in vacuo were almost the same as those under air. On the other hand, those exposed to alcohol vapor were exceedingly different from those under air. The sample exposed to ethanol is shown in Figure 2 as an example. The maximum degree of fluorescence decrease was about 80% of the intensity under air. The spectra recovered in both intensity and shape upon removal of vapor. The absorbances of R6G/Ht at 510 nm under both air and exposure to alcohol vapor were about the same (ca. 0.9), and the absorbance in vacuo was about 0.8. Therefore, it is clear that this difference in absorption does not cause a decrease in the fluorescence intensity. The fluorescence intensity of R6G/Ht was reversible with a periodic change in the atmosphere (under air \rightarrow in vacuo \rightarrow exposure to alcohol vapor) (Figure 3). The evacuation and exposure times were 30 and 10 min, respectively. The measurement under air after exposure to the vapor was carried

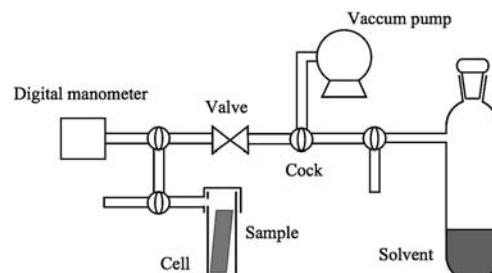


Figure 1. Schematic diagram of the apparatus.

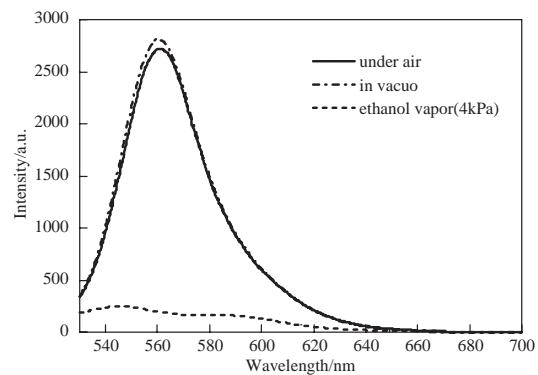


Figure 2. Fluorescence spectra of R6G/Ht (not corrected).

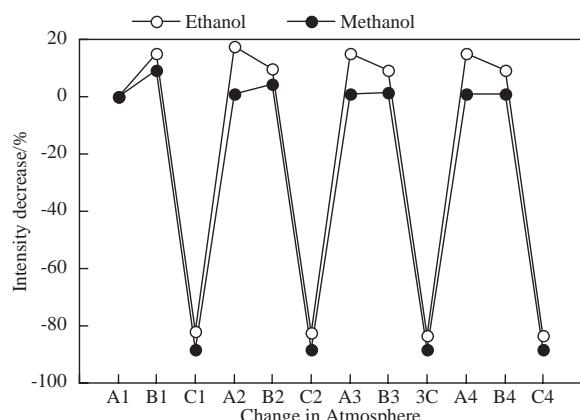


Figure 3. Change in fluorescence intensity of R6G/Ht with repeated change in atmosphere: A under air; B in vacuo; C exposure to alcohol vapor. The numbers following A, B, and C on the x axis express the cycle number.

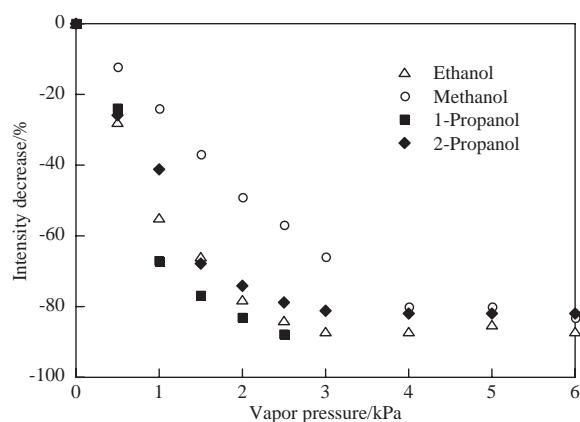


Figure 4. Dependence of fluorescence intensity of R6G/Ht on the vapor pressure of alcohol.

out after the cell was evacuated for 30 min, and the sample in the cell was exposed to air for 30 min. The fluorescence intensity was found to be dependent on the vapor pressure up to 3–4 kPa, as shown in Figure 4. The decrease in intensity seemed to be approximately linear with the increase in the vapor pressure. The degrees of decrease in the fluorescence intensity with the increase in vapor pressure were different according to the type of alcohol used. Our findings revealed that the higher the saturation vapor pressure of the alcohol,¹⁶ the smaller the degree in the decrease in intensity. Solvent vapors from acetonitrile, acetone, and benzene were also examined. These solvents resulted in a gradual increase in the fluorescence intensity with a periodic change in the atmosphere. These solvent vapors presumably remained after evacuation. The reversible change in fluorescence intensity was characteristic in the case of alcohol. This reversible change may be attributed to the hydroxy group of the

alcohol. Although it is not clear at present how R6G on the clay exists, the phenomena observed in this investigation are interesting from the viewpoint of using this material as an alcohol vapor sensor that is able to discriminate the type of alcohol.

Fluorescence intensity of R6G adsorbed on hydrotalcite¹⁷ was also affected by the atmosphere. However, the change was smaller than that for R6G/Ht. The intensity was the strongest under air, and it decreased to 70% in vacuo and to 90% under exposure to ethanol vapor. Although the absorbance of the sample used was not accurately measured because of the reflection of incident light, the order of absorption intensity at 510 nm is as follows: under air > under exposure to ethanol vapor > in vacuo. The fluorescence intensity of R6G adsorbed on hydrotalcite is expected to reflect this order.

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- 16 Saturated vapor pressures at 298 K of 1-propanol, 2-propanol, ethanol, and methanol are 2.73, 5.93, 7.89, and 12.69 kPa, respectively. These values were calculated from the Wagner equation, *Kagakubinran Kisohen II*, ed. by the Chemical Society of Japan, Maruzen, Tokyo, **2004**.
- 17 The adsorption of R6G was carried out by mixing aqueous R6G solution ($3.32 \times 10^{-4} \text{ mol dm}^{-3}$, 30 mL) with an aqueous suspension of Ht (30 mL). The mixture was stirred for 3 h and then filtered. The filtered sample (pale pink powder) was dried in vacuo at 333 K until a constant weight was obtained. The dye of only 2% in the solution was adsorbed on Ht.