

Humidity-Sensitive Color Changes of Ionic Dyes in Solid Thin Film of Sugar Gel

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Solid thin films of sugar gels containing ionic dyes, such as flavylum perchlorates and Methylene Blue, revealed reversible color changes toward the changes in temperature and humidity. Absorption spectra of the thin films revealed extended aggregates with only a weak shoulder of the dye monomer even at high temperature, as compared with aqueous hydrogel matrices which showed strong monomer band. The thin films revealed good reversibility toward temperature changes and moderate reversibility toward humidity changes.

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 by temperature or moisture through reversible dye aggregation phenomena have been reported, e.g., in bilayer membranes,¹⁻³ in alkane matrix,⁴ on helical DNA template,⁵ and in hemicyanine-based bichromophores.⁶ Recently, a novel thermochromism in polymeric hydrogels has been reported with a betain dye through a proton-transfer equilibrium between phenolate and phenol forms,⁷ while we reported thermochromism and solvatochromism of ionic dyes by reversible aggregation in aqueous sugar-gel matrices.⁸ Of particular interest is humidity-sensitive color changes through switching of the aggregation states of dyes (H- and J-aggregates) induced by adsorbed water molecules, e.g., with azobenzene derivatives in synthetic layered assemblies,^{9,10} and a polymethine dye in thin films.¹¹ The present paper is concerned with humidity- and temperature-sensitive color changes of ionic dyes in solid thin films of sugar gels, implying substantially different features from those observed in aqueous hydrogel matrices.⁸ Manipulation and operation in a solid thin film would be essential for practical use, e.g., in color sensors.

Solid thin films of sugar gels were obtained as follows: To a mixture of 3 ml ethanol solution containing 7-diethylamino-4'-dimethylaminoflavylum perchlorate (FC, 0.75 mM) and 7 ml aqueous solution at pH 4.0 (adjusted with dilute sulfuric acid and sodium acetate solutions), was added *kappa*-carrageenan (hereafter simply denoted as carrageenan) gel (0.1 g) with vigorous stirring. The aqueous hydrogel was pasted on a glass plate and air-dried overnight at room temperature, giving a transparent thin film.

Figure 1(b) illustrates the thermochromic behaviors of the thin film as compared with those of aqueous hydrogel (a). The aqueous gel (a) exhibits a strong monomer band of FC around 600 nm at elevated temperature, which blue-shifts due to aggregation upon cooling.⁸ Contrary, the thin film (b) exhibits more extensive aggregation bands with substantial decrease in the monomer band. Thus, the thin film exhibits only a weak shoulder around 600 nm (ascrivable to the monomeric species) even at 50 °C in contrast to the strong monomer band in the aqueous gel (a), while rather strong bands around 540 nm (ascrivable to H-

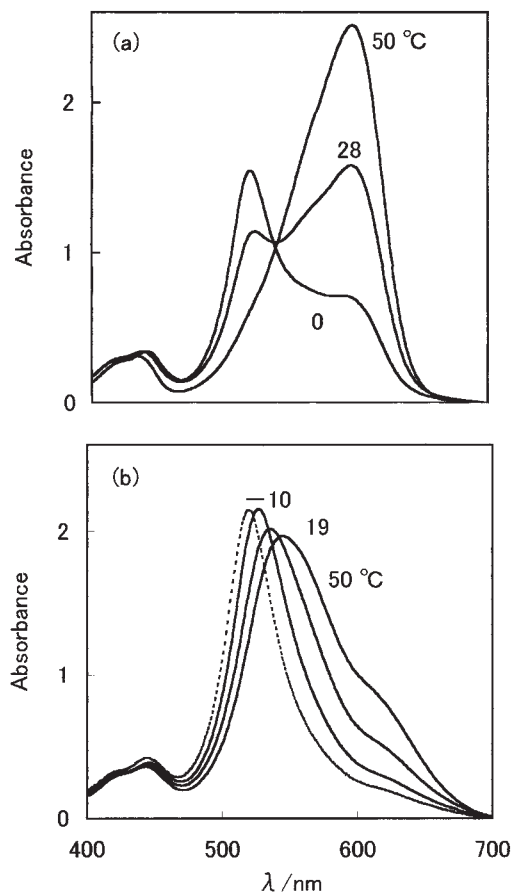


Figure 1. Thermochromic reactions of FC in (a) aqueous methanol and (b) solid thin film, of carrageenan gel. (a) FC $3.0 \cdot 10^{-5}$ M and carrageenan 1.0 wt% in 7 : 3 aqueous methanol solution at pH 4, (b) FC 0.9 wt% in carrageenan thin film. The broken curve refers to the spectrum of thin film dipped into water at 0 °C.

aggregates) which further blue-shifts with significant increase in its intensity upon cooling. This may imply that the aggregation is more extensively progressed in the thin film where the dye concentration is much higher than in the aqueous gel. By removal of the solvents (drying in the air) the dyes are concentrated while a trace or small amount of water should retain in the thin films in equilibrium with the atmospheric moisture, thus accelerating dye aggregation. When the thin film was dipped into cold water (0 °C), further blue shift was observed (broken curves in Figure 1b). Thus, in the thin films where aggregation is extensively progressed and monomeric species is of minor importance, the color changes are ascribable to the changes in the aggregation states or between lower and higher aggregates. In the aqueous gel the color changes are substantially ascribable to the changes between monomeric species (around 600 nm) and aggregates (around 530 nm) through dimer (slight shoulder around 570 nm).

Similar color changes were observed with FC in thin films of agar and agarose gels, while much less extensive color changes were found in films of pectin, amiropectin, and sodium alginate gels. Extensive color changes were also found with 4'-dimethylamino-flavylium perchlorate (FM) in thin films of carrageenan, agarose, agar, and pectin gels.

Thermochromic reversibilities of the thin films were examined toward repeated cycles of heating and cooling in the air. Thus, thin film of FC revealed good reversibility without significant fatigues: As illustrated in Figure 2a, the absorption spectra after 10 cycles of temperature change (open to the air) remained unchanged and overlapped with the initial ones. Thin film of FM, however, revealed rather poor reversibility, as illustrated in the broken curves in Figure 2b. This fatigue is ascribable at least partly to the tendency for hydration leading eventually to a chalcone.¹²

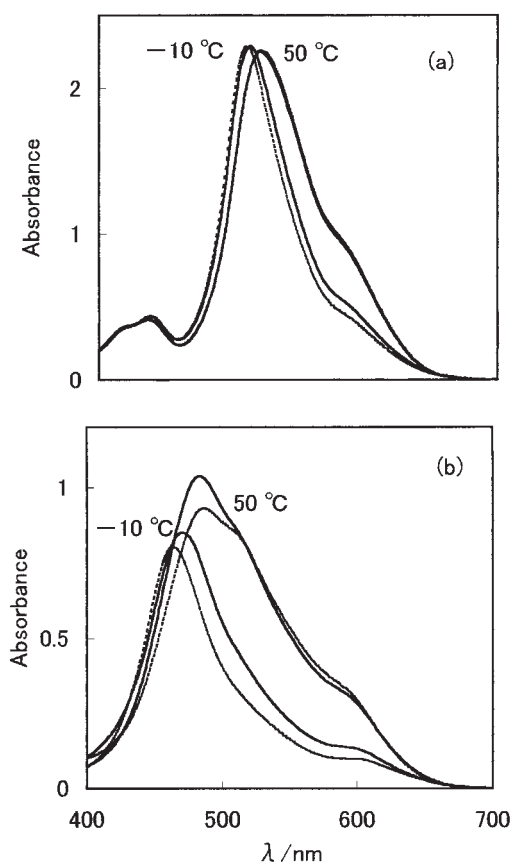


Figure 2. Absorption spectra of (a) FC and (b) FM in solid thin film of carrageenan gel before (solid curves) and after (broken curves) 10 cycles of alternate heating (50 °C) and cooling (−10 °C). (a) FC 0.9 wt%, (b) FM 0.5 wt%.

Thin films of carrageenan gel, dried over anhydrous calcium chloride overnight and sealed to keep air-tight in an optical cell, revealed extensive color changes upon exposure to a saturated vapor pressure of water in a sealed optical cell for 2 h at room temperature. Thus, the purple color (ca. 550 nm) of the dry film of FC changed gradually into red (ca. 520 nm), as illustrated in Figure 3. The color change could be repeated several times by alternate exposure to the dry (18 h) and the humid (2 h) atmospheres, with some fatigue (the broken curves refer to the

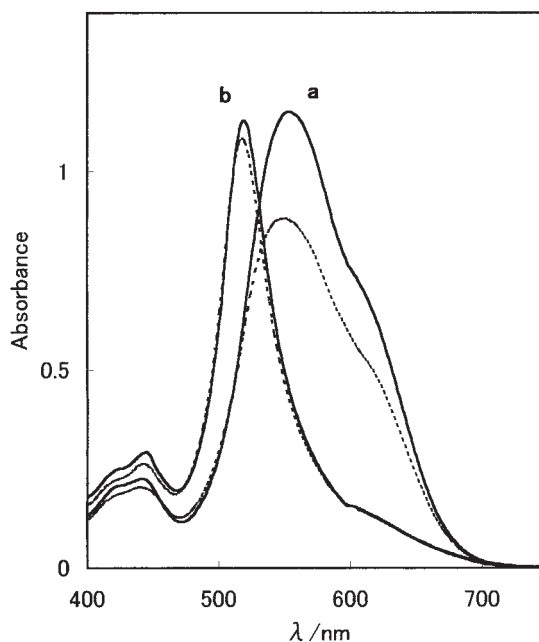


Figure 3. Absorption spectra of FC in thin film of carrageenan gel at room temperature. (a) Dried over anhydrous calcium chloride for 18 h, (b) exposed to the saturated vapor pressure of water at 20 °C for 2 h. The broken curves refer to the spectra after 5 cycles of alternate exposure to the dry and the humid atmospheres.

spectra after 5 repeated cycles). The remarkable influence of moisture in thin films (Figure 3) implies an important role of water molecule (with its high dielectric constant and hydrogen-bonding ability) to stabilize the aggregates of the charged dyes, to change aggregation states and/or the conformations of the host gels. A unique and important role of water has been demonstrated in controlling the aggregation of ionic dyes in layered assemblies^{9–11} as well as in zeolite.¹³

Similar humidity- and temperature-sensitive color changes have been observed in thin films with commercial ionic dyes, such as Methylene Blue and thionine, implying potential use in color sensors of temperature and humidity.

References and Notes

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