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Vapochromism of Ionic Dyes in Thin Films of Sugar Gels

Ryoka Matsushima,* Naoko Nishimura, Kuniaki Goto, and Yoshiumi Kohno

Department of Materials Science and Chemical Engineering, Faculty of Engineering, Shizuoka University,
Johoku 3-5-1, Hamamatsu 432-8561

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Solid thin films of sugar gels containing ionic dyes, such as flavylium and thionine salts, exhibit extensive and vapor-specific color changes upon exposure to volatile organic compounds, such as methanol, ethanol, acetone, benzene, ether, and pyridine. Some of them show good vapochromic reversibility after repeated exposures, although extensive degradation occurs with pyridine vapor. Vapochromism has been explained in terms of solvation and stabilization of the dye molecules by permeated vapors, resulting in a shift of dye aggregation–deaggregation equilibria.

Reversible color changes by environmental and/or physical changes have been actively studied for use in molecular sensors, switches, and information processing devices. Extensive color changes caused by temperature or moisture through reversible dye aggregation have been reported, e.g. in bilayer membranes,[1–3] in alkane matrices,[4] on helical DNA templates,[5] and in hemicyanine-based bichromophores.[6] A novel thermochromism in polymeric hydrogels has been reported with a betain dye through a proton-transfer equilibrium between phenolate and phenol forms.[7] We reported thermochromism and solvatochromism of ionic dyes by reversible aggregation in aqueous sugar-gel matrices, where cationic dyes tend to coagulate and condense on the negatively charged sugar-gel surface via electrostatic attractions.[8] Recently, humidity-sensitive color changes of organic polymer films have received considerable attention, e.g., those through switching of the aggregation states of dyes (H- and J-aggregates) induced by adsorbed water molecules in layered assemblies of azobenzene derivatives,[9,10] a polymethine dye in thin films,[11] and sulfophthalein-doped polymers.[12] An optical sensing host dye that responds to amine vapors has also been reported.[13] Of particular interest is the vapochromism towards environmentally hazardous substances such as volatile organic compounds (VOCs). Vapochromism of crystalline metal complexes has been extensively studied,[14–18] and a chemoselectively responsive sensor array of metallo-porphyrin dyes for odor visualization has been demonstrated.[19] In contrast, the vapochromism of dye-doped organic polymer films or matrices towards VOCs has been scarecely reported to our knowledge, despite their merit of easier fabrication and low cost.

In the course of our investigation on the humidity-sensitive color changes of ionic dyes in sugar-gel thin films,[20] extensive vapochromic responses towards some VOCs were observed.[21] This paper is concerned with vapochromism of ionic dyes doped in thin films of sugar gels through vapor-induced changes in the dye aggregation states.

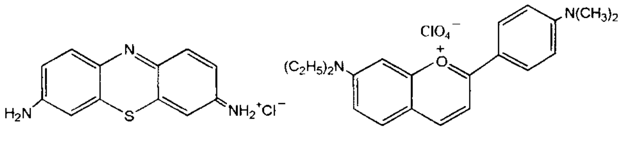
Experimental

Commercial thionine chloride (TH) (Tokyo Kasei), κ-carrageenan (hereafter denoted as carrageenan) and agarose gels (Wako), and all organic solvents of purest grade (Wako) were used as received, while water was de-ionized through ion-exchange resins. 7-Diethylamino-4′-dimethylaminoflavylium perchlorate (FV) was prepared by acid-catalyzed condensation of 4-diethylamino-2-hydroxybenzaldehyde and 4-dimethylaminoacetophenone (Scheme 1).[22]

To a mixture of 3 mL methanol solution containing FV (0.75 mM) or TH (1.5 mM) and 7 mL water was added carrageenan gel (0.1 g) or agarose gel (0.1 g) with vigorous stirring. The aqueous hydrogel was pasted on a silica glass plate and air-dried overnight at room temperature, giving a transparent thin film. The film was exposed to various vapors in a photometer cell sealed with a paraffin film for 2 h at room temperature. After each measurement of its absorption spectrum, the film was removed and exposed to air for 2 h. A dry film was prepared by transferring the air-dried film into a photometer cell with anhydrous calcium chloride and sealing with a paraffin film. Absorption spectra were recorded on a Hitachi U-3000 spectrophotometer.

Results and Discussion

Figure 1(a) illustrates the vapochromic responses of carrageenan film doped with FV upon exposure to various vapors for 2 h at room temperature. The shoulder around 600 nm is ascribable to the monomeric species and the 570 nm band to the dimeric or lower aggregates of FV.[8,20] In the air-dried film (broken curves) the 600 nm monomeric shoulder was much weaker as compared to the strong band of the aqueous hydrogel.[8] This implies that extensive aggregation had progressed during the removal of solvents from the aqueous hydrogel. Since water is a much better solvent for the sugar gel, the vapor-specific behaviors in Fig. 1 should be more reasonably rationalized by the relative affinities (solubilities) of



TH FV

Scheme 1. Structures and abbreviations of the dyes.

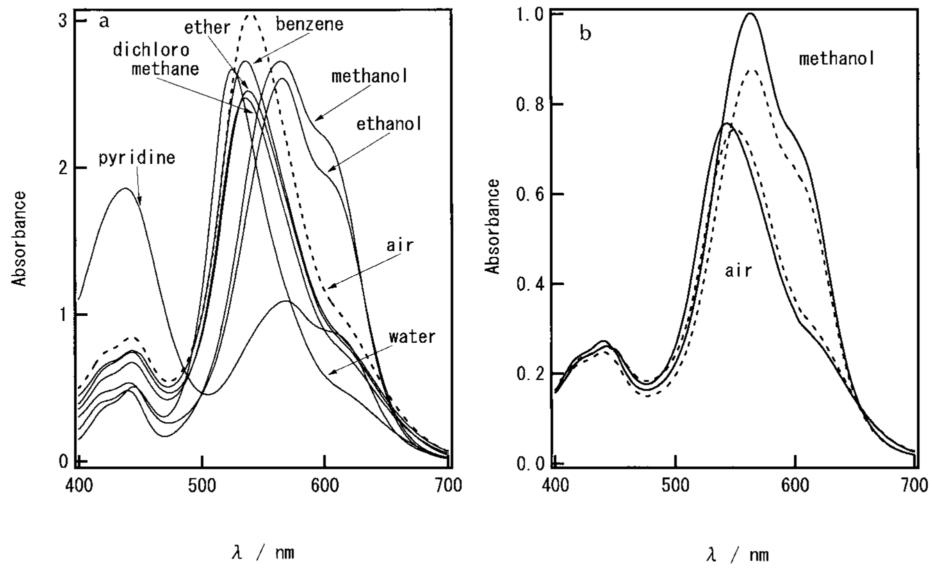


Fig. 1. (a) Vapochromic responses of FV-doped carrageenan film upon exposure to various vapors for 2 h at room temperature. The broken curve refers to a film exposed to the atmospheric air for 2 h. (b) Absorption spectra of the film before (solid curves) and after (broken curves) 5 cycles of repeated alternate exposures to methanol vapor and air.

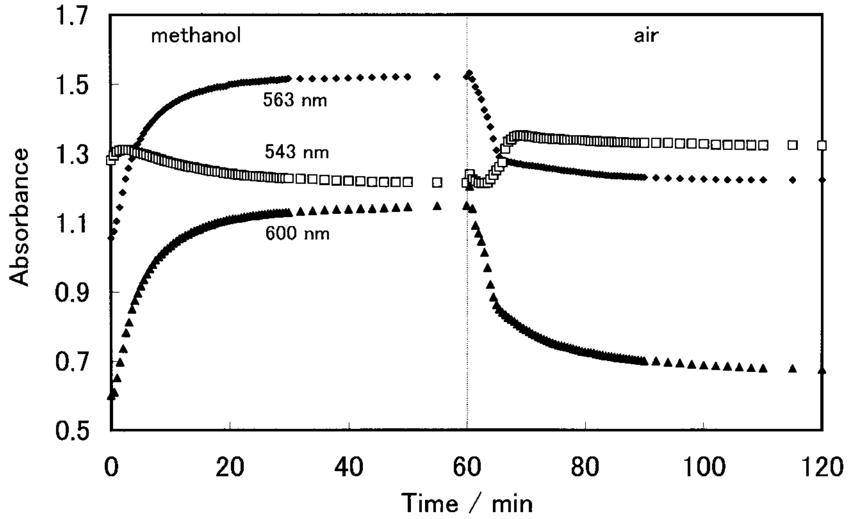


Fig. 2. Temporal changes in the absorbances of monomeric (600 nm) and aggregates (563, 543 nm) of FV-doped carrageenan film upon exposure to methanol vapor (left half) and atmospheric air (right half).

the permeated vapors with the dye rather than the gel. Upon exposure to vapors of methanol and ethanol (good solvents for FV), the monomeric shoulder and dimeric band increased markedly, whereas higher aggregation bands around 540 nm increased on exposure to benzene, ether, and water vapors (poor solvents for FV). Thus, with time of exposure to methanol vapor, the band of higher aggregates (543 nm) decreased and monomeric (600 nm) and dimeric (563 nm) bands increased in ca. 30 min. These changes were substantially reversed upon removal from the vapor and exposure to air, as illustrated in Fig. 2. Upon repeated alternate exposures to methanol vapor and air, however, the film revealed significant fatigue after several cycles under conditions not optimized, as illustrated in Fig. 1(b). Exposure to pyridine vapor resulted in the substantial decrease in the absorbance of FV, and a new band appeared around 430 nm of 4-diethylamino-4′-dimethylamino-2-hydroxychalcone. This implies partial conversion of FV into the chalcone due to an increase in the basicity.[22]

Figure 3 illustrates the vapochromic responses of carrageenan film (a) and agarose film (b) doped with TH upon exposure to various vapors. The absorption band around 600 nm is assigned to the monomeric species and the band around 550–570 nm to the dimeric or lower aggregates of TH.[23,24] Both films exhibited similar responses: vapors of methanol and ethanol (good solvents for TH) enhanced the monomer and dimer bands, and vapors of benzene and water (poor solvents) en-

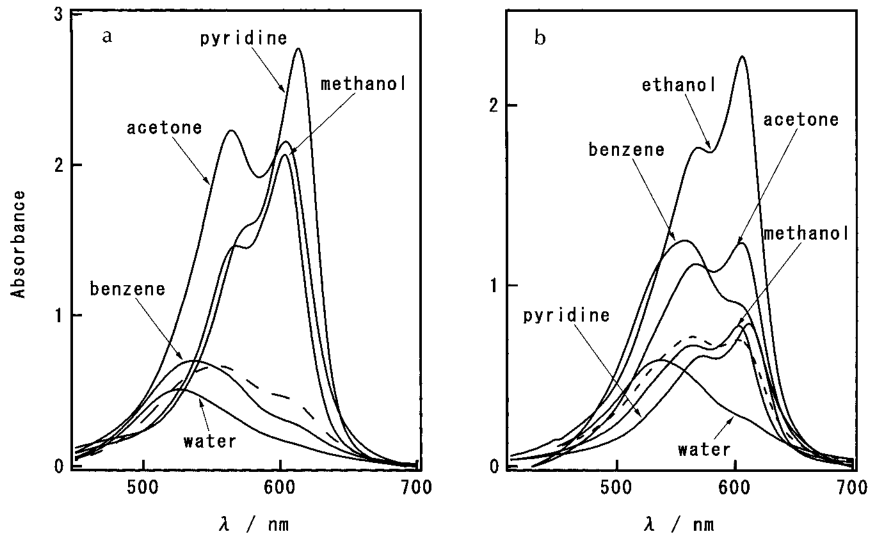


Fig. 3. Vapochromic responses of TH-doped carrageenan (a) and agarose (b) films, upon exposure to various vapors for 2 h at room temperature. The broken curves refer to films exposed to the atmospheric air for 2 h.

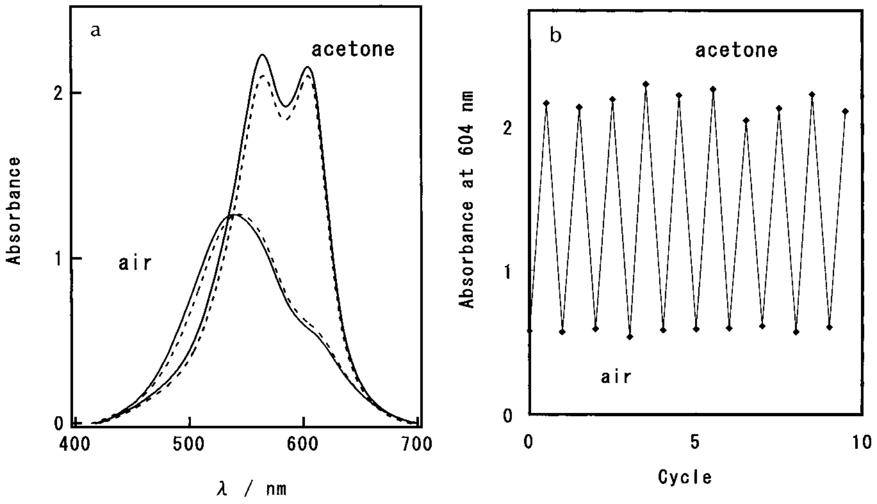
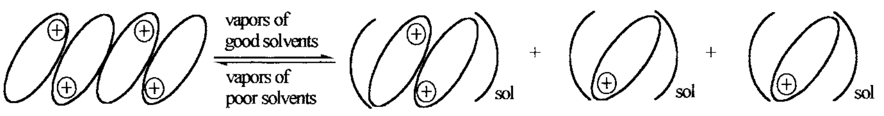


Fig. 4. (a) Absorption spectra of TH-doped carrageenan film before (solid curves) and after (broken curves) 10 cycles of repeated alternate exposures to acetone vapor and air. (b) Reversible color changes toward alternate 2 h-exposures to acetone vapor and air.



Scheme 2. A simplified model for the vapochromism of cationic dyes in thin films of sugar gels. Counter anions are omitted for simplification.

hanced the bands of higher aggregates. Thus, here again, the vapor-specific responses are ascribable to the solvation interactions that alter the dye aggregation states.

Good vapochromic reversibility was obtained with the TH-doped carrageenan film on exposure to acetone vapor, as illustrated in Fig. 4b. With time of exposure, both the 600 nm and 560 nm bands increased in pararell and attained a near maximum after ca. 20 min (data not shown). Upon alternate exposures to acetone vapor and atmospheric air, the color changed reversibly without substantial fatigues (Fig. 4b), and the spectra remained substantially unchanged after 10 repeated cycles (broken curves in Fig. 4a). Similarly, reversible color changes with exposures to methanol and water vapors are illustrated in Fig. 5, showing slight fatigue after 10 cycles. On the other hand, repeated exposure to pyridine vapor resulted in extensive degradation, and the film became almost colorless after 5 repeated cycles, which is not explainable as yet.

Vapochromism may be assumed to be a special case of solvatochromism, and a simplified mechanistic model may be proposed for the present vapochromism in terms of dye aggregation–deaggregation equilibria (Scheme 2), similar to that for the solvatochromism of the flavylium-doped aqueous hydro-

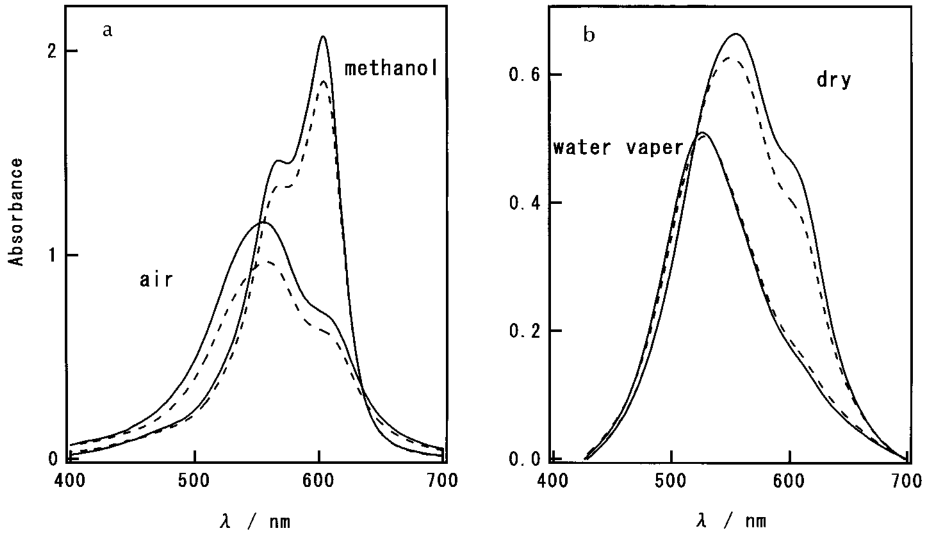


Fig. 5. Absorption spectra of TH-doped carrageenan film before (solid curves) and after (broken curves) 10 cycles of repeated alternate 2 h-exposures to methanol (a) and water (b) vapors.

gels.[8] However, vapochromic performances of doped dyes should be substantially different between a (dry) thin film and a volumed aqueous hydrogel. Thus, a high vapochromic response is expected in a thin film where permeated VOCs can effectively make contact with the dye molecules, but not in a volumed hydrogel where VOCs are diluted in the bulk solvent before interacting with the dye molecules. Further, dyes in thin films are constrained in small spaces, causing the dye molecules to aggregate more extensively than in a volumed hydrogel. Such strain should also exert a higher sensitivity (reactivity) to the VOCs upon contact. The restricted mobility of the aggregates in thin films can be substantially relaxed and/or the aggregates can dissociate upon exposure to the VOCs of good solvents, such as methanol and ethanol, to become strongly solvated and stabilized. If the solvation energy is larger than the aggregation energy, then deaggregation into lower aggregates and/or monomeric species would proceed.

When vapors of poor solvents permeate a gel, they cannot effectively solvate or they may even destabilize the dye molecules to enhance higher aggregation (backward).

Similarly, extensive vapochromism has been observed in a dye-doped Nafion film upon exposure to various vapors of VOCs, and a comparative study with the present sugar-gel films is in progress. Thin films of FV-doped carrageenan gels revealed *apparent* thermochromic behavior under air upon changes in temperature, as reported in a previous letter.[20] The spectral features were very similar to those obtained for the humidity changes at constant temperature. However, no significant thermochromism was observed when the film was placed over anhydrous calcium dichloride and sealed in a cell. Thus, the apparent thermochromism observed under air should be ascribed to the temperature-dependent changes in the amount of adsorbed water vapor.

In summary, ionic dye-doped thin films of sugar gels exhibit extensive vapor-specific vapochromism. On exposure to vapors of good solvents for dyes, the monomeric and dimeric bands remarkably increase, while the weak bands of higher aggregates shift to the blue on exposure to vapors of poor solvents. This phenomena can be explained in terms of solvation and stabilization of the dye molecules by the permeated vapors, resulting in a shift of the dye aggregation–deaggregation equilibria.

Interactions of the matrices with dye molecules and VOCs should be investigated, including microscopic examinations.

References

1 N. Nakashima and T. Kunitake, *J. Am. Chem. Soc.*, **104**, 4261 (1982).

2 E. Ando, J. Miyazaki, K. Morimoto, H. Nakahara, and K. Fukuda, *Thin Solid Films*, **133**, 21 (1985); E. Ando, J. Hibino, T. Hashida, and K. Morimoto, *Thin Solid Films*, **160**, 279 (1988).

3 T. Seki and K. Ichimura, *J. Phys. Chem.*, **94**, 3769 (1990).

4 N. DiCesare, M. Belletete, C. Marrano, M. Leclerc, and G. Durocher, *J. Phys. Chem.*, **103**, 795 (1999).

5 M. Wang, G. L. Silva, and B. A. Armitage, *J. Am. Chem. Soc.*, **122**, 9979 (2000).

6 S. Zeena and K. G. Thomas, *J. Am. Chem. Soc.*, **123**, 7859 (2001).

7 A. Seeboth, J. Kriwanek, and R. Vetter, *J. Mater. Chem.*, **9**, 2277 (1999).

8 R. Matsushima, A. Ogiue, and S. Fujimoto, *Chem. Lett.*, **2000**, 590; R. Matsushima, H. Okuda, M. Aida, and A. Ogiue, *Bull. Chem. Soc. Jpn.*, **74**, 2295 (2001).

9 K. Okuyama, M. Ikeda, S. Yokoyama, Y. Ochiai, Y. Hamada, and M. Shimomura, *Chem. Lett.*, **1988**, 1013.

10 T. Seki, T. Fukuchi, and K. Ichimura, *Langmuir*, **16**, 3564 (2000).

11 L. Daehne, J. Tao, and G. Mao, *Langmuir*, **14**, 565 (1998).

12 Y. Sadaoka, Y. Sasaki, and M. Yamada, *J. Mater. Chem.*, **3**, 877 (1993).

13 K. Yoshida, Y. Ooyama, S. Tanikawa, and S. Watanabe, *Chem. Lett.*, **2000**, 714.

14 C. L. Exstrom, J. R. Sowa, C. A. Daws, D. Janzen, and K. R. Mann, *Chem. Mater.*, **7**, 15 (1995).

15 C. A. Daws, C. L. Exstrom, J. R. Sowa, and K. R. Mann, *Chem. Mater.*, **9**, 363 (1997).

16 J. K. Evju and K. R. Mann, *Chem. Mater.*, **11**, 1425 (1999).

17 M. A. Mansour, W. B. Connick, R. J. Lachicotte, H. J. Gysling, and R. Eisenberg, *J. Am. Chem. Soc.*, **120**, 1329 (1998).

18 C. E. Buss, C. E. Anderson, M. K. Pomijie, C. M. Luts, D. Britton, and K. R. Mann, *J. Am. Chem. Soc.*, **120**, 7783 (1998).

19 N. A. Rakow and K. S. Suslick, *Nature*, **406**, 710 (2000).

20 R. Matsushima, A. Ogiue, and Y. Kohno, *Chem. Lett.*, **2002**, 436.

21 Annual Meeting on Photochemistry, Kyoto, September 2002, Abstr. p. 65.

22 R. Matsushima, S. Fujimoto, and K. Tokumura, *Bull. Chem. Soc. Jpn.*, **74**, 827 (2001).

23 S. Hamai, *Bull. Chem. Soc. Jpn.*, **73**, 861 (2000).

24 S. A. John and R. Ramaraj, *J. Appl. Polym. Sci.*, **65**, 777 (1997).