Thermochromic Properties of Flavylium Salts in Agar-Gel Matrix

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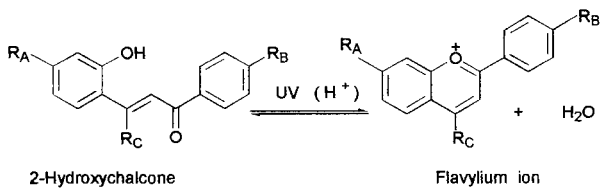
Flavylium salts exhibited a reversible thermochromism in an agar-gel matrix. Thus, by the temperature change from –3 to 50 °C, the absorption band around 600 nm of 7-diethylamino-4'-dimethylaminoflavylium perchlorate increased by a factor of ca. 1.5, while the band around 520 nm substantially decreased. Upon repeated cycles of the color change no significant fatigues were observed. The thermochromic behaviors were tentatively rationalized to the dye aggregation phenomenon enhanced by the sol-gel matrix.

Despite that the excellent color properties (e.g., high color purity, intensity, and variation) have long been recognized, it is only recently that the variation and stabilization of naturally occurring anthocyanins have been successfully rationalized to the molecular stacking phenomena, such as copigmentation and self-association (aggregation), via hydrophobic interactions.[1, 2] We have attempted to develop new and environmentally suitable functional dyes by least modifications of the anthocyanidine dyes.[3, 4] In the course of our investigation on the photochromism of the chalcone-flavylium system (R_C = H in the following Scheme),[3]



unusual spectral features, such as a large deviation from the Beer-Lambert rule, were observed on the colored forms (flavylium ions) in solution[5] and in sol-gel matrix.[6] Figure 1(a) illustrates the thermochromism of 7-diethylamino-4'-dimethylaminoflavylium perchlorate (**1**) (30 μM) in an agar-gel matrix at pH 4.8. At temperatures above 30 °C a strong band appears around 600 nm (blue), which is substantially decreased and a new band appears around 520 nm (magenta) by cooling down to –3 °C. Under these conditions spectral changes of the flavylium **1** due to hydration are unlikely, since its absorption spectrum in aqueous methanol solution at pH below 5.0 was fairly stable and unchanged at room temperature for over a week and only slightly decreased on heating at 50 °C for a week. The relative intensities of the two bands change significantly by the change in the water content of the gel (Figure 1(b)). Figure 2 illustrates the reversible color change of the gel toward repeated cycles for warming and cooling, demonstrating excellent thermochromic reversibility. Similar thermochromic features were also found with many other flavylium salts. Among others 4-phenyl derivatives (R_C = phenyl) are chemi-

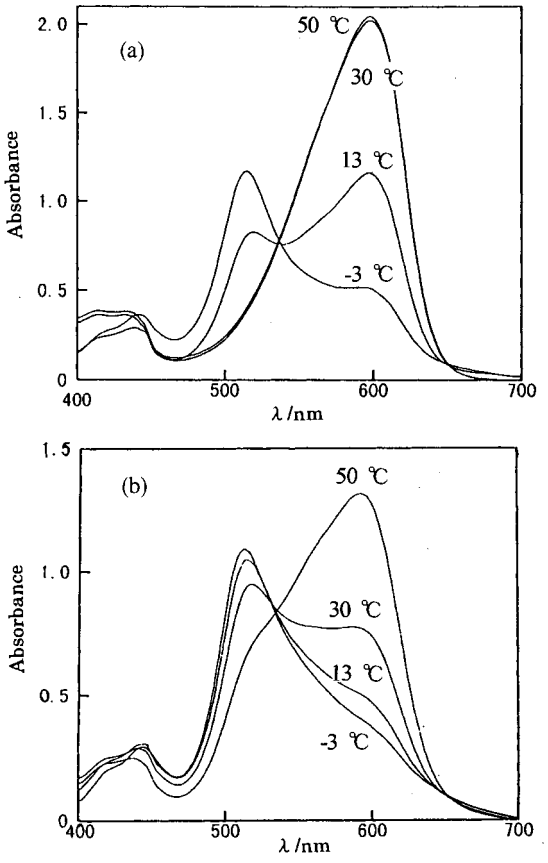


Figure 1. Thermochromism of the agar-gel of flavylium **1** at pH 4.8 containing **1** in 30 μ M and agar 2.0 wt% in a mixture of water : methanol in 7:3 ratio (a) and in 9:1 ratio (b).

cally more stable and hence more favorable models for study in a wide pH range, since they are reluctant to hydration in a wider pH range, while many flavylium ions with R_C = H tend to undergo hydration at a higher pH region leading to chemical bleaching.[1, 3]

The thermochromic responses were much less extensive in fluid solution in the absence of agar. Figure 3 illustrates the spectral changes of 7-diethyl-4'-dimethylamino-4-phenylflavylium *p*-toluenesulfonate (**2**) toward the changes in temperature and dye concentration in a fluid aqueous methanol solution, measured under conditions that the products (dye concentration times cell-depth) were kept constant. In a lower concentration (3 μM × 50 mm-depth) a single band appears around 600 nm (a), but in a higher concentration (150 μM × 1 mm-depth) the band is reduced and a new shoulder appears around 570 nm (b). Upon cooling the latter solution the 570 nm band increases and the

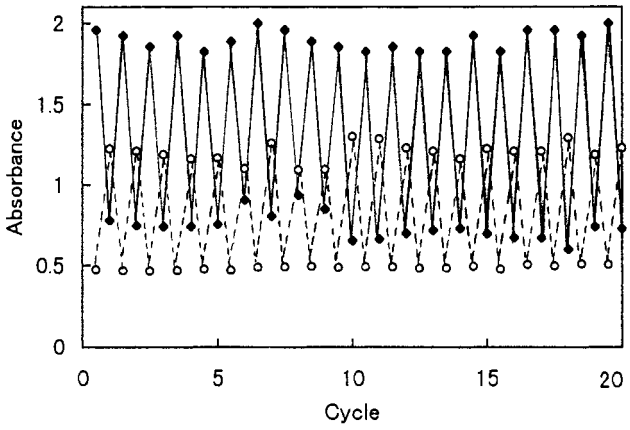


Figure 2. Thermochromic reversibility of the agar-gel of flavylium **1** toward repeated cycles of warming (50 ℃) and cooling (-3 ℃) in 7:3 aqueous methanol mixture at pH 4.8. (■) : 595 nm, (○) : 516 nm.

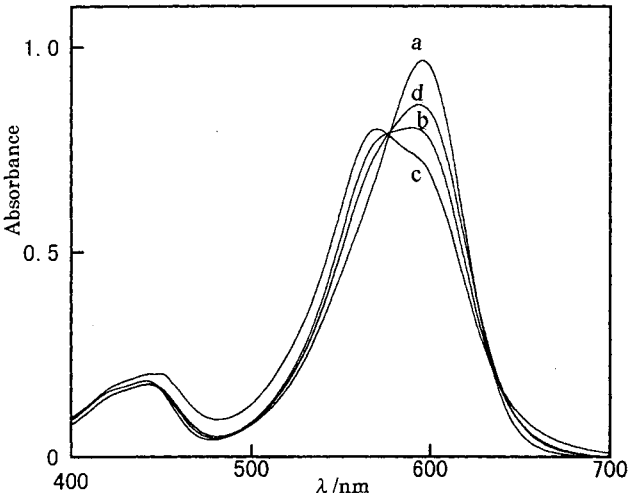


Figure 3. Effects of the dye concentration and temperature on the absorption spectra of flavylium **2** in the absence of agar in 7:3 aqueous methanol solution at pH 4.0. Concentration of **2**, depth of the cell, and temperature of the gel were (a) 3 μM, 50 mm-depth, 20 ℃; (b) 150 μM, 1 mm-depth, 20 ℃; (c) 150 μM, 1 mm-depth, -3 ℃; (d) 150 μM, 1 mm-depth, 50 ℃; respectively.

600 nm band decreases (c), whereas the reverse changes are seen on warming (d), demonstrating a small but significant thermochromism even in the absence of agar.

$$\text{dye} + \text{dye} \rightleftharpoons (\text{dye})_2$$

$$(\text{dye})_2 + (\text{dye})_2 \rightleftharpoons (\text{dye})_4 \quad \text{etc.} \qquad (1)$$

Aggregation-dissociation phenomena (eq 1) of cyanine-type dyes have been extensively studied in solution[7] and matrices.[8, 9] Usually head-to-tail (J-type) aggregation causes red-shifts and side-by-side (H-type) aggregation causes blue-shifts in the absorption bands. Either the increase in the dye concentration or the increase in the water content tends to accelerate aggregation. At a higher temperature the equilibrium tends to shift to the left and the monomer bands become dominant, while at a low temperature the bands of aggregates become dominant. In the present case, the long wavelength bands around 600 nm may be ascribed to the monomeric species and the shorter wavelength bands to dimeric and/or aggregates of H-type. The remarkable thermochromic responses of the flavylium salts in the agar-gel matrix, as compared to small responses in fluid solution, imply crucial influence of the hydrogel matrix on the dye aggregation. Matrix properties such as the hydrophilic-hydrophobic changes (as well as the size and viscosity) of the dye environments may be involved, in the similar manner to the natural anthocyanins whose stability and stacking properties are assisted by hydrogen bonding in the hydrophilic sugar moieties.[1, 2]

References and Notes

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