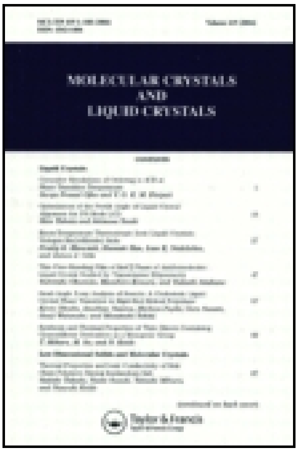

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High-Order Aggregation of Crystal Violet in the Chromonic Lyotropic Mesophases of 7,7′-Disodiumchromoglycate

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High-Order Aggregation of Crystal Violet in the Chromonic Lyotropic Mesophases of 7,7′-Disodiumchromoglycate

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Electronic absorption spectra of Methylene Blue (MB), Crystal Violet (CV), and Ponseau BS (PBS) have been measured in the host of the 7,7′-disodiumchromoglycate (7,7′-DSCG)-water system. In the chromonic mesophases of the 7,7′-DSCG-water system, the metachromasy bands of MB (rod-like cationic guest) is weakened compared with that in water, that of CV (disk-like cationic guest) largely blue-shifted up to 504 nm, and that of PBS (anionic guest) was unchanged. This observation indicates that the association behavior of a guest in these phases depends on the shape and polarity of the guest. The large blue shift observed for CV indicates that the CV molecules are forced to associate in the chromonic lyotropic mesophases of 7,7′-DSCG forming an aggregate with a high aggregation order. A possible mechanism of this high-order aggregation of CV in these mesophases is proposed; a hollow formed by the columns of the stacked 7,7′-DSCG molecules incorporates such a cationic disk-like guest as CV by a cooperative action of the electrostatic force causing a binding of guest molecules to the anionic sites on the surface of the hollow and the dispersion force causing formation of sandwich aggregates of guest molecules.

Keywords: aggregation, crystal violet, chromonic mesophase, lyotropic liquid crystal, disodiumchromoglycate

I. INTRODUCTION

Some aromatic compounds in water exhibit “chromonic” mesophases in spite of the absence of alkyl chains.[1–5] The chromonic mesophases were suggested to be a new breed of lyotropic liquid crystals on the ground that chromonic lyotropic mesophases are not miscible with the amphiphilic lyotropic mesophases, and were recognized as lyotropic discotic phases.[6] The 5,5′-disodiumchromoglycate (5,5′-DSCG)-water system was the first to be found to form the chromonic mesophase.[1] It is, however, suggested[6] that chromonic mesophases are widespread and have been repeatedly encountered in the past.[7–12] Some models[13–15] of columnar structures were proposed for the molecular arrangement emerged in the chromonic mesophase on the bases of NMR, X-ray diffraction, FTIR and optical microscopy studies.[1–5,15–21] Aiming to verify these models, we have recently investigated the association behavior of guests in the host of the 5,5′-DSCG-water system by observing the behaviors of the metachromasy (*D*) bands in their electronic absorption spectra.[22] It was found that the disk-like cationic guests (Crystal Violet (CV) and Malachite Green (MG)) exhibits *D*-bands in the mesomorphic host of the 5,5′-DSCG-water system, whereas no *D*-band is observed for a rod-like cationic guest (Methylene Blue (MB)) in that host. This observation implies that the associations of CV and MG molecules are favored by the molecular arrangement in the chromonic mesophase of the 5,5′-DSCG-water system. This unexpected phenomenon can be explained in terms of some crucial structural parameters of the guests and a lyotropic columnar structure[14] of the host.

The 7,7′-disodiumchromoglycate (7,7′-DSCG)-water system exhibits chromonic mesophases (N and H mesophases) similar to those (N and M mesophases) observed in the 5,5′-DSCG-water system.[21] In this paper, we have observed the behavior of the *D*-bands of an anionic dye (Ponseau BS (PBS)) as well as cationic dyes (MB and CV) in the host of 7,7′-DSCG-water system to investigate the association behavior of the dyes in this host. This study shows, as an extension of our investigation mentioned above, how the charge polarity and the shape of the guest molecule influence the association of the guest in the chromonic mesophsaes of the host. We have also aimed to clarify the similarity or difference of molecular arrangements in the chromonic lyotropic mesophases of 7,7′-DSCG and 5,5′-DSCG from the viewpoint of the association behavior of the guest.

II. EXPERIMENTAL

7,7′-DSCG was kindly provided by the Pharmaceutical Division of Fison Ltd. (Loughborough, U.K.) and was used without further purification. All the dyes, whose structures are shown in Figure 1, were used as purchased. 7,7′-DSCG was dried in vacuum and introduced into the mother aqueous solution of the dye with a dye concentration of 2.17 mmol/l to yield the 7,7′-DSCG concentration of 10 wt% (ca. 200 mmol/l). The mixture thus prepared was made homogeneous by sonication and stirring. This sample was sandwiched between two borosilicate glass plates with a gap adjusted to 10–50 μm by using a polyethylene or teflon spacer. The sample cell was sealed with epoxy resin. The temperature of the sample cell was controlled by circulating water or alcohol when the polarizing microphotographs and absorption spectra were measured. To compensate for the Rayleigh scattering by a sample cell containing a mesomorphic host and a guest, an absorption

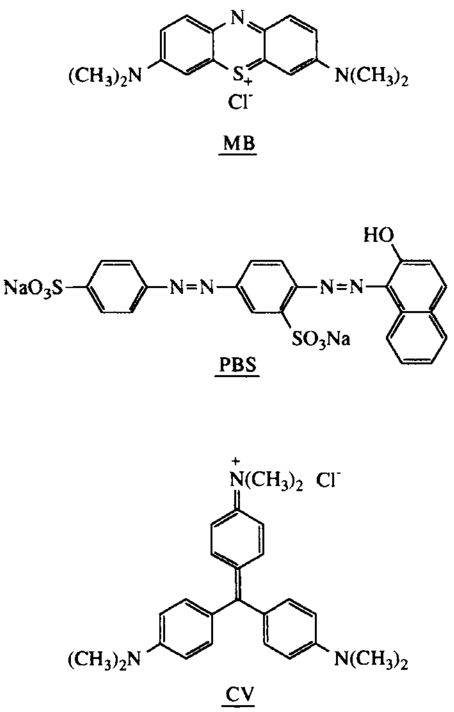

FIGURE 1 Molecular structures of MB, PBS and CV.

spectrum due to the Rayleigh scattering by a reference cell containing the host only was subtracted from the apparent absorption spectrum of the sample cell in the visible region. By use of the polarizing-microscopic method, the following transition temperatures were observed for the 7,7′-DSCG-water system whose concentration is 10 wt%[21]:

$$\text{I phase} \underset{41^\circ\text{C}}{\rightleftarrows} \text{R phase} \underset{19^\circ\text{C}}{\rightleftarrows} \text{N phase} \underset{\text{ca.}\,8^\circ\text{C}}{\rightleftarrows} (\text{N+H})\ \text{phase} \underset{\text{ca.}\,1^\circ\text{C}}{\rightleftarrows} \text{H phase}$$

Thus, the absorption spectra of the dyes in the I phase were measured at 50°C, in the R phase at 30°C, in the N phase at 15°C, and in the H phase at −5°C.

III. RESULTS

The spectral data for MB, PBS, and CV are summarized in Figures 2, 3, and 4, respectively. In aqueous solutions, all the dyes concerned exhibit the metachromasy (*D*) bands due to dimers or higher aggregates of sandwich types at the shorter wavelength side of the monomer (*M*) bands. In all the mother solutions with higher dye concentrations (2.17 mmol/l), the intensities of the *D*-bands are much higher than those of the *M*-bands (see Figures 2b, 3b and 4b). At 50°C, however, the *D*-

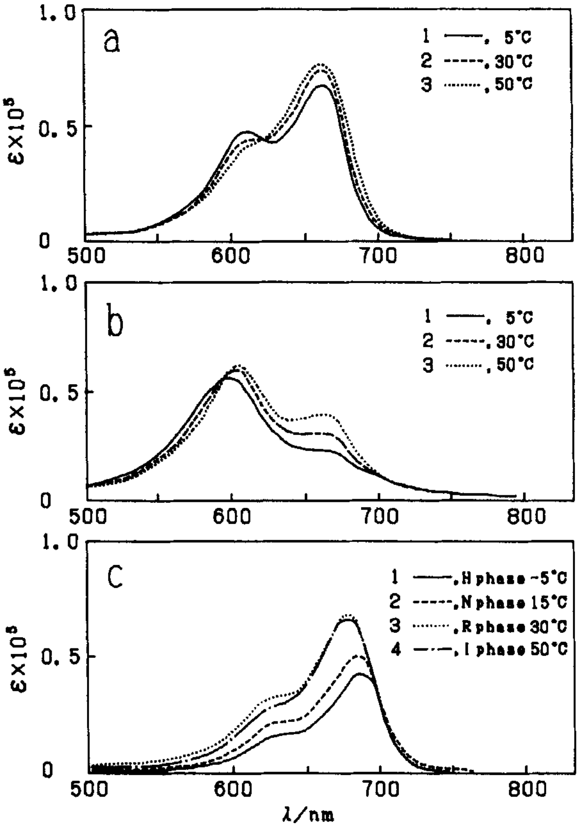

FIGURE 2 Temperature and phase dependences of the electronic absorption spectra of MB in different media: (a)–(b), in water; (c), in 7,7′-DSCG-water system. The concentrations of MB are as follows: (a), 2.17 × 10^{-5} mol/l; (b)–(c), 2.17 × 10^{-3} mol/l.

and *M*-bands of PBS in a dilute aqueous solution appear to be overlapped with equal intensities to give a single band (see spectrum 3 in Figure 3a).

In the 7,7′-DSCG-water system, the association behavior of PBS and CV is very different from that of MB as described below. The association behavior of a dye in the 7,7′-DSCG-water system is known from the relative intensity of the *D*-band compared with that of the *M*-band. The molecular arrangement of 7,7′-DSCG in the chromonic lyotropic mesophases may influence the association of the dye, and this influence can be disclosed by a comparison of the spectral change shown in (c) with that for the mother solution shown in (b). The *D*-band of MB in the 7,7′-DSCG-water system decreases in intensity to a great extent in all phases in comparison with that of MB in the mother solution (compare Figure 2c with Figure 2b). This observation indicates that the association of MB is suppressed simply by the presence of the 7,7′-DSCG molecules (the suppression effect by the host) just as in the case of MB in the 5,5′-DSCG-water system.[22]

In the I phase at 50°C, PBS exhibits the *M*-band which slightly outweighs the *D*-band (spectrum 4 in Figure 3c), while the *D*-band outweighs the *M*-band in the mother solution at 50°C (spectrum 3 in Figure 3b), demonstrating that there appears

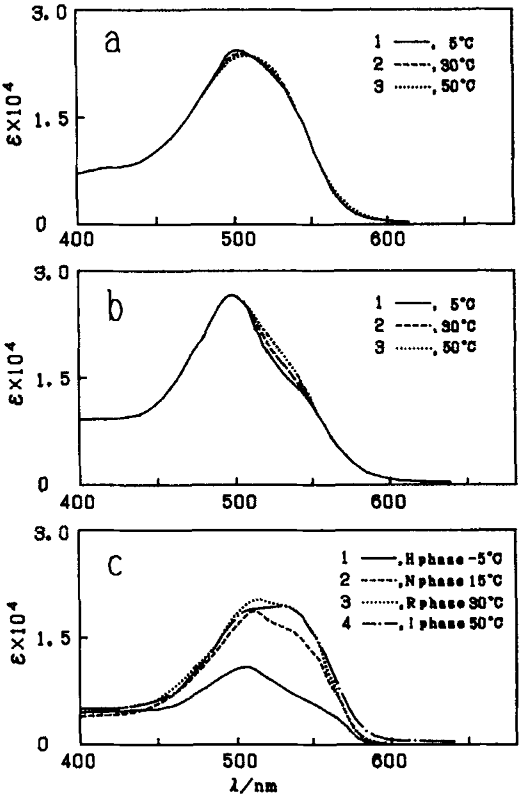

FIGURE 3 Temperature and phase dependences of the electronic absorption spectra of PBS in different media: (a)–(b), in water; (c), in the 7,7′-DSCG-water system. The concentrations of PBS are as follows: (a), 2.17×10^{-5} mol/l; (b)–(c), 2.17×10^{-3} mol/l.

the suppression effect by the host in the I phase. This suppression is known to be so effective as to result in a large shift of the monomer-dimer equilibrium to the monomer side, which is never effected even in a dilute aqueous solution (compare spectrum 4 in Figure 3c with spectrum 3 in Figure 3a). On lowering the temperature, the phase transitions occur from the I phase to the N and H phases, causing a large shift of the equilibrium to the aggregate side to result in the predominance of the *D*-band (spectra 1,2 in Figure 3c). This spectral change is much more drastic than the temperature dependence (Figure 3b) of the spectrum of PBS in the mother solution, indicating that the association of the PBS molecules is encouraged by the molecular arrangements of 7,7′-DSCG in the N and H phases, and thereby the suppression effect by the host weakens. This encouragement, however, is not so great as in the case of CV in the N and H phases described below.

Roughly, the association behavior of CV in the 7,7′-DSCG-water system, which is shown in Figure 4c, is similar to that of PBS described above. Namely, it is demonstrated that the association of CV molecules is encouraged in the N and H mesophases, where the suppression effect by the host weakens. In contrast to the case of PBS, however, the associatoin behavior of CV is quite unusual in that in

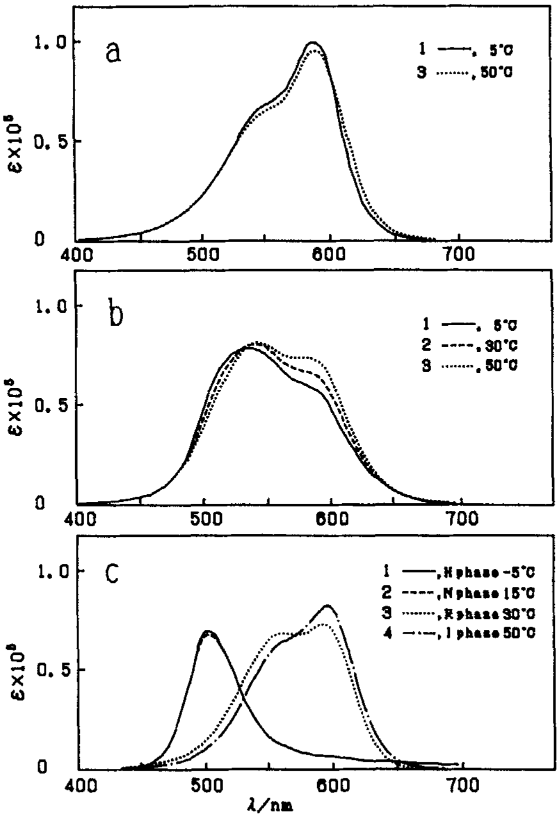

FIGURE 4 Temperature and phase dependences of the electronic absorption spectra of CV in different media: (a)–(b), in water; (c), in the 7,7′-DSCG-water system. The concentrations of CV are as follows: (a), 2.17×10^{-5} mol/l; (b)–(c), 2.17×10^{-3} mol/l.

the N and H phases only the *D*-band appears at a very short wavelength (504 nm) and the *M*-band is missing (see spectra 1 and 2 in Figure 4c). In the aqueous solutions of CV, the *D*-band seems never to be blue-shifted up to about 500 nm even at high concentrations. It is well known that the *D*-band due to an aggregate of a sandwich type is blue-shifted as the aggregation order is increased. Therefore, the large blue shift of the *D*-band of CV in the N and H phases gives evidence that the CV molecules are forced to associate quite highly in these phases.

The *D*-band of CV in the R phase is less intense than the *M*-band and remains at the same position as that in the I phase (cf. spectra 3 and 4 in Figure 4c), indicating that such a high-order aggregate of CV as formed in the N and H phases is never formed in the R phase. Therefore, the association behavior of the CV shows that the molecular arrangement of 7,7′-DSCG in the R phase is quite different from those in the N and H phases, in agreement with the NMR and X-ray analyses.[21] The molecular arrangement of 7,7′-DSCG in the N phase is considered to be similar to that in the H phase from the viewpoint of the association behavior of CV. On the other hand, the molecular arrangement of 7,7′-DSCG in the N and H phases may be somehow different from that of 5,5′-DSCG in the N and M phases because the former encourages the association of CV much more greatly than the latter.

IV. DISCUSSION

As described above, in the N and H lyotropic mesophases of 7,7′-DSCG the associations of a rod-like cationic guest (MB), a rod-like anionic guest (PBS), and a disk-like cationic guest (CV) are suppressed, moderately encouraged, and greatly encouraged, respectively, compared with the cases of aqueous solutions. Therefore, the association behavior of a guest in the chromonic mesophases of the 7,7′-DSCG-water system seems to depend not only on the shape of the guest, as pointed out in our previous paper,[22] but also on the polarity of the guest. Thus, the anionic sites on the surface of the columns formed by stacked 7,7′-DSCG molecules are considered to influence the association of the guest, because the anionic sites interact with the cationic guests attractively and with the anionic guests repulsively.

The suppression mechanism of the association of MB in the N and H mesophase of 7,7′-DSCG is considered to be the same as that in the N and M mesophases of 5,5′-DSCG proposed in our previous work[22]; the number of anionic sites to which the cationic MB molecules are bound is much larger than that of the MB molecules because the molar ratio of host (7,7′-DSCG) molecules to guest (MB) molecules is about 90 (see Experimental section).

The association mechanism of CV in the N and H mesophases of 7,7′-DSCG might also be basically the same as that of CV in the N and M mesophases of 5,5′-DSCG, which was proposed rather ambiguously in our previous work.[22] Since the association of CV is encouraged much more greatly in the N and H mesophase of 7,7′-DSCG than in the N and M mesophases of 5,5′-DSCG, it is necessary to visualize the circumstances unambiguously, where the association of CV is encouraged so greatly as to result in the formation of a high-order aggregate. As discussed in our previous work, if the cationic guest molecules are fewer than the anionic binding sites as in the present case, it is required for the association of guest molecules to confine them in a certain region of the column surface and to bind them to the anionic sites located in that region.[22] There may be the following circumstances where this requirement is fulfilled: a hollow formed by the columns of the stacked 7,7′-DSCG molecules[14] incorporates such a cationic disk-like guest as CV in a cooperative way, as explained below. The CV molecule has the shape of a disk with a positively charged periphery on account of its charge-resonance structures (see Figure 6 in Reference 22). This structural feature may allow multi-site binding of such a disk-like guest to the surface of the hollow mentioned above with its molecular plane normal to the hollow surface. When the first guest molecule is fixed in the inlet region of the hollow with such a conformation, this molecule is expected to attract the second guest molecule and so on because the guest tends to form an aggregate of the sandwich type, as evidenced by the blue shift of the *M*-band by association.[23–26] As a result, other guest molecules are accumulated on both ends of the hollow to result in sandwich aggregates as illustrated in Figure 5. The incorporation of cationic disk-like guest molecules on both ends of the hollow

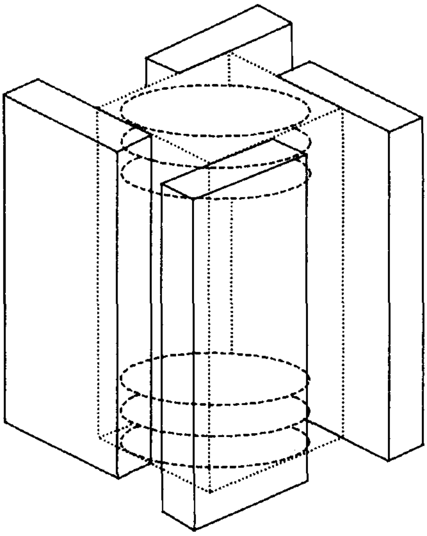

FIGURE 5 The proposed model which assumes cooperative incorporation of disk-like guest molecules on both ends of the hollow formed by columns of stacked 7,7′-DSCG molecules.

may, therefore, be promoted by a cooperative action of the electrostatic force causing multi-site binding of guest molecules to the hollow surface and the dispersion force causing formation of sandwich aggregates of guest molecules. In other words, the association of CV is cooperatively (hence greatly) encouraged in the N and H mesophases of 7,7′-DSCG. This cooperative encouragement seems to be less effective in the N and M mesophases of 5,5′-DSCG due to differences in the lyotropic columnar structures of these hosts.

In contrast to the case of a cationic disk-like guest, a cationic rod-like guest such as MB can penetrate deeply into the hollow, so that there is no possibility of accumulation in a specific region of the hollow or exclusion from the hollow. This may be the reason why MB does not exhibit association in the chromonic lyotropic mesophases of 7,7′-DSCG and 5,5′-DSCG.

The association mechanism of PBS in the chromonic lyotropic mesophases of 7,7′-DSCG is considered to be different from that of CV discussed above. There are two possible explanations for that the association of PBS is encouraged by the molecular arrangements of 7,7′-DSCG in the N and H mesophases. Firstly, anionic PBS molecules cannot penetrate into the hollow because they are repelled by the anionic sites on the interior surface of the hollow, resulting in accumulation of all PBS molecules in the exterior region of the hollow and thus encouraging the association of PBS molecules. Secondly, anionic PBS molecules in the N and H mesophases may behave like those in the mother solution because they are free from binding to anionic sites of the hollow and hence equally distributed in the aqueous regions of the lyotropic columnar structure[14] of the host.

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