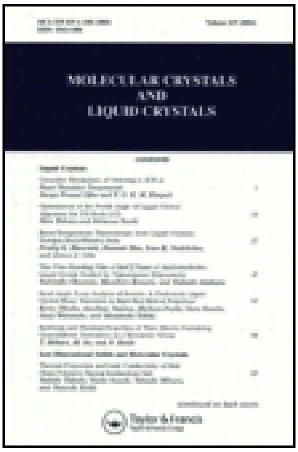


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Photoacoustic and FT-IR Study upon Molecular Forms of Rhodamine B Dye Adsorbed on KCl and SiO_2 Substrates

E. Kanezaki [a]

[a] Department of Chemical Science and Technology, Faculty of Engineering, University of Tokushima Minamijosanjima 2-1, Tokushima, 770, JAPAN

To cite this article: E. Kanezaki (1996): Photoacoustic and FT-IR Study upon Molecular Forms of Rhodamine B Dye Adsorbed on KCl and SiO_2 Substrates, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 275:1, 225-231

To link to this article: http://dx.doi.org/10.1080/10587259608034076

Mol. Cryst. Liq. Cryst., 1996, Vol. 275, pp. 225–231
Reprints available directly from the publisher
Photocopying permitted by license only

Photoacoustic and FT-IR Study upon Molecular Forms of Rhodamine B Dye Adsorbed on KCl and SiO_2 Substrates

E. KANEZAKI

Department of Chemical Science and Technology, Faculty of Engineering, University of Tokushima
Minamijosanjima 2-1, Tokushima 770, JAPAN

(Received November 8, 1994; in final form April 27, 1995)

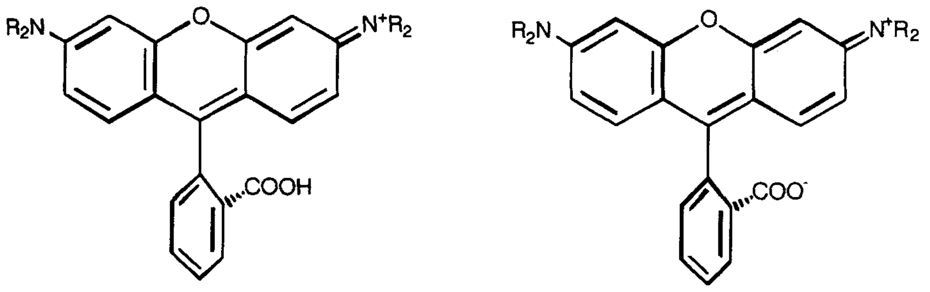
Solid state rhodamine B which is adsorbed on KCl or on SiO_2 substrate is studied by means of photoacoustic spectroscopy (PAS) and by FT-IR diffuse reflectance spectroscopy (FT-IR/DRS) in order to investigate the effect of substrate on the molecular form of the dye. Depth profile of the PAS spectrum for the dye on porous silica surface reveals that the molecular form is indifferent to the depth of pores on the substrate where the adsorbed dye molecules are located. The zwitterionic form is concluded for the dye on KCl whereas the cationic one is assigned on SiO_2. Gradual fading of color in the powder of the dye on KCl is elucidated by reversible formation of the lactonic form.

Keywords: Photoacoustic spectroscopy, rhodamine B, adsorption

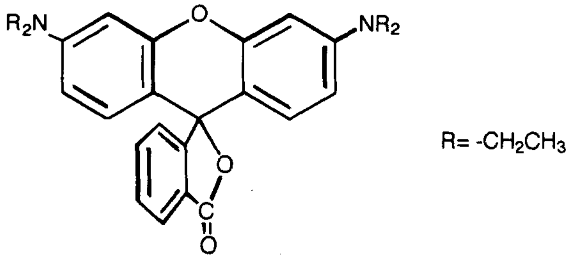
1. INTRODUCTION

Rh B is a typical cationic dye compound in which cationic, zwitterionic and lactonic forms (*C*-, *Z*- and *L*-forms, respectively; Figure 1) have been detected in absorption and in fluorescence spectra of solutions.[1,3] The *Z*-form with a dissociated -COO^- group is in the ground state equilibrium with the *L*-form and the *C*-form with a protonated -COOH group is produced in the lactone-ring opening of the *L*-form associated with the protonation by some proton donors(s).[3] In solutions, both the *Z*- and the *C*-forms have an intense π, π^* absorption in the visible region showing a vivid red color. The length of the conjugated π-electron system in the xanthene moiety is shortened in the *L*-form owing to the cyclic addition by a neucleophilic attack of the anionic oxygen in the carboxylate group to the ninth carbon atom thereby resulting in a shift of the absorption to the high energy side and in a colorless nature of this form.[3]

Unlike in solutions, a molecular form of the dye on inorganic solid substrates has been rarely studied so far[4] because of lack of an appropriate technique to study solids in ordinary conditions. Since SiO_2 is used as a carrier for reaction catalysis, it is important to know the structure of adsorbates on the solid. PAS has been used recently to obtain the depth analysis of adsorbed Rh B molecules on porous SiO_2 particles and has been applied to some solid dye compounds thus proving a powerful tool for powder samples.[5,6]



Cationic Form Zwitterionic Form



Lactonic Form

FIGURE 1 Multiformity in rhodamine B molecular form.

In this paper, a depth profile of the absorption spectrum is demonstrated for Rh B dye molecules which are located in surface pores of SiO_2 particles (Rh B/SiO_2) by means of PAS. The molecular form of the dye is determined by FT-IR/DRS and is compared with that of the dye on KCl substrate (Rh B/KCl). Color fading of the Rh B/KCl powder is observed in two days exposure to moisture.

2. EXPERIMENTAL

KCl pellets (WAKO, reagent grade, 1 g) were dissolved into 20 ml of Rh B (NIPPON KANKO SIKISO, 99.999%) aqueous solution ($C \sim 10^{-4}\,\mathrm{mol\,dm^{-3}}$). After being roughly dried in air, the colored sludge was heated at $T = 50°\mathrm{C}$ for several hours; then the red granules were crushed by using an agate mortar and pestle. Finally a red-purple powder (Rh B/KCl) was obtained. The estimated molecular ratio of the dye to the equivalent of KCl in the powder is 4.7×10^{-4} mol/eq. Thermal decomposition of the adsorbed dye by heating was not feasible because absorption spectra of the two following aqueous solutions were identical: one was prepared by using a part of the colored powder and the other by using the dye and KCl reagents added separately. The preparation for Rh B/SiO_2 red powder has been described before.[5] The specific surface area of SiO_2 solid substrate by the BET method with N_2 gas was $3.76 \times 10^2\,\mathrm{m^2\,g^{-1}}$ and the average occupied surface area (A_0) by a dye molecule in the Rh B/SiO_2 powder was estimated $A_0 = 5.04 \times 10^2\,\mathrm{nm^2\,(molecule)^{-1}}$.[5]

An outline of the PAS apparatus has been published.[5] Frequency in the range of $2.2 - 1 \times 10^3\,\mathrm{s}^{-1}$ generated by a mechanical chopper was adopted for the modulation of the exciting radiation. Intensity of the photoacoustic signal of samples was normalized through the established procedure[7] to the intensity of a reference carbon black with the interval at very 0.5 nm between $\lambda = 300$ to 700 nm.

FT-IR/DRS was performed by using a NICOLET 170SX FT-IR Spectrometer equipped with an MCT detector in the region of wavenumber $(\sigma)\,400 \le \sigma/\mathrm{cm}^{-1} \le 4000$ and with a polystyrene film for wavelength calibration.

3. RESULTS AND DISCUSSION

Figure 2 shows a series of photoacoustic spectra of the Rh B/SiO_2 powder where their shapes are dependent on the modulation frequency of radiation. It has been indicated that this dependence results from the change of thermal diffusion length (μ) which is a function of the modulation frequency.[5,7] Analysis has revealed that the dye molecules, which are located in shallow pores, are detected at higher modulation frequencies whereas those molecules, which are located in deep pores, are additively detected at lower frequencies.[5] A higher A_0 value than an estimated occupied area of the dye molecule enables us to observe solution-like spectra[6] in Figure 2 although some minor differences are noticed. Background signal increases in the whole spectral region with the increase of modulation frequency owing to the decrease of the signal intensity from the dye molecles. This decrease results from the reduced amount of dye molecules which are detected at higher modulation frequencies as described above. A gradual signal rise in the high energy region is noted in all spectra of Figure 2. It has been verified that the signal rise results from additive photoacoustic signal generation in the SiO_2 substrate which absorbs the UV-radiation.[6] On the other hand, it is another prominent feature that an intense absorption at $\lambda_{max} = 545$ nm is commonly observed in these spectra. Two weak bands at $\lambda_{max} = 350$ and 400 nm, a shoulder at $\lambda = 510$ nm are also commonly observed. The shoulder band has been assigned to a dimer absorption in solutions[8] which species are not discussed here. Considering the common location of absorption in the spectra of Figure 2 it is strongly suggested that the monomeric Rh B dye has uniformly the same molecular form in this powder; depth of the surface pores in which the dye molecules are located has little influence on the uniformity in the molecular form of the dye.

Results of FT-IR/DRS measurements of the Rh B/SiO_2 powder in the fingerprint region are summarized in Table 1. Though absorption by the substrate disturbs the observation of the dye originated absorption, a band appears at $\sigma = 1750\,\mathrm{cm}^{-1}$ with medium intensity. Grauer *et al.* have studied Rh B molecules adsorbed on some clay minerals containing the SiO_4^{4-} skeleton and have concluded that the dye exists as the *C*-form which has a characteristic IR absorption at $\sigma = 1715\text{–}1757\,\mathrm{cm}^{-1}$.[9] With this assignment, the *C*-form with a protonated -COOH group is concluded in the Rh B/SiO_2 powder. It is reasonable to suppose that the surface pores in which the dye molecules are located act as proton donors because the Rh B molecule also takes this form in protic solutions.[3,9]

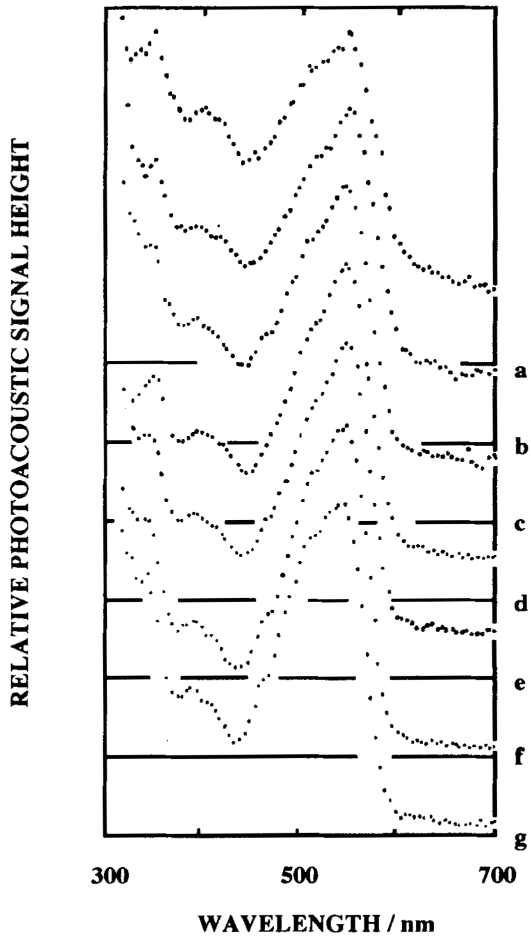


FIGURE 2 Depth profile in photoacoustic spectra of the Rh B/SiO$_2$ powder with a series of modulation frequency of excitation: a; 1.0×10^3, b; 5.9×10^2, c; 2.4×10^2, d; 1.0×10^2, e; 66, f; 5.56 and g; 2.2 s^{-1}. Baselines are indicated for all spectra. The intensity of each spectrum is normalized at the maximum which is located at $\lambda_{max} = 545$ nm.

TABLE 1

Peak locations in FT-IR/DRS spectra of RhB powders in 1200–1800 cm^{-1} region

Samples	σ/cm^{-1}			
	1634(sr)	1611(sh)	1536(w)	1506(w)
Rh B/KCl	1464(sh)	1406(w)	1360(sh)	1326(w)
	1290(sh)	1261(m)		
Rh B/SiO$_2$	1750(br)	1592(m)	1410(sh)	1383(br, sr)
	1350(br, sr)			

sr: strong, m: medium, sh: shoulder, w: weak, br: broad

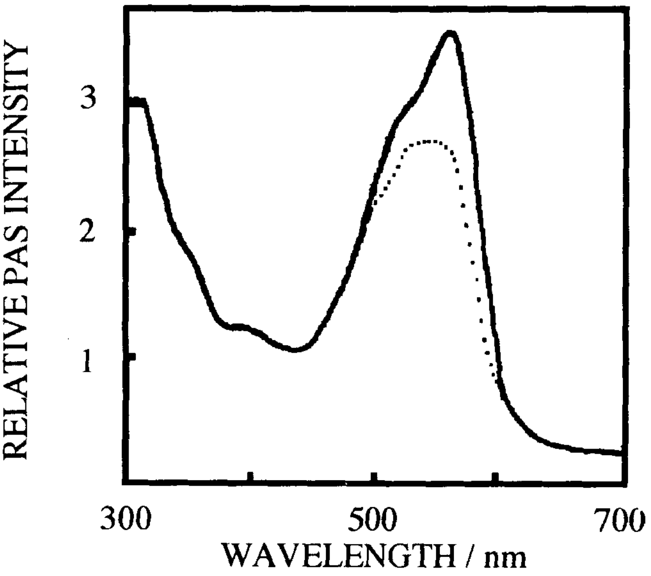


FIGURE 3 Photoacoustic spectra of the Rh B/KCl powder immediately (solid line) and two days (dotted line) after the sample preparation; see text.

Figure 3 shows two PAS spectra of the Rh B/KCl powder. Immediately after the sample preparation (solid line), an intense absorption at $\lambda = 560$ nm is observed with a weak shoulder band at the high energy side of the maximum. A gradual signal rise due to absorption of the UV-radiation by the KCl substrate is also observed in the high energy region of both spectra. Besides the difference in location of the intense absorption, two weak and broad bands which are located at around $\lambda_{\max} = 350$ and 400 nm in Figure 2 are almost missing in Figure 3, though the dimer shoulder is still observed. It is known that solvatochromism may be responsible for energy shift in the absorption spectra in solutions but the total profile of the spectrum remains unchanged.[3] Therefore, the spectral change in Figure 3 strongly suggests that the predominant molecular form of the dye in the Rh B/KCl powder is different from that in the Rh B/SiO_2 when Figures 2 and 3 are compared.

Figure 4 shows the FT-IR/DRS spectrum of the Rh B/KCl powder in which the absorption at around $\sigma = 1750\,\text{cm}^{-1}$ is missing. Taking into account that the intense absorption is located in the visible region in Figure 3, it is concluded that the dye molecule in the Rh B/KCl powder does not have the *L*-form. Although a large shift in band location beyond the scope of this figure cannot be excluded completely, it is the author's opinion that the absorption due to -COOH group disappears owing to the change in molecular form from the *C*-form on SiO_2 to the Z-form on KCl. Absorption of the *Z*-form in Figure 3 ($\lambda_{\max} = 560$ nm) red-shifts by 491 cm^{-1},[10] from that of the *C*-form in Figure 2 ($\lambda_{\max} = 545$ nm), which suggests that the ground state of the former is more unstable than the state of the latter.

An interesting change is noted in the photoacoustic spectrum of the Rh B/KCl powder. After exposing this powder to the atmosphere at room temperature for two

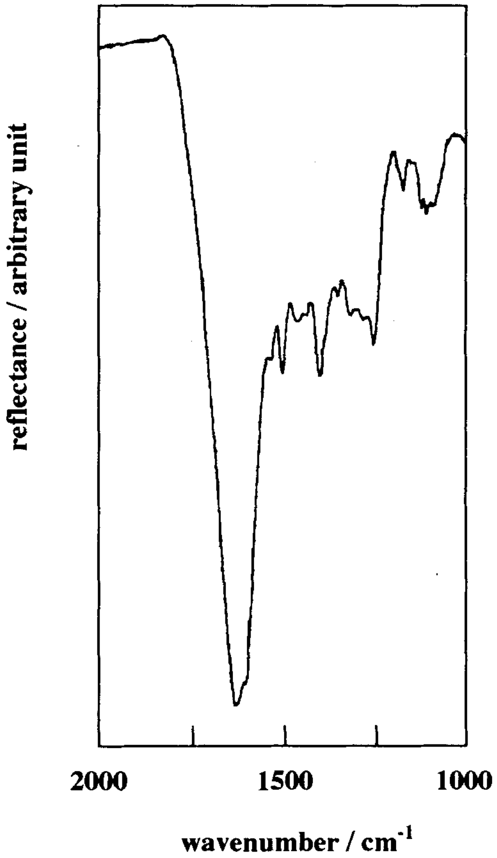


FIGURE 4 FT-IR/DRS spectrum of the Rh B/KCl powder.

days the absorbance of the band at $\lambda_{max} = 560$ nm decreases and the band shape becomes obscure (Figure 3, dotted line) although no significant change is observed after the same treatment of the Rh B/SiO_2 powder in particular. The absorbance at $\lambda = 560$ nm is reduced to 73% of that before the exposure. The absorbance of the dimer band also apparently decreases although absorbance of the latter band is reduced in a lesser degree (88%) than that of the former one. The spectrum recovers after drying the exposed sample in an electric furnace at $T = 50°C$ for 1 h. An absorption by water appears so intense in the FT-IR/DRS spectrum of the exposed powder that it completely covers the fingerprint region in the spectrum of the dye thus making it impossible to assess what is produced in the exposure by this method.

This change on the exposure is elucidated as follows. The absorbance at $\lambda = 560$ nm decreases because a part of the Z-form molecules change to the L-form, which results from absorption of water vapor by the sample powder during the exposure. Under the dry condition, the Z-forms are fixed in the rigid salt matrices. However, in a wet atmosphere, the outer part of the hosting KCl microcrystal dissolves in the airborne water; thus the carboxylate group in the Z-form on the dissolved microcrystal is set free from the restriction by the lattice. It becomes feasible that the neucleophilic attack, which is described before, occurs to produce the *L*-form that is in the equilibrium with the *Z*-form in various solutions. Although the colorless lactone formation at the surface of the KCl microcrystals decreases the absorbances of the band at $\lambda_{max} = 560$ nm, this band is still predominant in the spectrum of Figure 3, (dotted line). This is partly due to the thermal nature of the solid substrate; the thermal diffusion length of KCl is eight times as large as that of SiO_2 at the same modulation frequency.[7] Furthermore, the shape of the band at $\lambda_{max} = 560$ nm in this spectrum becomes obscure after two day's exposure. A reason for this is that a part of the dye molecules change their forms from the *Z*- to the *C*-form because of the introduction of the proton donating water molecules to the sample powder on exposure. Since the *C*-form has the intense band at $\lambda_{max} = 545$ nm (Figure 2), the absorbance at the shorter wavelength side of the band at $\lambda_{max} = 560$ nm increases on the formation of this form. These two kinds of change in molecular form seem reversible with the change of water content in the Rh B/KCl powder. The decrement of the dimer band indicates the relatively smaller yield of the *L*-form from the dimer which suggests a unique structure of the Rh B dimer on the lattice of ionic crystals.[4]

4. CONCLUSION

Indifferent to the depth of location in surface pores, Rh B molecules are cationic uniformly on the SiO_2 substrate. This is in contrast with the zwitterionic form of the dye molecules on the KCl substrate, which results from the difference in polarity of two solid substrates. The combination of PAS and FT-IR/DRS proved complementary and effective in studying the adsorbed dye molecules on solid substrates.

Acknowledgements

The author expresses sincere gratitude to Dr. Kenta Ooi, Government Industrial Research Institute, Shikoku, for kind permission to use the FT-IR/DRS and BET facilities.

References

1. K. H. Drexhage, *Dye Lasers* Springer, Berlin, Chap. 4, (1973)
2. M. Koizumi, *Photosensitized Reaction* Kagakudojin, Kyoto, (1978).
3. I. Rosenthal, P. Peretzand A. Muszkat, *J. Phys. Chem.*, **83**, 350 (1979); D. A. Hinckley and P. G. Seybold, *Spectrochim. Acta*, **44A**, 1053 (1988); J. Karpiuk, Z. R. Grabowski and F. C. De Schryver, *J. Phys. Chem.*, **98**, 3247 (1994).
4. (a) L. Ernst, *Ber. Bunsenges. Phys. Chem.*, **87**, 63 (1983); (b) K. Kemnitz, N. Nakashima, K. Yoshihara and H. Matsunami, *J. Phys. Chem.*, **93**, 6704 (1989).
5. E. Kanezaki, *Chem. Phys Lett.*, **138**, 352 (1987).
6. E. Kanezaki, *Mol. Cryst. Liq. Cryst.*, **166**, 245 (1989).
7. A. Rosencwaig, *Photoacoustics and Photoacoustic Spectroscopy* Wiley, New York, (1980).
8. J. E. Selwyn and J. I. Steinfeld, *J. Phys. Chem.*, **76**, 762 (1972); M. E. Gal, G. R. Kelly and T. Kurucsev, *J. Chem. Soc., Faraday Trans. 2*, **69**, 395 (1973).
9. Z. Grauer, A. B. Malter, S. Yariv and D. Avnir, *Colloids and Surfaces*, **25**, 41 (1987).
10. With estimated experimental error ± 300 cm^{-1} due to the band width in excitation.