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INVITED ARTICLE

Molecular aggregation and chromonic liquid crystals

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Almost 30 years ago, when the study of chromonic liquid crystals was in its infancy, Alfred Saupe and L.J. Yu investigated disodium cromoglycate using deuteron magnetic resonance spectroscopy. Among their findings were that the quadrupolar splitting of the D_2O spectrum increased with decreasing temperature and that the addition of salt to the solution increased the temperature stability of the nematic phase. A good deal of research on chromonic liquid crystals has been reported since that time, and therefore a lot more is known. However, it is also interesting that some of the questions from that time remain unanswered.

Keywords: chromonic; lyotropic; liquid crystal; aggregation

1. Introduction

Although the fact that many dyes spontaneously aggregate in aqueous solutions, with some forming a liquid crystal phase at sufficiently high concentrations, had been known for many years, the discovery that an asthma drug named Cromolyn (disodium cromoglycate or DSCG) did this brought renewed attention to these systems during the latter half of the 20th century. Hartshorne and Woodard [1] had used polarising microscopy and X-ray diffraction to determine that there were two phases, a nematic or N phase that they described in a fashion similar to the discotic nematic phase elucidated by Chandrasekhar five years later for a thermotropic system, and a hexagonal M phase in which the molecules stack on top of each other in columns. An alternative picture of the nematic phase followed from Lydon, who described the N phase as a nematic phase of columnar aggregates, perhaps with a structure containing water in the centre of the columns [2]. Yu and Saupe [3] decided to study this system with deuteron magnetic resonance spectroscopy, so they dissolved DSCG in D_2O. Some of the D_2O molecules associate with the aggregates and are partially ordered. This produces a quadrupolar splitting of the deuteron magnetic resonance that reveals information about the degree of D_2O association and the orientational order in the liquid crystal phase.

At the time that Yu and Saupe began their investigation, there was a good deal of confusion about the dye systems that possessed liquid crystal phases. In fact, most liquid crystal researchers were unaware that this type of material formed liquid crystal phases. Lyotropic liquid crystals were well-known, but these were the amphiphilic systems of soaps and phospholipids. Some researchers thought that materials such as DSCG were similar to the amphiphilic systems. Others considered the DSCG liquid crystal phases to be typical thermotropic phases. This confusion is evident in the article by Yu and Saupe when they refer to the M phase as a smectic phase [3].

Yu and Saupe's results confirmed the phase diagram of Hartshorne and Woodard, but included two new results. As the temperature was decreased in the liquid crystal phase, the quadrupolar splitting also increased, indicating that the degree of association and/or the amount of orientational order increased. Also, the addition of sodium chloride increased the temperature of the liquid crystal to the isotropic liquid transition and decreased the temperature dependence of the splitting. They concluded that the presence of sodium chloride makes the aggregates stiffer. Finally, they did not find evidence for hollow, water-filled columns.

In the time since Yu and Saupe reported their results, there have been many investigations of the DSCG–water system as well as many other aggregating dyes. Phase diagrams have been determined and many are similar to that of DSCG. Order parameters have been measured and the aggregates have been probed by investigating how they scatter light. Experiments have been carried out in the liquid crystal phases and in the isotropic phase near the coexistence region. In short, a good deal more is known about both the properties of these aggregating systems and the extent of the variation from one system to another. However, one of the questions Yu and Saupe asked is still largely unanswered. What is the detailed structure of the aggregates?

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The history of the work on chromonic liquid crystals is first briefly reviewed, with an emphasis on how interest in these systems varied and how two paths of inquiry developed simultaneously. A discussion of the most simple theoretical ideas follows, in order to show why there can be significant variation in the behaviour of these systems. A few examples of recent experimental results are described along with a discussion of what is known and unknown.

2. A brief history of chromonic liquid crystals

Research into aggregating systems with liquid crystal properties is known to be almost a hundred years old. In 1915 Sanquist investigated aqueous solutions of some sulphonic acids and noticed the presence of threads when polarised light was used [4]. Many years later, Jelly [5] and Scheibe *et al.* [6] independently reported on the liquid crystal properties of pseudo-isocyanine dyes in solution. After the introduction of the antiasthmatic drug disodium cromoglycate to the market in 1967, Cox and co-workers began to investigate it in order to increase its effectiveness. Their report described two liquid crystal phases and noted the 3.4 Å X-ray reflection without ascribing it to the stacking repeat distance [7]. The work of Hartshorne and Woodard, of Lydon, and of Yu and Saupe followed shortly thereafter.

The absorption spectra of both the sulphonic acid and pseudo-isocyanine dyes change with increasing concentration, but in different ways. In the sulphonic acid dyes, there is a change in the shape of the absorption spectrum and a general decrease in the absorption coefficient, but nothing occurs as the concentration increases and aggregation takes place. In the pseudo-isocyanine dyes, in addition to the changes that take place in the sulphonic dyes, at a certain concentration an intense, narrow peak appears at higher wavelength. This J- or Scheibe-band occurs in other aggregating systems, and has been the subject of considerable research itself. For example, in porphyrin systems, aggregation in extremely low concentration samples can be initiated by lowering the solution pH, with a narrow, intense red-shifted peak appearing at a threshold concentration [8, 9]. The appearance of the new peak is usually attributed to interactions of the electrons on different molecules of the aggregate, in some sense forming an extended, coupled array. This can be modelled using exciton coupling between the excited states of molecules in an aggregate. There are no liquid crystal phases associated with this aggregation, because the concentrations are too low. Thus from a very early time, there were two paths of investigation. One path concentrated on drugs and dyes that aggregated and possessed liquid crystal phases. The other path was concerned with dyes that showed dramatic changes in their absorption spectra upon aggregation. Some of these dyes possessed liquid crystal phases and some precipitated out of solution at too low a concentration for a liquid crystal phase to form. The communication between investigators in these two groups was not always good, with one group more interested in the liquid crystal properties and the other more interested in the aggregation behaviour that caused the large changes in the absorption spectra.

Disodium cromoglycate is a highly investigated chromonic liquid crystal system. See [10–16] for examples. Likewise, pseudo-isocyanine has been extensively investigated, with [17–23] being just a few examples. However, over the years many other dyes have been investigated for their liquid crystal properties. The sodium salts of naphthalenesulfonic acids have quite an extensive history [24–32, 34, 54]. Other examples include xanthone derivatives [35], porphyrin compounds [36], other cyanine dyes [37], phthalocyanines [38] and derivatives of perylenetetracarboxylic and naphthalenetetracarboxylic acids [14, 39–41].

The understanding that has come from this research is that many of these systems have common properties. For example, there is almost universal evidence that the aggregation process involves the stacking of polyaromatic groups 3.4 Å away from each other, and that the shape of the aggregates is columnar. Another example is that almost always two liquid crystal phases are present, the nematic or N phase with orientational order only and the M phase with both orientational and translational order. Changes to the absorption spectrum with concentration are usually present. What does seem to differ is the aggregate structure, with evidence for cross-sections of 1, 2, and more molecules and with other evidence for extremely large aggregates (micrometre sized), perhaps containing water in their central core. There is also some evidence that these larger structures are layered instead of columnar [37]. What is also unclear is the aggregation process, with a good deal of evidence for isodesmic aggregation with no critical aggregation concentration, but with other evidence for a critical aggregation concentration.

The brief history just outlined is quite incomplete. Several excellent reviews, with far more extensive discussion of the history of research into chromonic systems, have been written and should be consulted for further information [42–45].

3. Aggregation theory

In any theory of aggregation, the shape of the aggregates is extremely important. For example, consider a system in which there is a free energy cost for every molecule at certain locations on the outside of the aggregate. For a one-dimensional aggregate, the free energy increase might be for every molecule on the ends of the aggregate. For a two-dimensional aggregate, the free energy increase might be for every molecule on the perimeter of the aggregate. For a three-dimensional aggregate, the free energy increase might be for every molecule on the surface of the aggregate. For the one-, two- and three-dimensional aggregates, the number of the molecules causing an increase in the free energy is proportional to the number of molecules in the aggregate to the 0, 1/2 and 2/3 powers, respectively. Therefore, in an expression for the free energy per molecule of the aggregate, this term will vary as the number of molecules in the aggregate to the −1, −1/2 and −1/3 powers, for the one-, two- and three-dimensional aggregates, respectively. This different dependence on the number of molecules in the aggregate has far reaching consequences. For example, one-dimensional aggregates of many sizes can coexist in equilibrium with each other, whereas two-dimensional aggregates tend to form one extremely large aggregate.

Besides changes to the free energy for molecules at certain locations on the outside of the aggregate, there are free energy changes for molecules joining the interior of the aggregate. Attractive interactions between neighbouring molecules as well as hydrophobic effects can serve as the driving forces for aggregation. A simple formulation of a theory for columnar aggregates that allows for some robustness in its behaviour is described in a review article by Gelbart and Ben-Shaul [46]. The free energy difference for all molecules in an aggregate of N molecules relative to a free molecule contains a negative term for all of the molecules in the aggregate and a positive term for those molecules at the two ends of the column,

$$\frac{\Delta\mu_N}{k_B T} = -N\alpha + \delta = -(N-1)\alpha + (\delta - \alpha). \quad (1)$$

Here α and δ are free energy parameters in units of $k_B T$, k_B is the Boltzmann constant and T is the temperature. The parameter α represents the stacking free energy change and $\delta - \alpha$ represents the scission free energy (the free energy difference between the two ends of an aggregate relative to the two sides of a molecule). In order for this theory to describe systems such as the aggregating dyes and J-aggregates, δ must be greater than or equal to α.

While casting the theory in terms of the dimensionless parameters α and δ makes the mathematics less cumbersome, it does eliminate temperature as an explicit variable. Thus it should be remembered that the theory is attempting to describe the behaviour of molecules in a solvent, so the temperature at which the theory is applicable is the range of temperatures for which the solvent is a liquid.

This expression for the free energy of an aggregate can be used to calculate the equilibrium distribution of aggregate sizes in several ways. McKitterick *et al.* [47] describe how this is done using the partition function. If the volume fractions of aggregates of different size, χ_N, are calculated, the following relationship results:

$$\chi_N = N(z\chi_1)^{N-1} e^{\alpha-\delta} \chi_1. \quad (2)$$

The parameter z is equal to $(L^3/V)e^{\alpha}$, where L^3/V is the appropriate factor stemming from a consideration of phase space and the external degrees of freedom of the molecules (V is the sample volume). For simplicity, many theories set L^3/V equal to v/V, where v is the volume of a single molecule. Note that Equation (2) cannot be used as an expression for χ_1, which complicates the algebra somewhat. If the volume fraction of the dye is ϕ, then it must equal the sum of the volume fractions for each size of aggregate,

$$\phi = \sum_{N=1}^{\infty} \chi_N. \quad (3)$$

Thus given values for α, δ and ϕ, values for the χ_N can be found using Equations (2) and (3).

Two sets of distributions of aggregates are shown in Figure 1, each of which tends toward a limiting case. When $\delta = \alpha$, there is a gradual shift of the distribution to larger aggregates as the volume fraction increases. There is no volume fraction at which aggregates begin to form in large numbers, i.e. there is no critical aggregation volume fraction (in analogy to a critical micelle concentration). We can define a critical aggregation volume fraction as the volume fraction when half of the dye molecules exist as free molecules in solution, but there is no dramatic change in the number of aggregates in passing through this volume fraction. When $\delta = \alpha$, only one term is present in the free energy expression, implying that the change in free energy for a molecule joining an aggregate is independent of aggregate size. This is called isodesmic aggregation and seems to apply to some of the aggregating dye systems.

The other set of distributions in Figure 1 is for cases when $\delta \gg \alpha$. As can be seen in the figure, there is a critical aggregation volume fraction at which significant aggregation takes place over a relatively small range of volume fraction. For this case, there are a number of approximations that hold quite well. The average aggregation number, $\langle N \rangle$, is given by

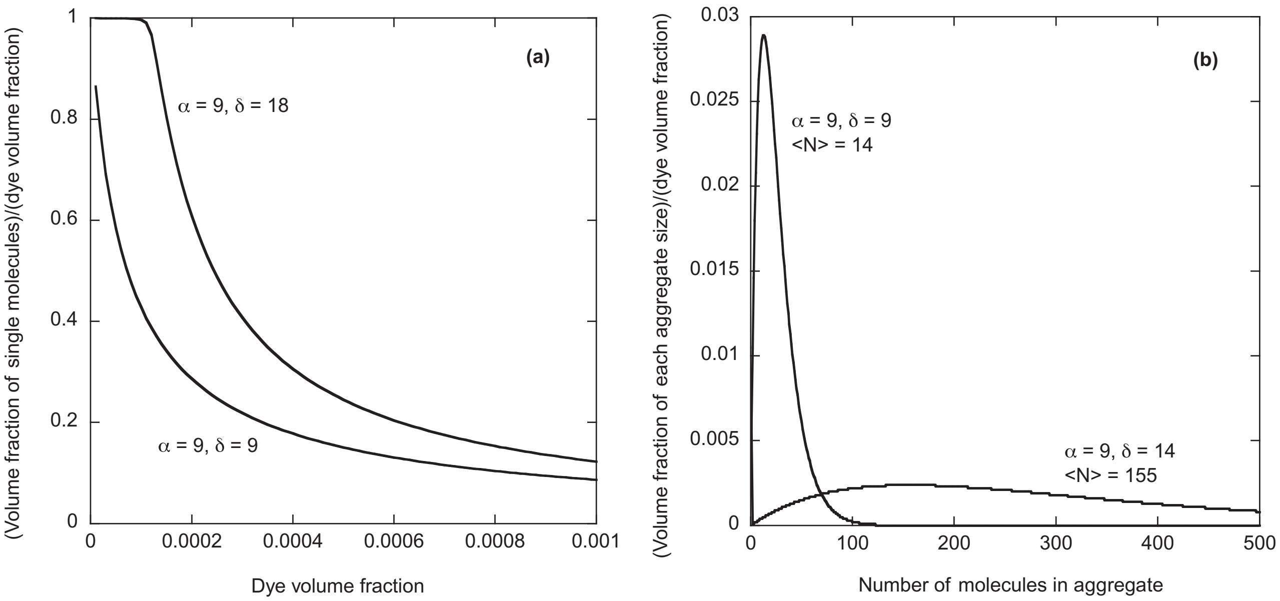

Figure 1. Predictions of the aggregation theory described in the text: (a) dependence of the volume fraction of single molecules on the dye volume fraction for cases of both isodesmic and non-isodesmic aggregation; (b) the distribution of aggregate size for cases of both isodesmic and non-isodesmic aggregation ($\phi = 0.02$). As explained in the text, isodesmic aggregation occurs when $\alpha = \delta$.

$$\langle N\rangle = \frac{\sum_{N=1}^{\infty} i(\chi_N/N)}{\sum_{N=1}^{\infty}(\chi_N/N)} \approx \sqrt{\phi}\,e^{\delta/2}, \qquad (4)$$

where (L^3/V) has been set to v/V. If, instead of the volume fraction for aggregates of different size, the number of aggregates of different size is plotted, the distribution is proportional to χ_N/N and is approximately an exponential, varying as $\exp(-\mathrm{N}/\langle\mathrm{N}\rangle)$. There is also a simple approximation for the critical aggregation volume fraction, ϕ_C:

$$\phi_C \approx e^{-\alpha}. \qquad (5)$$

These theoretical considerations should apply to the initial stages of aggregation when there is little interaction between the aggregates. In order to understand the transition to the liquid crystal phase, a more sophisticated theory is required. Unfortunately, there has not been a great deal of theoretical work directed specifically toward chromonic liquid crystals. If the aggregates are considered to be hard spherocylinders interacting through the excluded volume effect, then the calculations of Lee [48] are applicable. According to this theory, the volume fraction change is about 8% and the orientational order parameter equals about 0.7 at the nematic–isotropic transition for a volume fraction of about 0.28 and a length-to-diameter ratio of 9. Taylor and Herzfeld consider self-assembling systems of linear aggregates, including in the calculation hard-core potentials, short-range repulsions and an energy contribution for each pair of molecules [49, 50]. In this theory, a typical system with a volume fraction of about 0.28 has about six molecules in an aggregate on average and an orientational order parameter of 0.7 at the transition. More recently, a Monte Carlo simulation of a mixture of model chromonic and water molecules has been performed [51]. Both attractive and repulsive interactions are employed among the model units for the chromonic molecule and the water molecule. In the simulation, the average number of molecules per aggregate gradually increases with increasing volume fraction, reaching about ten at a volume fraction of about 0.1.

4. Experimental results

Perhaps the most direct evidence for the structure of chromonic liquid crystals comes from X-ray diffraction studies. Although the intensity of the peak varies from system to system, all chromonic liquid crystals that have been investigated with X-rays show a concentration independent peak representing a repeat distance of 3.4 Å. Since this is the distance between both the planes in graphite and the base pairs of DNA, the presence of this peak has been interpreted as coming from the stacking of the polyaromatic parts of the chromonic molecules. With this interpretation, the basic building block of the aggregates in all chromonic liquid crystals is a spontaneous tendency for the molecules to stack with the planar parts of the molecules parallel to each other.

Another finding from the X-ray work is that there is often, but not always, a broad, concentration-dependent peak that represents a longer repeat distance in the structure. In oriented samples, the position of this peak differs from the position of the 3.4 Å peak by an azimuthal angle of 90°. Therefore, this concentration dependent peak has been interpreted as stemming from the distance between aggregates, which is expected to vary with concentration. If the aggregate–aggregate distance and the volume fraction of the dye are both known, then some basic conclusions about the geometry of the aggregates can be drawn. For example, if the aggregates are basically infinite planes of thickness a and separation d, then the volume fraction ϕ is just a/d. Since the scattering wavevector of the aggregate–aggregate peak q_0 equals $2\pi/d$, then as the concentration is changed, q_0 should depend linearly on ϕ (that is, a log–log graph of q_0 *vs.* ϕ should have a slope of one). This same type of argument can be used if the aggregates are infinite cylinders with radius R and separation d. In this case ϕ is proportional to the square of R/d, so a log–log graph of q_0 *vs.* ϕ should have a slope of one-half.

X-ray data on many systems have been incorporated into Figure 2, which is a log–log plot of q_0 *vs.* ϕ. Most of the linear fits to the data have a slope consistent with one-half, which is strong evidence for columnar aggregates. For these systems, a model of stacked molecules forming a long, slender aggregate seems appropriate. The analysis can be taken further and the cross-sectional area of the aggregates estimated. When this is done, we find cross-sectional areas of one, two and more molecular areas [52].

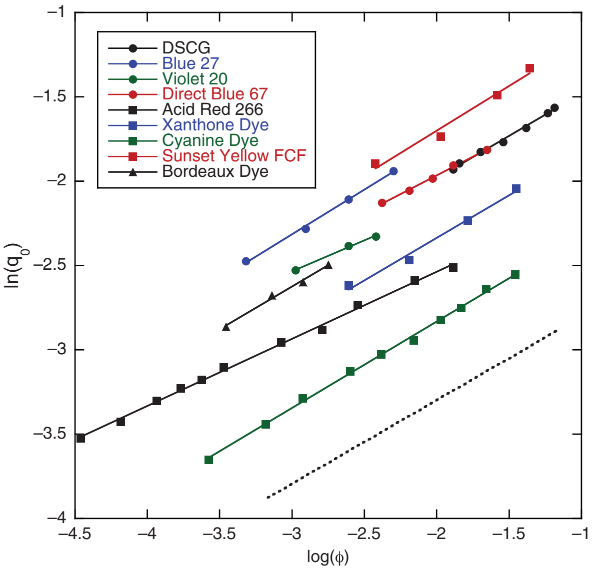

Figure 2. Log–log plot of the peak X-ray scattering wavevector q_0 *vs.* volume fraction ϕ. Aggregates that grow in only one dimension, like columnar aggregates, produce a slope of 1/2. The dotted line has slope 1/2. The data are taken from the following references: DSCG [1], Blue 27 [39], Violet 20 [39], Direct Blue 67 [30], Acid Red 266 [27], Xanthone Dye [35], Cyanine Dye [37], Sunset Yellow FCF [31] and Bordeaux Dye [41] (colour version online).

It should be remembered, however, that not all of the data in Figure 2 have slopes consistent with the anticipated value of one-half. These systems have slopes smaller than one-half, indicating that the aggregate structure is more complicated. When this finding is combined with the fact that the X-ray peak due to molecular stacking varies significantly in intensity between systems, the conclusion is that not all chromonic liquid crystals have as simple a structure as stacked molecules.

The optical properties of chromonic liquid crystals also reveal a great deal about the structure of the phases. Unaligned samples show the defects typical of the nematic phases of small molecule thermotropic liquid crystals, as can be seen in the photomicrograph of Sunset Yellow FCF shown in Figure 3. Although more difficult to align than small molecule thermotropic liquid crystals, it is possible to align chromonic liquid crystals in a thin cell planar geometry by proper treatment of the glass surfaces. Magnetic fields are also capable of aligning some chromonic liquid crystals. When this is done, noticing that there is no change in the birefringence when the cell is rotated slightly around the rubbing direction confirms that the director is oriented along the rubbing direction and demonstrates that the liquid crystal phase is uniaxial [14]. Birefringence values turn out to be small and negative, increasing with increasing concentration and decreasing with increasing temperature. For

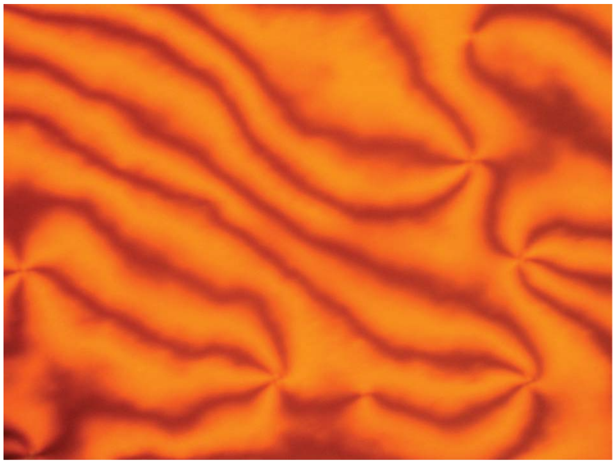

Figure 3. Microscopy image of Sunset Yellow FCF in the nematic phase between crossed polarisers. The thickness of the sample is 10 μm and the glass surfaces have been coated for homeotropic alignment of thermotropic liquid crystals. While this surfactant allows the cell to be filled easily with an aqueous solution, the result is that the director is unaligned and defects form.

molecules that absorb light polarised in the plane of the molecule (Sunset Yellow FCF is an example), the absorption of light polarised along the director is less than the absorption of light polarised perpendicular to the director. This observation is strong evidence that the plane of the molecule tends to be oriented perpendicular to the director. A structure with the director parallel to stacks of planar molecules is consistent with this observation and is further evidence for this simple structure for some chromonic liquid crystals. If it is assumed that the absorption occurs for light polarised along a single axis in the plane of the molecule, then the order parameter can be calculated. Values range generally from 0.6 to 0.8, showing a slow decrease with increasing temperature [14, 31].

A number of investigations have tried to examine the aggregation process instead of the structure and properties of the liquid crystal phases. Since aggregation affects the absorption spectrum of the molecules, absorption measurements are revealing. What is found is that there are changes to the absorption spectrum at concentrations far below that at which the liquid crystal forms. For Sunset Yellow FCF, for example, the liquid crystal phase forms at a concentration of about 24 wt% at room temperature, but changes to the absorption spectrum are clearly evident below 0.1 wt% [31]. Likewise, for Bordeaux dye, changes to the absorption spectrum can easily be seen below 0.04 wt% whereas the liquid crystal phase forms around a concentration of 6 wt% [41]. This could be an indication that the process is isodesmic, with aggregation starting at very low concentrations, but with the liquid crystal phase only forming when the aggregates become large enough. On the other hand, the aggregation process may have more than one stage. For example, the molecules might form dimers at a low concentration, causing the observed changes in the absorption spectrum. Then at a higher concentration, the dimers begin to form larger structures, which eventually grow large enough to form a liquid crystal phase. The results of the absorption measurements are consistent with both of these scenarios.

More recently, light scattering experiments have been carried out in the isotropic phase that show quite convincingly that in at least one system the aggregation process seems to have at least two stages. DSCG shows changes to the absorption spectrum at concentrations as low as 0.2 wt% when the liquid crystal phase forms at about 11 wt% [52]. Yet careful static and dynamic light scattering measurements on a 14 wt% DSCG sample showed that a new scattering mode consistent with the formation of molecular aggregates appears in the isotropic phase about 11°C above the start of the coexistence region [16]. When similar measurements are performed on both DSCG and Bordeaux dye in the isotropic phase, the difference between these two chromonic systems becomes very evident. Figure 4 shows intensity data for polarised scattering on both materials. Notice that the DSCG scattering is weak and relatively constant at high temperature, but starts to increase around 12°C above the coexistence region as the temperature is decreased. On the other hand, the polarised scattering in Bordeaux dye shows a fairly uniform variation with temperature, approaching low values only at very high temperatures. Dynamic light scattering measurements are just as revealing. Figure 5 shows the correlation functions over a range of temperatures for both DSCG and Bordeaux dye. The change in the correlation function for DSCG around 36°C (13°C above the upper limit of the coexistence region) is clearly evident and consistent with the experimental data and more extensive analysis of [16]. There is no corresponding change to the correlation function for Bordeaux dye. In fact, all the correlation functions for Bordeaux dye are well-described by a stretched exponential,

$$C(t) = C_0 e^{-(t/\tau)^{\beta}}, \qquad (6)$$

where τ is a correlation time and β is the stretching parameter. The fits to the Bordeaux dye data have τ values that decrease from around 46 μs to 14 μs as the

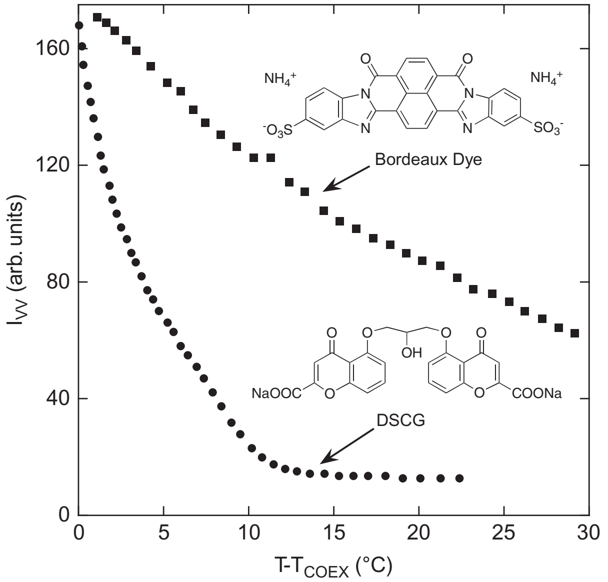

Figure 4. Polarised light scattering in the isotropic phase of a 10 wt% DSCG sample and a 3 wt% Bordeaux dye sample. T_{COEX} is the upper limit of the nematic–isotropic coexistence region. The data for DSCG are taken from [16]. The wavelength of the light and the scattering angle for the DSCG experiment are 633 nm and 30°, respectively, and for the Bordeaux dye experiment are 647 nm and 90°, respectively. The chemical structures for DSCG and Bordeaux dye are also shown.

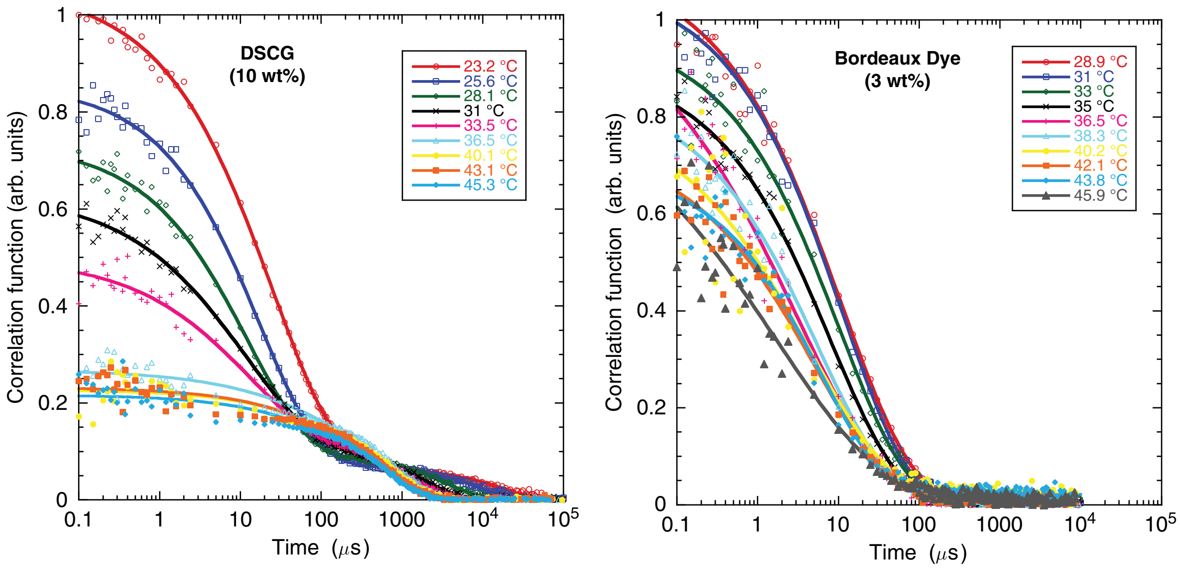

Figure 5. Polarised scattering correlation functions for a 10 wt% sample of DSCG and a 3 wt% sample of Bordeaux dye. The correlation functions have been scaled according to the measured scattering intensity. The wavelength of the light and the scattering angle are 514.5 nm and 90°, respectively, for the DSCG experiment, and 647 nm and 45°, respectively, for the Bordeaux dye experiment. The upper limit of the coexistence region is 23°C for DSCG and 26°C for Bordeaux dye. The solid lines are to aid the eye in the DSCG plot and are fits to Equation (6) in the Bordeaux dye plot (colour version online).

temperature is increased, but the β values show no trend with temperature and are in the 0.4 to 0.5 range. These β values are consistent with those found for the faster orientational mode in DSCG [16].

The fact that there is a change in the aggregation process in the DSCG system is also revealed by absorption measurements. Figure 6 shows how the absorption changes with temperature in the isotropic phase of a 12 wt% sample of DSCG. There is a small change in slope when the wavelength is near the maximum of the absorption spectrum (328 nm), but a dramatic change in slope when the wavelength is at the high wavelength edge of the absorption spectrum (380 nm). When these experiments were repeated for DSCG concentrations between 10 and 14 wt%, the results shown in Figure 7 were obtained. Notice that the change evident in the temperature dependence of the absorption occurs approximately 15°C above the transition for a 10 wt% sample and decreases to about 10°C above the transition for a 14 wt% sample. This is consistent with the light scattering results. Whether this aspect of aggregation in DSCG is common is an open question. There is evidence that it is not universal, however, since absorption measurements on Sunset Yellow FCF do not show any change in the temperature dependence (see Figure 8), just as was the case for the light scattering measurements for Bordeaux dye.

Finally, important information on chromonic liquid crystals is obtained from studying how these systems respond to the presence of electrolytes and changes to the solution pH. Recent experiments report that the liquid crystal phase is stabilised by mono- and divalent salts, but destablised by the presence of weakly hydrated cations and multivalent additives or by an increase in pH [15, 53, 54]. The screening of the charges on the ionic dyes by these additives is an important aspect of this behaviour, but there is also evidence for some incorporation of the additives into the aggregate structure and even the possibility of additional aggregation stages.

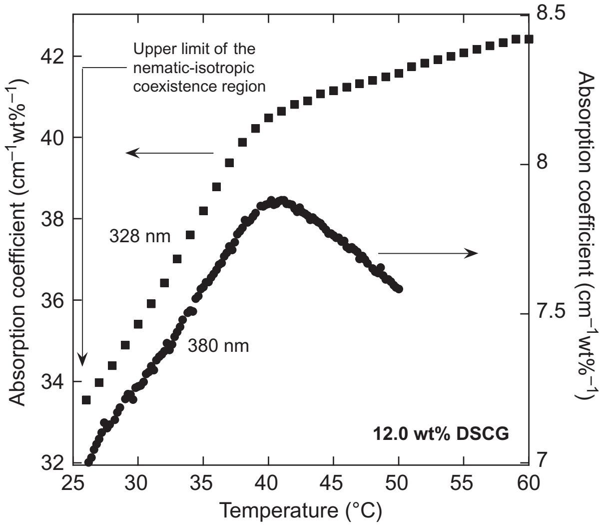

Figure 6. The absorption coefficient at 328 nm and 380 nm of a 12.0 wt% sample of DSCG as a function of temperature in the isotropic phase. Both sets of data show a change in temperature dependence 13 or 14°C above the upper limit of the nematic–isotropic coexistence region.

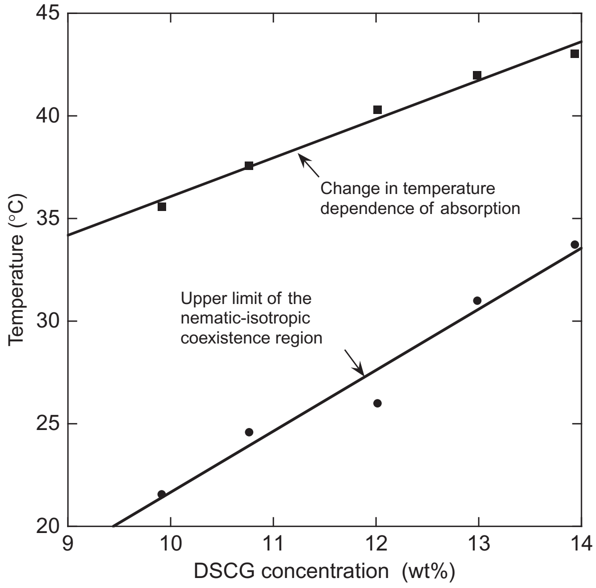

Figure 7. Concentration dependence of both the upper limit of the nematic–isotropic coexistence region and the change of the absorption temperature dependence for DSCG. The change in the temperature dependence of the absorption occurs closer to the nematic–isotropic coexistence region as the DSCG concentration increases.

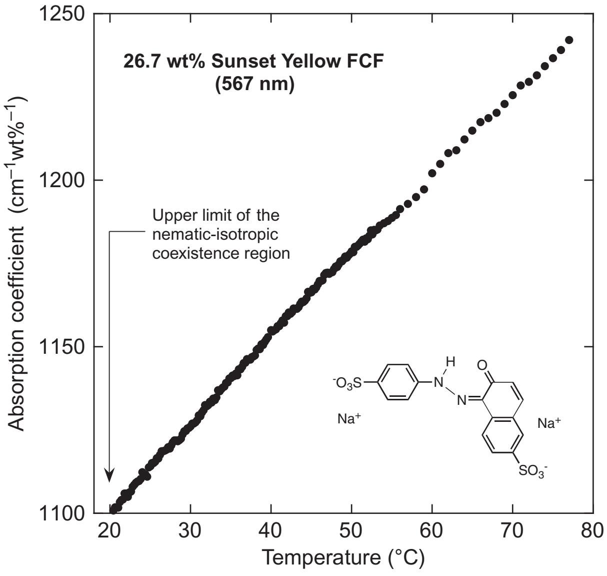

Figure 8. The absorption coefficient as a function of temperature in the isotropic phase of Sunset Yellow FCF. The chemical structure of Sunset Yellow FCF is also shown.

5. Discussion

It is clear from the research done over many decades that chromonic liquid crystals represent a class of materials of wide-ranging properties and robust behaviour. The evidence is strong that some of the systems, Sunset Yellow FCF for example, aggregate in stacks of single molecules, perhaps according to an isodesmic process. However, for many of the other systems, the aggregation process and/or the aggregate structure seems to be more complicated. Those systems in which the cross-section is two molecules may act similarly, but one such system, DSCG, exhibits what appears to be a critical aggregation temperature. Is there a connection between a more complicated aggregate structure and the presence of a critical temperature or critical concentration at which aggregation begins? This is an important question that needs to be answered.

There is some evidence that some of the aggregates contain water in their structure. Perhaps the best candidates for this are the systems that form a liquid crystal phase when the concentration of the dye is 1 wt% or less [27]. With so little dye in solution, it is difficult to imagine that aggregates composed only of dye would interact strongly enough to stabilise a liquid crystal phase. However, if the aggregates contain water that cannot easily move in and out of the aggregate, the effective volume fraction of the aggregates increases, making the formation of a liquid crystal phase much easier to understand. Recent confocal microscopy images of aggregates in a system that forms a liquid crystal at 0.4 wt% are consistent with this hypothesis [47]. However, this system may not be representative, since there is also evidence that these phases in other compounds possess a layered rather than columnar structure [27].

The average length of the aggregates is a difficult property to determine experimentally. The results range from 17 nm for DSCG from a light scattering experiment [13] to 8 nm for Bordeaux dye from a stacking free energy determination [52] to 4 nm for Sunset Yellow FCF from an X-ray study [54]. The problem with these estimates is that they seem much too small to create the anisotropic interactions necessary to stabilise a liquid crystal phase. Using these numbers, we obtain length-to-width ratios between 4 and 12. However, the Onsager theory for hard rods [55] predicts that the length-to-width ratio times the volume fraction must be greater than 4 for a liquid crystal phase to form. For DSCG, Bordeaux dye and Sunset Yellow FCF, this product is approximately 1.5, 0.3 and 0.7, respectively, which are all significantly less than 4. Of course, the interactions in these systems do not resemble hard rods, but the discrepancy is so great that we must wonder what is being missed. Even a theory that incorporates much more realistic interactions predicts that the product of the length-to-width ratio and the volume fraction should be around 1.4 [49, 50], which two of the three systems do not come close to. This discrepancy has prompted the idea that perhaps the aggregates have defects in them, that destroy the stacking correlation but maintain a single aggregate [54]. Perhaps the measurements are sensitive to the stacking correlation distance, while the liquid crystal phase is sensitive to the physical length of the aggregates.

Finally, the question of the formation of even larger aggregates must be raised. There is evidence that a number of these systems form structures such as fibres and bundles under certain conditions. These appear in both the traditional J-aggregate systems [22] and the more recent chromonic liquid crystal systems [53]. How are these related to the initial aggregate structure? Does a structure different from the initial aggregate structure become stable under some conditions? Does the initial aggregate structure itself become the building block for a larger and more complicated structure? Answers to these questions are required to understand completely the behaviour of these systems.

6. Conclusions

Chromonic liquid crystals have been known to exist and have been the subject of investigations for many, many years. Recent interest in these systems has added to the understanding of this unique phase of matter, but it is clear that some fundamental aspects of these systems, not to mention a myriad of specific details, are not fully understood. Future research, undoubtedly utilising new theoretical and experimental methods, will continue to shed light on chromonic liquid crystals and perhaps allow for a number of unique applications.

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References

[1] Hartshorne, N.H.; Woodard, G.D. *Mol. Cryst. Liq. Cryst.* **1973**, *23*, 343–368.
[2] Lydon, J.E. *Mol. Cryst. Liq. Cryst. Lett.* **1980**, *64*, 19–24.
[3] Yu, L.J.; Saupe, A. *Mol. Cryst. Liq. Cryst.* **1982**, *80*, 129–134.
[4] Sanquist, H. *Ber. Dtsch. Chem. Ges.* **1915**, *48*, 2054–2055.
[5] Jelly, E.E. *Nature* **1936**, *138*, 1009–1010; *Nature (London, UK)* **1937**, *139*, 631–632.
[6] Scheibe, G.; Kandler, L.; Ecker, H. *Naturwissenschaften* **1937**, *25*, 75.
[7] Cox, J.S.G.; Woodard, G.D.; McCrone, W.C. *J. Pharm. Sci.* **1971**, *60*, 1458–1465.
[8] Fleischer, E.B.; Palmer, J.M.; Srivastava, T.S.; Chatterjee, A. *J. Am. Chem. Soc.* **1971**, *93*, 3162–3167.
[9] Pasternack, R.F.; Huber, P.R.; Boyd, P.; Engasser, G.; Francesconi, L.; Gibbs, E.; Fascella, P.; Venturo, G.C.; Hinds, L. de C. *J. Am. Chem. Soc.* **1972**, *94*, 4511–4517.
[10] Hui, Y.W.; Labes, M.M. *J. Phys. Chem.* **1986**, *90*, 4064–4067.
[11] Perahia, D.; Luz, Z.; Wachtel, E.J.; Zimmermann, H. *Liq. Cryst.* **1987**, *2*, 473–489.
[12] Mundy, K.; Sleep, J.C.; Lydon, J.E. *Liq. Cryst.* **1995**, *19*, 107–112.
[13] Nastishin, Y.A.; Liu, H.; Shiyanovskii, S.V.; Lavrentovich, O.D.; Kostko, A.F.; Anisimov, M.A. *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.* **2004**, *70*, 051706.
[14] Nastishin, Y.A.; Liu, H.; Schneider, T.; Nazarenko, V.; Vasyuta, R.; Shiyanovskii, S.V.; Lavrentovich, O.D. *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.* **2005**, *72*, 041711.
[15] Kostko, A.F.; Cipriano, B.H.; Pinchuk, O.A.; Ziserman, L.; Anisimov, M.A.; Danino, D.; Raghavan, S.R. *J. Phys. Chem. B* **2005**, *109*, 19126.
[16] Betrand, C.E.; Linegar, K.L.; Kostko, A.F.; Anisimov, M.A. *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.* **2009**, *79*, 041704.
[17] Kopainsky, B.; Hallermeier, J.K.; Kaiser, W. *Chem. Phys. Lett.* **1981**, *83*, 498–502.
[18] Rehage, H.; Platz, G.; Struller, B.; Thunig, C. *Tenside Surf. Det.* **1996**, *33*, 242–248.
[19] Stegemeyer, H.; Stockel, F. *Ber. Bunsenges. Phys. Chem.* **1996**, *100*, 9–14.
[20] von Berlepsch, H.; Bottcher, C.; Dahne, L. *J. Phys. Chem. B* **2000**, *104*, 8792–8799.
[21] Neumann, B *J. Phys. Chem. B* **2001**, *105*, 8268–8274.
[22] von Berlepsch, H.; Bottcher, C. *J. Phys. Chem. B* **2002**, *106*, 3146–3150.
[23] Herzog, B.; Huber, K.; Stegemeyer, H. *Langmuir* **2003**, *19*, 5223–5232.
[24] Reeves, R.L.; Maggio, M.S.; Harkaway, S.A. *J. Phys. Chem.* **1979**, *18*, 2359–2368.
[25] Hamada, K.; Take, S.; Iijima, T.; Amiya, S. *J. Chem. Soc. Faraday Trans. 1* **1986**, *82*, 3141–3148.
[26] Hamada, K.; Mitshuishi, M.; Ohira, M.; Miyazaki, K. *J. Phys. Chem.* **1993**, *97*, 4926–4929.
[27] Tiddy, G.J.T.; Mateer, D.L.; Ormerod, A.P.; Harrison, W.J.; Edwards, D.J. *Langmuir* **1995**, *11*, 390–393.
[28] Neumann, B.; Huber, K.; Pollmann, P. *Phys. Chem. Chem. Phys.* **2000**, *2*, 3687–3695.
[29] Ichimura, K.; Fujiwara, T.; Momose, M.; Matsunaga, D. *J. Mater. Chem.* **2002**, *12*, 3380–3386.
[30] Ruslim, C.; Matsunaga, D.; Hashimoto, M.; Takashi, T.; Ichimura, K. *Langmuir* **2003**, *19*, 3686–3691.
[31] Horowitz, V.R.; Janowitz, L.A.; Modic, A.L.; Heiney, P.A.; Collings, P.J. *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.* **2005**, *72*, 041710.
[32] Prasad, S.K.; Nair, G.G.; Hegde, G.; Jayalakshmi, V. *J. Phys. Chem. B* **2007**, *111*, 9741–9746.
[33] Park, H.-S.; Kang, S.-W.; Tortora, L.; Nastishin, Y.; Finotello, D.; Kumar, S.; Lavrentovich, O.D. *J. Phys. Chem. B* **2008**, *112*, 16307–16319.
[34] Edwards, D.J.; Jones, J.W.; Lozman, O.; Ormerod, A.P.; Sintyureva, M.; Tiddy, G.J.T. *J. Phys. Chem. B* **2008**, *112*, 14628–14636.
[35] Perahia, D.; Wachtel, E.J.; Luz, Z. *Liq. Cryst.* **1991**, *9*, 479–492.

[36] Usol'Tseva, N. *Mol. Cryst. Liq. Cryst*. **1996**, *288*, 201–210.

[37] Harrison, W.J.; Mateer, D.L.; Tiddy, G.J.T. *J. Phys. Chem*. **1996**, *100*, 2310–2321.

[38] Eichhorn, H.; Bruce, D.W.; Wohrle, D. *Adv. Mater.* (*Weinheim, Ger.*) **1998**, *10*, 419–422.

[39] Ignatov, L.; Lazarev, P.I.; Nazarov, V.; Ovchinnikova, N.A. *Proc. SPIE* **2002**, *4658*, 79–90.

[40] Tam-Chang, S.-W.; Iverson, I.K.; Helbley, K. *Langmuir* **2004**, *20*, 342–347.

[41] Tomasik, M.R.; Collings, P.J. *J. Phys. Chem. B* **2008**, *112*, 9883–9889.

[42] Lydon, J. *Curr. Opin. Colloid Interface Sci*. **1998**, *3*, 458–466.

[43] Lydon, J. In *Handbook of Liquid Crystals*: Demus, D., Goodby, J., Gray, G.W., Spiess, H.-W., Vill, V., Eds.; Wiley–VCH: Weinheim, 1998; Vol. 2B, p 981.

[44] Lydon, J. *Curr. Opin. Colloid Interface Sci*. **2004**, *8*, 480–490.

[45] Tam-Chang, S.-W.; Huang, L. *Chem. Commun.* (*Cambridge, UK*) **2008**, *195*, 1957–1967.

[46] Gelbart, W.M.; Ben-Shaul, A. *J. Phys. Chem*. **1996**, *100*, 13169–13189.

[47] McKitterick, C.B.; Erb-Satullo, N.L.; LaRacuente, N.D.; Dickinson, A.J.; Collings, P.J. *J. Phys. Chem. B* **2010**, *114*, 1888–1896.

[48] Lee, S.D. *J. Phys. Chem*. **1987**, *87*, 4972–4974.

[49] Taylor, M.P.; Herzfeld, J. *Langmuir* **1990**, *6*, 911–915.

[50] Taylor, M.P.; Herzfeld, J. *Phys. Rev. A: At., Mol., Opt. Phys*. **1991**, *43*, 1892–1905.

[51] Maiti, P.K.; Lansac, Y.; Glaser, M.A.; Clark, N.A. *Liq. Cryst*. **2002**, *29*, 619–626.

[52] Dickinson, A.J.; LaRacuente, N.D.; McKitterick, C.B.; Collings, P.J. *Mol. Cryst. Liq. Cryst*. **2009**, *509*, 751–762.

[53] Tortora, L.; Park, H.S.; Antion, K.; Finotello, D.; Lavrentovich, O.D. *Proc. SPIE* **2007**, *6487*, 6487OI-1–6487OI-15.

[54] Park, H.; Kang, S.W.; Tortora, L.; Nastishin, Y.; Finotello, D.; Kumar, S.; Lavrentovich, O.D. *J. Phys. Chem. B* **2008**, *112*, 16307–16319.

[55] Onsager, L. *Ann. N. Y. Acad. Sci*. **1949**, *51*, 627–659.