

Thermochromism and Solvatochromism by Reversible Dye Aggregation in Sugar-Gel Matrices

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Upon changes in temperature or solvent, extensive and reversible color changes (e.g., blue to pink) were observed with a cationic flavylium dye in sugar-gel matrices, such as agar, agarose, pectin, sodium alginate, and carrageenan gels, whereas only small spectral changes were found in methylcellulose gel or in the absence of any sugar gels. During many repeated cycles of warming and cooling no indications of significant fatigue were observed, demonstrating a high thermochromic reversibility. Comparable thermochromism and solvatochromism were observed with the well-known cationic dye Methylene Blue in the sugar-gel matrices. In the presence of an anionic surfactant in place of sugar gel, extensive color changes were also observed while no changes were observed at all in the presence of a cationic surfactant, thus implying an important role of the electrostatic interactions between the cationic dye and anionic surfaces or species. It has been assumed that the cationic dyes are reversibly coagulated or condensed on the negatively charged colloid-gel surface to enhance dye aggregation.

Intermolecular aggregation of cyanine dyes are well known to cause remarkable spectral changes. Usually, head-to-head (J-type) aggregation causes red-shifts and side-by-side (H-type) aggregation causes blue-shifts.[1–6] Methylene Blue (MB), which is popular due to use in the "blue bottle" experiment,[7,8] is one of the most extensively studied dyes; it forms both H-type and J-type aggregations. Thus, H-dimer formation within zeolite cavities by the aid of water has been reported,[9] while time-dependent spectral changes of MB in silica sol-gel matrix have demonstrated the occurrence of the monomer and dimeric species after sol-gel preparation.[10] The color changes[11] and stability[12] are strongly affected by the electrostatic interactions with oppositely charged species of additives. Thus, substantial changes in the absorption and fluorescence spectra of cationic dyes via complex formation with organic anions[13] and anionic dyes[14] in the presence and absence of cyclodextrins have been reported. The electrostatic attractions between opposite charged species are strong enough to retain self-assembled adsorption layers on polyions for a long term.[15–17]

Recently, the color variation and stability of naturally occurring anthocyanins have been successfully explained by the molecular stacking phenomena, such as copigmentation and self-association (aggregation) via hydrophobic interactions.[18,19] In the course of our investigation on the photochromism of the chalcone-flavylium system,[20] strong solvent effects and deviations from the Beer-Lambert law were observed on the colored form (flavylium ions).[21] And we reported a new thermochromism and solvatochromism of cationic flavylium ions based on the reversible aggregation on the negatively charged sugar colloid-gel surfaces through electrostatic attractions.[22] Recently, a novel thermochromism has been reported with a betaine dye in polymeric hydrogels by a proton-transfer equilibrium between the phenolate and phenol forms.[23] Contrary to the thermochromism based on a chemical process (proton transfer),[23] our thermochromic system is based on a physical process (dye aggregation).[22] We expect essentially better reversibility for a physical process than a chemical one, since a physical process is less susceptible to irreversible side reactions and decompositions. In the present work, thermochromism and solvatochromism of 4′,7-bis(dimethylamino)-4-phenylflavylium (FV) perchlorate and MB (for comparison) were studied in various sugar-gel matrices in some detail.

Experimental

Materials. Water was deionized and distilled, while organic solvents of guranteed grade (Wako) were used as received. Methylene Blue (MB) tetrahydrate, hexadecyltrimethylammonium bromide (HTAB, cmc = 0.8 mmol dm^{-3}), agar powder, agarose-III, sodium alginate, pectin from apple, κ-carrageenan, and methylcellulose were purchased (Wako) and used without purification. Sodium dodecylbenzenesulfonate (SDS, Kanto, cmc = 8.2 mmol dm^{-3}) was used as received. 4′,7-Bis(dimethylamino)-4-phenylflavylium (FV) perchlorate was prepared from 4′-dimethylaminochalcone and *m*-dimethylaminophenol with dry hydrogen chloride and chloranil (2,3,5,6-tetrachloro-2,5-cyclohexadiene-1,4-dione) in ethanol.[24]

Apparatus and Procedures. Electronic absorption spectra were recorded on a Hitachi U-3000 spectrophotometer and pH values were measured with a HM-30S pH meter (Toa Denpa). After the pH values of aqueous methanol solutions containing FV or MB (20–100 μM, 1 M = 1 mol dm^{-3}) were adjusted with aqueous solutions of 0.01 M sodium acetate and 0.01 M sulfuric acid, sugar gels (usually 2 wt%) were dissolved. The dye-dispersed sugar-gel matrices were placed in a 10 mm- or a 1 mm-thickness cell and these cells were immersed in a water bath or a refrigerator for 20 min before measurements of absorption spectra. No equipment for temperature control was available in the sample chamber of

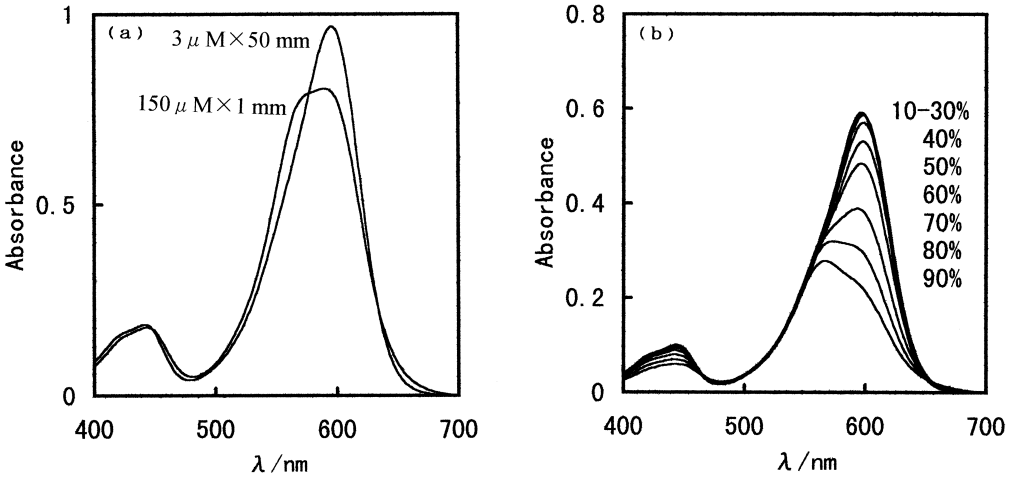

Fig. 1. Spectral changes of FV in solution in the absence of sugar gels. (a) Concentration-dependent absorption spectra (deviation from the Beer–Lambert law) of FV measured under a constant optical density (3 μM in a 50 mm-thickness cell vs 150 μM in a 1 mm-thickness cell) in 7:3 aqueous methanol solution at pH 4.8, (b) solvatochromism of FV (50 μM in a 1 mm-thickness cell) upon change in the water content (v/v%) in aqueous methanol solution at pH 4.0.

the spectrometer, and some errors in temperature are assumed.

Results and Discussion

Spectral Changes of FV in the Absence of Sugar gels. Figure 1a illustrates a concentration-dependent spectral change (or a deviation from the Beer-Lambert law) of the flavylium ion (FV) in the absence of sugar gels measured under a constant optical density, implying intermolecular interactions such as dye aggregations at higher concentration. Figure 1b illustrates spectral changes (solvatochromism) of FV in the absence of sugar gels with the change in the solvent. The band around 600 nm is decreased and a new band appears around 560 nm with the increase in the water content. Figure 2a demonstrates a small but significant thermochromism in solution in the absence of sugar gels. It should be noticed that significant spectral changes do occur due to aggregation at high FV concentration even in the absence of sugar gels.

Aggregation-dissociation phenomena (Eq. 1) of cyanine-type dyes have been extensively studied in solution and matrices, and usually, J-type (head-to-tail)

$$\begin{aligned} &\text{dye} + \text{dye} \rightleftarrows (\text{dye})_2 \\ &(\text{dye})_2 + (\text{dye})_2 \rightleftarrows (\text{dye})_4 \text{ etc.} \end{aligned} \quad (1)$$

aggregation causes red shifts and H-type (side-by-side) aggregation causes blue shifts in the absorption bands.[1–6] Either an increase in the dye concentration[25] or a lowering of temperature tends to enhance aggregation.[26] Increase in the water con-

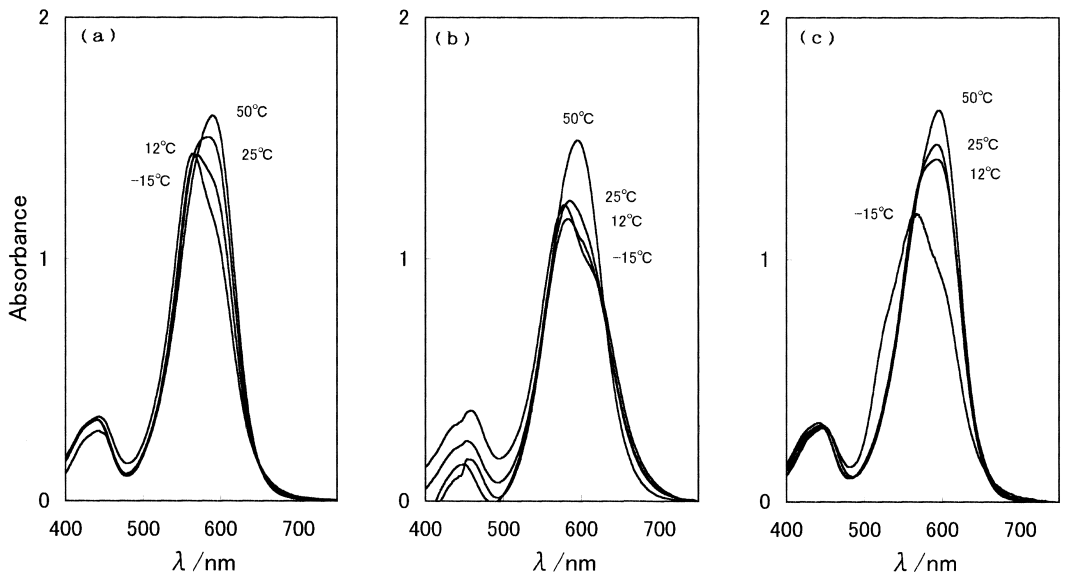

Fig. 2. Thermochromism of FV (30 μM) in the absence and presence of sugar gels at pH 7.0. (a) In the absence of sugar gels in 9:1 aqueous methanol, (b) in the presence of pectin gel (2 wt%) in 7:3 aqueous methanol, and (c) in the presence of methylcellulose gel (2 wt%) in 9:1 aqueous methanol.

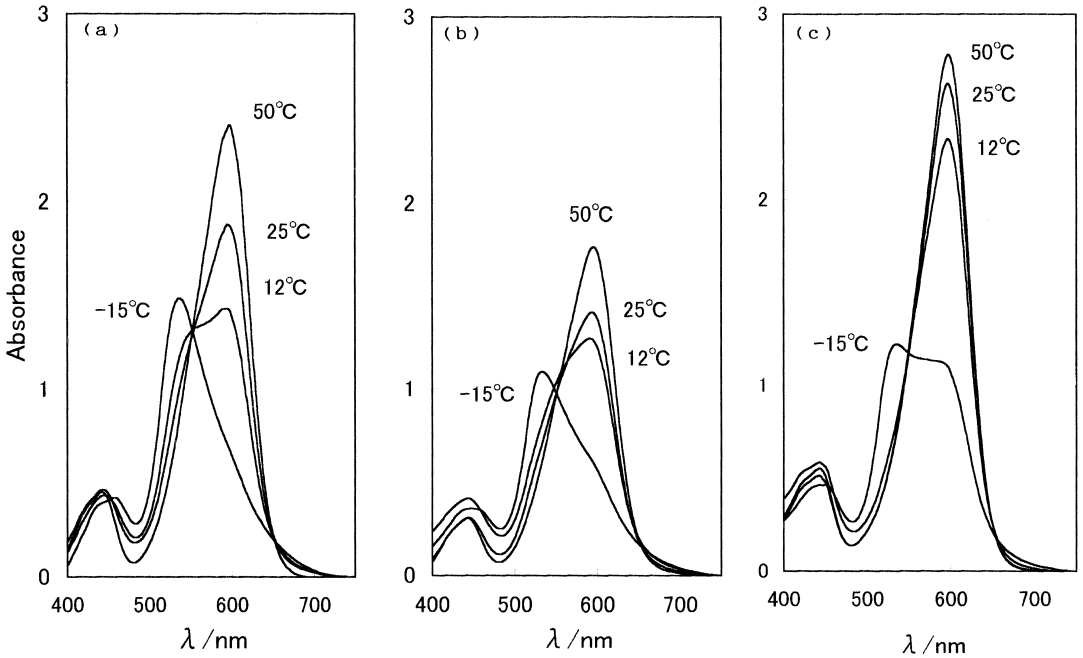

Fig. 3. Thermochromism of FV (30 μM) in various sugar gel matrices. (a) In agar gel (2 wt%) in 6:4 aqueous methanol at pH 6.0, (b) in agarose gel (2 wt%) in 7:3 aqueous methanol at pH 7.0, (c) in sodium alginate gel (2 wt%) in 6:4 aqueous methanol at pH 4.0.

tent also tends to lower the solubility of FV, enhancing aggregation. Thus, the band of FV around 600 nm is ascribable to the monomeric species and the shorter wavelength bands to H-aggregated species. The spectral changes are substantially enhanced in the presence of polysaccharide gels, as described below.

Thermochromism of FV in Sugar-Gel Matrices. Figure 2 illustrates spectral changes of FV in the absence (a) and in the presence of pectin gel (b) and methylcellulose gel (c), in 9:1 aqueous methanol, all showing rather small thermochromism. The band shifts are relatively small (from ca. 600 to 560 nm) in the absence of sugar gels and in the presence of pectin and methylcellulose gels (Figs. 1 and 2). The band around 560 nm may be assigned to lower aggregates such as H-dimers, while the shoulder around 520 nm (Fig. 2c) may be due to higher H-aggregated species.

In the gel matrices of agar, agarose, and sodium alginate, on the other hand, much more extensive themochromisms were observed, as shown in Fig. 3. Thus, the 520 nm bands of higher aggregates are stronger, while the 560 nm band or shoulder is less clear. Similarly, extensive thermochromism and solvatochromism were observed with 4-diethylamino-4′-dimethylaminoflavylium (FV-H with R_C = H) perchlorate in sugar gels, as illustrated in Fig. 4. Besides the sharp 520 nm bands, small

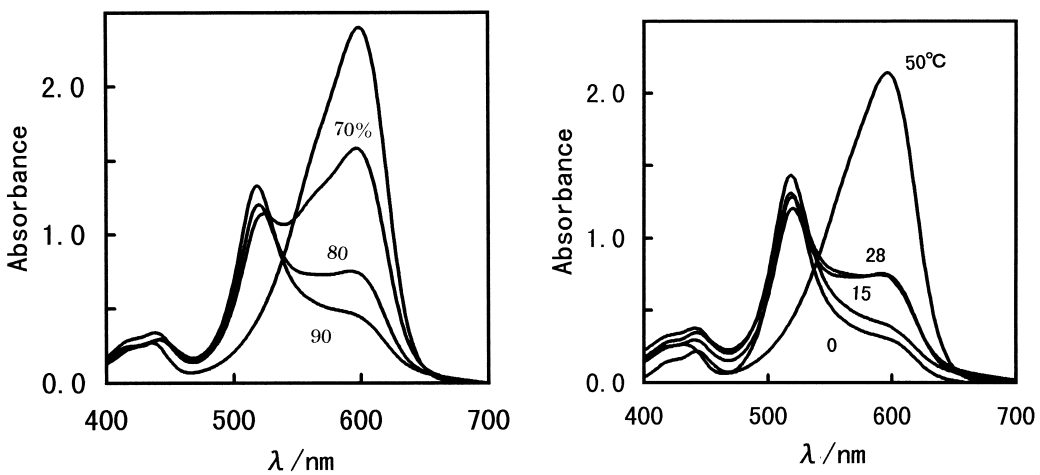

Fig. 4. Solvatochromism (left) and thermochromism (right) of 4-diethylamino-4′-dimethylaminoflavylium perchlorate (30 μM) in the presence of κ-carrageenan (1 wt%) in 8:2 aqueous methanol solution at pH 4.0. Figures in the left-hand side refer to the water content (v/v%) in the solvent.

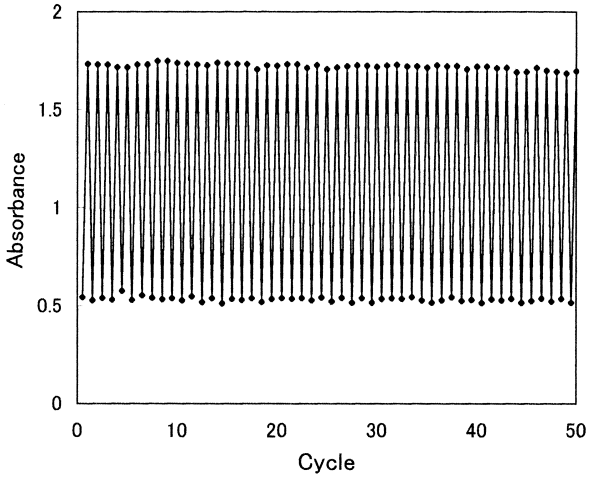

Fig. 5. Thermochromic reversibility of FV (30 μM) in sodium alginate gel (2 wt%) upon repeated cycles of warming (50 °C) and cooling (−15 °C) in 6:4 aqueous methanol at pH 7.0. The vertical axis refers to the absorbance at 595 nm.

shoulders can be seen around 560 nm, suggesting a stepwise and rapid growth of higher aggregates through dimers.

Upon many repeated cycles of warming and cooling no indications of significant fatigue were found, as demonstrated in Fig. 5. The spectra after repeated color changes were well overlapped with those of the initial gels. Similar thermochromic reversibilities were obtained in agar, agarose, and κ-carrageenan gels. The κ-carrageenan gel of FV-H also showed high thermochromic reversibility upon many repeated temperature changes at pH 4, though conversion into 2-hydroxychalcone derivative could take place at higher pH region via hydration.

Figure 6 illustrates a solvatochromism of FV in sodium alginate gel toward the change in the water content, demonstrating more extensive color changes as compared with those observed in the absence of sugar gels (Fig. 1b). Similar solvatochromisms were observed with agar, agarose, and κ-carrageenan gels. Absorption spectra of FV in non-aqueous solvents were examined, too, as illustrated in Fig. 7. While a strong monomer band appeared around 600 nm in a good solvent (acetone), this band disappeared and a weak band appeared around 530 nm in a poor solvent (9:1 ether-acetone). When the ether solution was kept standing at room temperature for a few days, dark precipitates were obtained. After light washing and drying, the precipitates were pasted on a piece of fine paper and were subject to the measurement of the reflection spectrum. The spectra (b) and (c) in Fig. 7 are fairly comparable. This implies that the 530 nm band is ascribable to higher aggregated species, and also supports the above assignment of the 520 nm band to higher aggregates formed in aqueous hydrogels.

The colloid-gel surfaces of agar, agarose, sodium alginate and κ-carrageenan are assumed to bear significant negative charges (which are associated with positive counterions), whereas the gel surfaces of methylcellulose and pectin bear nil or little charges since their hydroxy groups are totally or substantially methylated, respectively. Through electrostatic forces the cationic FV ions would be coagulated and/or condensed

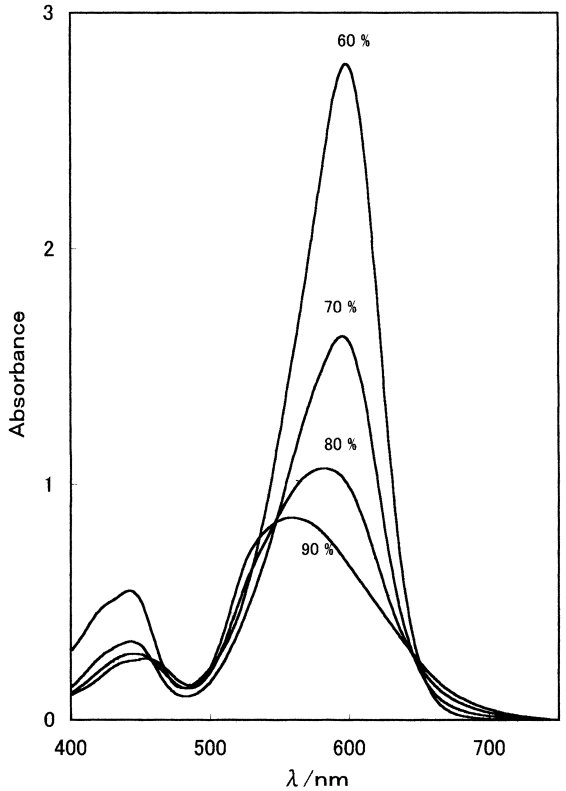

Fig. 6. Solvatochromism of FV (30 μM) in sodium alginate gel (2 wt%) upon change in the water content (v/v%) in aqueous methanol at pH 4.0 at 25 °C.

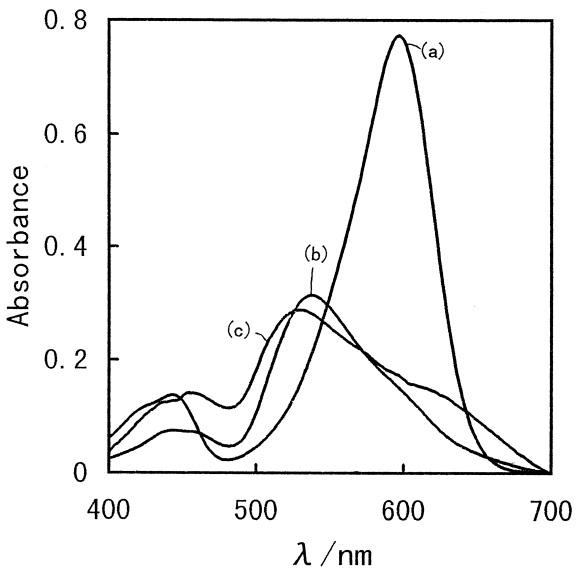

Fig. 7. Comparison of the absorption spectra of FV in acetone (a) and 1:9 acetone–ether solution (b), with reflection spectra of the precipitates (c) obtained from the ether solution on standing for a few days.

on the anionic colloid surfaces, thus enhancing dye aggregations. A schematic model is illustrated in Fig. 8.

In support for the role of the electrostatic interactions between opposite charges, addition of an anionic surfactant

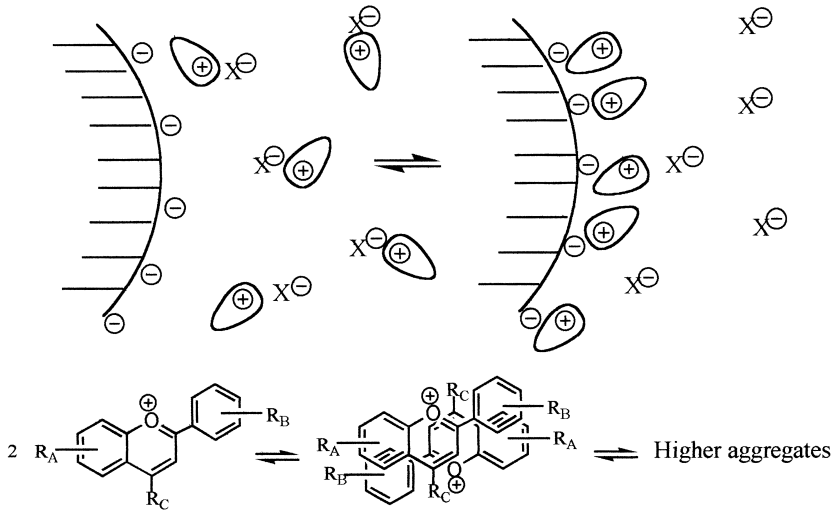

Fig. 8. Assumed model for reversible coagulation and/or condensation of the cationic FV ions on the negatively charged colloid-gel surface to enhance dye aggregation. The counter cations on the colloid surface are omitted for simplicity.

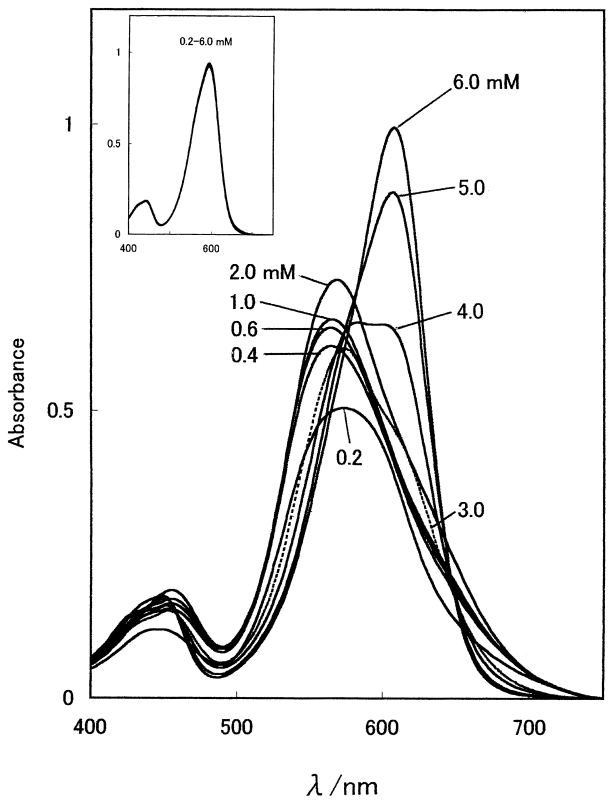

Fig. 9. Effects of anionic surfactant (SDS) on the spectra of FV (20 μM) in 4:1 aqueous methanol solution at pH 7. The inset illustrates the nil effect of cationic surfactant (HTAB) under similar conditions.

(SDS) caused extensive spectral changes, whereas cationic surfactant (HTAB) caused no changes at all, as illustrated in Fig. 9. Thus, it is apparent that the interactions between the cationic FV and the anionic micelle surface play a crucial role for the spectral changes. Thus, on closer inspection at low SDS concentration (0.2–1.0 mM), the dimer band appears around 560 nm at 0.2 mM SDS; this is blue-shifted (formation of higher aggregates) with increasing SDS. At higher SDS concentration (2.0–6.0 mM), contrary, dissociation of the aggregates into monomers would become dominant, since the solubility or dispersibility of the dye is increased in the presence of a large amount of SDS. Spectral changes of a cationic dye due to interaction with negative sugar-gel surfaces has been reported earlier,[11] but related reversible thermochromism has not been reported before 2000,[22] to the best of our knowledge. The substantial color changes of FV by aggregation in sugar-gel matrices may draw special interest in relation to the mechanisms (copigmentation, association, and stacking) for the color variation of the natural anthocyanin dyes in flowers and fruits containing aqueous sugar-gels.[18,27]

Thermochromism of MB in Sugar-Gel Matrices. The structures and shapes of the cationic FV and MB dyes are fairly comparable with each other, and hence comparable thermochromic and solvatochromic behaviors would be expected in the sugar-gel matrices. Figure 10 illustrates the thermochromism of MB in κ-carrageenan gel, demonstrating extensive color changes and good reversibility. Similar color changes and reversibilities were obtained in the gel matrices of agar and sodium alginate, while very small changes were found in pectin and agarose gels and nil changes in methylcellulose gel. The blue band around 660 nm has been assigned to the MB monomer and the new band around 600 nm to the H-type aggregates in acid aqueous solution.[10] Similar blue shift of thionine dye (shift from ca. 600 to 550 nm) has been assigned to the formation of H-aggregates within a zeolite in the presence of coadsorbed water.[9] From these facts, we consider that the reversible thermochromism of MB in the sugar gels shown in Fig. 10 are ascribable to the formation of H-aggregates enhanced by the electrostatic interactions with negative charges on the colloid-gel surfaces.

Both FV and MB dyes undergo H-type aggregation leading to the blue shifts, perhaps because their molecular structures are fairly comparable to each other.

Additive Effects and Solvatochromism of MB. In sugar-gel matrices (such as agarose and sodium alginate), exten-

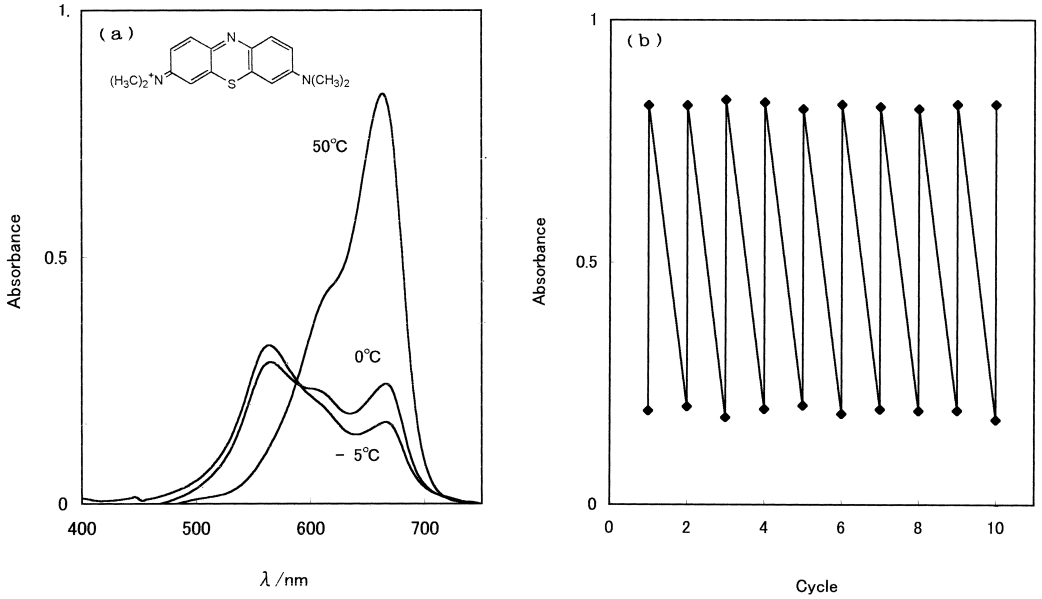

Fig. 10. Thermochromism of MB (10 μM) in a gel matrix of κ-carrageenan (2 wt%) in 8:2 aqueous methanol at pH 7. (a) Spectral changes, (b) thermochromic reversibility upon repeated cycles of warming (50 °C) and cooling (−5 °C). The vertical axis in (b) refers to the absorbance at 663 nm.

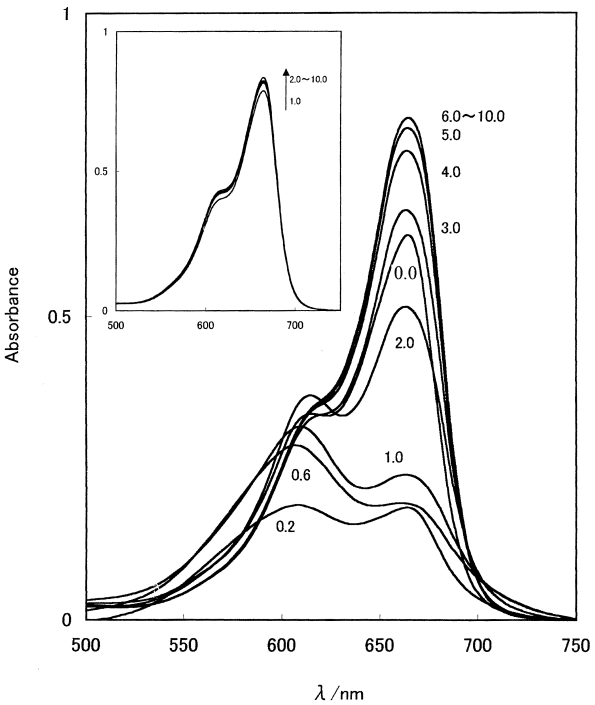

Fig. 11. Effects of anionic surfactant (SDS) on the spectra of MB (10 μM) in aqueous solution at pH 7. The inset illustrates the nil effect of cationic surfactant (HTAB) under similar conditions. Figures refer to the concentrations/mM of the surfactants.

sive solvatochromisms (blue shifts by the increase in the water content) were observed (data not shown). Further, extensive spectral changes were observed in solution upon addition of SDS while nil changes were obtained for HTAB, as illustrated in Fig. 11. On addition of a small amount of SDS (0.2–1.0 mM), aggregation of MB is enhanced (increase in the 610 nm band) as expected. At higher amounts of SDS, however, the solubility or dispersibility of the dye would be increased, and dissociation of the aggregates into monomers would become dominant (increase in the 660-nm monomer band). On the other hand, extensive spectral changes were observed with an anionic dye (Acid Orange 7) upon addition of the cationic HTAB whereas nil changes were found by the anionic SDS (data not shown). These results demonstrate the importance of the electrostatic interactions of the cationic MB dye with opposite charges on the colloid micelles (or oligomers).

In summary, extensive thermochromism and solvatochromism of cationic dyes (FV and MB) were observed in polysaccharide-gel matrices by reversible coagulation and aggregation on the negatively charged colloid-gel surfaces through electrostatic attractions. Any other cationic and anionic dyes should generally exhibit extensive chromisms by reversible aggregation on the oppositely charged surfaces.

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