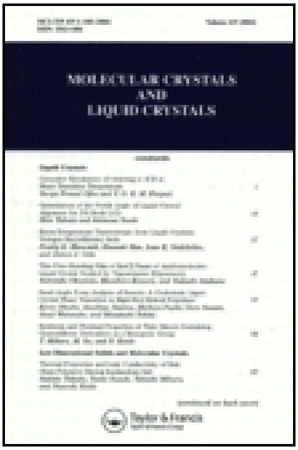

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Aggregate Structure and Free Energy Changes in Chromonic Liquid Crystals

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To cite this article: Alexandra J. Dickinson, Nicholas D. LaRacuente, Christopher B. McKitterick & Peter J. Collings (2009): Aggregate Structure and Free Energy Changes in Chromonic Liquid Crystals, Molecular Crystals and Liquid Crystals, 509:1, 9/[751]-20/[762]

To link to this article: http://dx.doi.org/10.1080/15421400903051044

Mol. Cryst. Liq. Cryst., Vol. 509, pp. 9/[751]–20/[762], 2009
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400903051044

Aggregate Structure and Free Energy Changes in Chromonic Liquid Crystals

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Past and recent x-ray and absorption data on chromonic liquid crystals are analyzed in a consistent manner to reveal both the cross-sectional areas and stacking free energy changes for a number of systems. Two tentative conclusions result from this study. First, the locations of the charged groups on the dye molecule determine the number of molecules in the cross-section of the aggregate. Second, among systems with the same aggregate structure, the higher the stacking free energy change as measured in dilute solutions, the lower the concentration at which a room temperature liquid crystal phase forms at higher concentrations.

Keywords: aggregation; chromonic; liquid crystals; supramolecular assembly

I. INTRODUCTION

Although the existence of chromonic liquid crystals has been known for some time [1], interest in them has recently increased [2–10]. The reasons for this are numerous, but surely the fact that these systems represent an aqueous, ordered phase of weakly bound supramolecular assemblies is largely responsible for the interest among both basic and applied researchers. Theoretical and experimental

The partial support of this work by the Petroleum Research Fund of the American Chemical Society is acknowledged, as is additional support from the Howard Hughes Medical Institute and the Research Experiences for Undergraduates Program at the Laboratory for Research in the Structure of Matter at the University of Pennsylvania. Fruitful discussions with Oleg Lavrentovitch, Gordon Tiddy, Krishna Prasad, and Michelle Tomasik are warmly acknowledged.

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investigations have revealed a good deal about the structure, behavior, and properties of these phases. But there are many questions of fundamental importance that are still unanswered. Among them are (1) what is the structure of the aggregates, (2) what is the nature of the aggregation process, and (3) why do these systems react to changes in pH, ionic strength, and the presence of other molecules in the ways that have been observed?

The experimental results, both past and recent, provide enough information that a review of this work is quite revealing. While such a review is not capable of definitively answering any of the questions posed above, it can indicate trends that provide considerable insight into the nature of the answers. To that end, past experimental results have either been used directly or re-analyzed in a consistent manner for a number of chromonic liquid crystals. For some systems, the free energy change driving aggregation has been estimated. For even more systems, the cross-sectional areas of the aggregates have been determined and compared to the molecular area. As a result, two tentative conclusions are presented concerning the reasons why different aggregate structures are formed and why the liquid crystal phase occurs at concentrations that vary significantly.

II. WELL ESTABLISHED RESULTS

Every chromonic liquid crystal that has been examined through an x-ray diffraction investigation shows a peak in the intensity at a value of the scattering wavevector corresponding to a distance of 0.34 nm. Figure 1 shows such a peak for Bordeaux dye, a dye derived from naphthalenecarboxylic acid [11]. In all cases, the value of the peak scattering wavevector does not change with dye concentration, indicating that the 0.34 nm distance represents a basic feature of the aggregate structure. Since this distance is the same as is found between base pairs of nucleic acids and between graphite layers, it is reasonable to conclude that the polyaromatic cores of the dyes are stacked on top of one another and separated by this distance. When the sample is partially aligned due to shear as a x-ray capillary tube in filled, this peak is oriented in the plane of the tube axis, indicating that the molecular stacks are oriented along the tube axis. It has therefore been concluded by many researchers that the stacking of the molecules results in long, columnar aggregates that develop orientational order of their long axes. This conclusion is strengthened by absorption measurements made on the liquid crystal phase of chromonic systems. For example, the visible absorption of azo- dyes is almost entirely due to the nitrogen-nitrogen double bond, which is

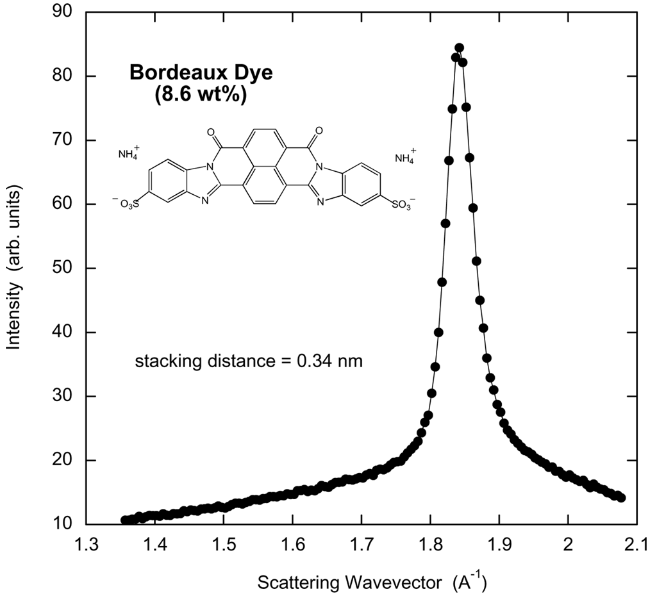


FIGURE 1 X-ray scattering peak due to the stacking of molecules in an aggregated solution of Bordeaux dye. The molecular structure of Bordeaux dye is also shown.

extremely sensitive to the polarization state of the light. If the incident light is polarized along the nitrogen-nitrogen double bond, there is considerable absorption, while incident light polarized perpendicular to the double bond is hardly absorbed at all. Thus when one measures the absorption of a chromonic liquid crystal and notices that the absorption is much greater for light polarized perpendicular to the director than for light polarized parallel to the director [6,7], one must conclude that the nitrogen-nitrogen double bonds are oriented perpendicular to the long axes of the aggregates. This is just the situation expected if the molecules stack into columns and the long axes of the columns are preferentially oriented along the director.

While the conclusion that the basic structure of the aggregates is one of molecular stacking is strongly supported by experimental evidence, the simplest extension of this, namely that the aggregates are columnar stacks much longer than they are wide, may not be warranted. The width of the x-ray peak can be used to determine the distance over which the stacking is coherent, which surely cannot be larger than the length of the aggregates. If the coherence length in the stacking direction, which is equal to 2π divided by the full-width-at-half-maximum of the scattering wavevector peak, is calculated from the data in Figure 1, one obtains 15 nm or about 44 molecules. This represents a length-to-width ratio of approximately 7.5. To get some sense of this number, according to the Onsager theory of hard rods [12], the length to width ratio times the volume fraction should be more than 4 for the liquid crystal phase to be stable. The volume fraction of Bordeaux dye when its concentration is 8.6 wt% is 0.064 and thus the product of it and the length-to-width ratio is about 0.5, much less than 4. Clearly these aggregates of ionized molecules in aqueous solution do not act like the hard rods of Onsager's calculation. Still the discrepancy is so large that one must wonder if something is being missed. To that end, Lavrenovitch and co-workers have suggested that the aggregates may possess defects and branches, where the x-ray coherence is lost but a physical connection remains [13]. This would explain the existence of a liquid crystal phase when the x-ray evidence suggests that the aggregates are too short.

It is worthwhile pointing out an aspect of this length estimate that will be relevant when the stacking free energy change is discussed later. If the aggregation process is considered to be isodesmic, that is, if the change in free energy when a molecule joins an aggregate is independent of aggregate size, then a simple relationship between the average number of molecules in an aggregate and the stacking free energy change results,

$$\langle \mathrm{n} \rangle = \sqrt{\phi}\, \mathrm{e}^{-\alpha/2},$$

where $\langle \mathrm{n} \rangle$ is the average number of molecules in an aggregate, ϕ is the volume fraction of dye, and α is the stacking free energy change in units of the Boltzmann constant times the temperature [14]. Using the volume fraction of the sample for Figure 1, an estimate of α of about 10 results. Unlike the analysis described in the next section, this estimate of α is determined from data at higher concentration in the liquid crystal phase, rather than in very dilute solutions in the isotropic phase.

III. CROSS-SECTIONAL AREA OF THE AGGREGATES

Another finding that is found to be true for most investigated chromonic liquid crystals is the existence of a concentration-dependent peak in the x-ray scattering at a value of the scattering wavevector smaller than that for the concentration-independent peak discussed earlier. In partially aligned samples, this peak represents a repeat distance perpendicular to the stacking repeat distance and has been interpreted as a measure of the distance between the columnar aggregates.

If the aggregation is in columns and the lengths of the columns grow as the concentration of dye increases, then the peak scattering wavevector q_0 should be proportional to the square root of the volume fraction [6]. The inset of Figure 2 shows a log-log plot for the dye Blue 27 [11], for which the slope is 0.53 ± 0.02. With this in mind, the square of the peak scattering wavevector can be graphed against the volume fraction and the slope used to determine the cross-sectional area of the aggregates. The only assumption needed is that the packing symmetry that best represents the average arrangement of these columns is hexagonal. Since hexagonal close packing in two dimensions has the highest density, then when the packing is not close, each column has the largest area to explore and thus the maximum entropy, if on average they occupy a two dimensional hexagonal lattice. With this assumption, the relationship between the peak scattering wavevector

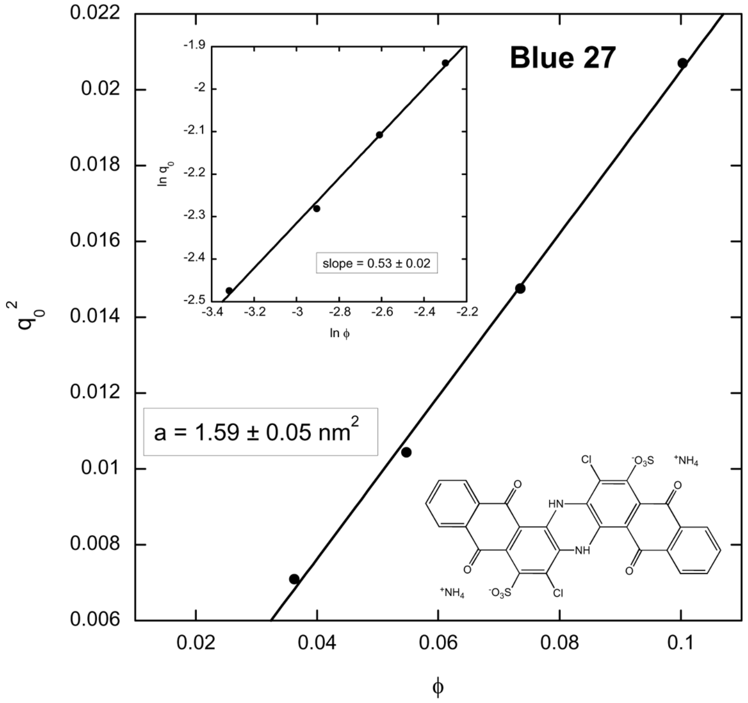


FIGURE 2 Inset: log-log plot of the peak scattering wavevector versus volume fraction for Blue 27. The slope is very close to one-half, indicating columnar assemblies. Full graph: square of the peak scattering wavevector vs. volume fraction. The cross-sectional area of the aggregates, a, can be calculated from the slope.

TABLE 1 Results from X-ray Scattering Experiments for Nine Chromonic Liquid Crystals

Compound	Slope of log-log plot	Area (nm^2)	Area/molecular area
Sunset Yellow FCF [6]	0.53 ± 0.06	1.21 ± 0.12	1.0
Blue 27 [11]	0.53 ± 0.02	1.59 ± 0.05	1.0
Direct Blue 67 [15]	0.44 ± 0.01	2.67 ± 0.08	1.1
Disodium Cromoglycate [16]	0.50 ± 0.02	2.39 ± 0.08	1.8
Bordeaux Dye [17]	0.51 ± 0.03	3.24 ± 0.04	1.9
Violet 20 [11]	0.37 ± 0.03	4.06 ± 0.40	2.2
Xanthone Dye [18]	0.50 ± 0.04	4.70 ± 0.25	3.3
Acid Red 266 [19]	0.45 ± 0.03	8.00 ± 0.20	6.0
Cyanine Dye [20]	0.51 ± 0.01	12.9 ± 0.30	6.3

q_0 and the volume fraction ϕ is

$$q_0^2 = \frac{2\sqrt{3}\,\pi^2}{a}\,\phi,$$

where a is the cross sectional area of the aggregates. As Figure 2 demonstrates, the value of a for Blue 27 is $1.59 \pm 0.05\,\mathrm{nm}^2$.

It is instructive to compare the cross-sectional area of the aggregates to the area of a single molecule. This can be done by determining the structure of the molecule through an energy minimization program and from it calculating the cross sectional area. Since the dyes are ionized in solution, it is the area of the ion that should be used for this calculation. When this is done for Blue 27, one obtains a value of approximately $1.6\,\mathrm{nm}^2$, or a ratio between the aggregate area and molecular area of about 1.0.

When this procedure is carried out for the data published on nine chromonic liquid crystals, the values listed in Table 1 result. Notice that the slope of the log-log plot is consistently close to one-half, and that the ratios of aggregate area to molecular area fall into three categories (close to 1, close to 2, and more than 3).

IV. STACKING FREE ENERGY CHANGES

Another finding that is present for most investigated chromonic liquid crystals is a change in the absorption coefficient as the dye concentration of dilute solutions is increased. Although slightly different for each system, this change amounts to a decrease in the value of the maximum absorption coefficient and a shift of the absorption maximum to higher or lower wavelength. One way this change can be understood is through exciton theory. The absorption of a single molecule is modeled as a two state system. When molecules join an aggregate, the excited states of neighboring molecules in the aggregate are coupled. This results in an absorption coefficient that decreases together with a shift in the wavelength of maximum absorption as the number of molecules in an aggregate increases [6]. The decrease of the absorption coefficient at the peak wavelength or the absorption coefficient at a fixed wavelength near the wavelength of maximum absorption as the number of molecules in an aggregate increases can be shown to closely follow a simple relationship,

$$a_n = a_1 + (a_\infty - a_1)\cos\left(\frac{\pi}{n+1}\right),$$

where a_n is the absorption coefficient of an aggregate composed of n molecules, a_1 is the absorption coefficient of a single molecule in solution, and a_∞ is the absorption coefficient of an aggregate of an

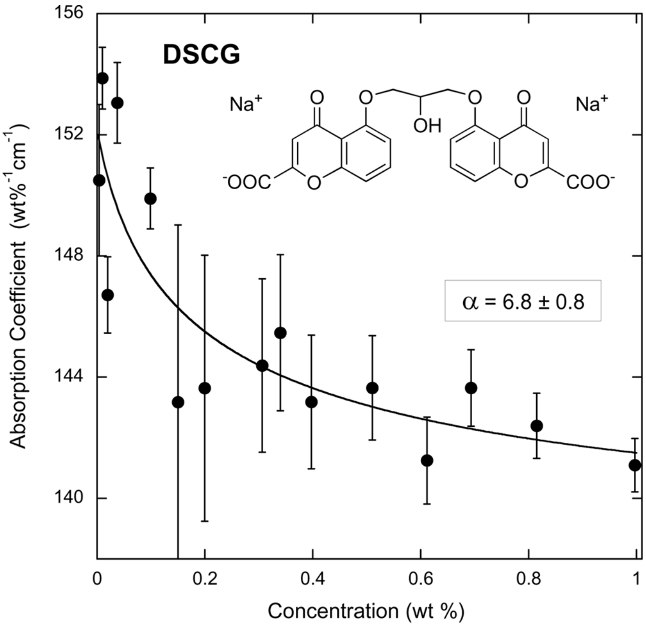


FIGURE 3 Absorption coefficient of disodium cromoglycate (DSCG) as a function of concentration. The line is a fit to the theory as described in the text, yielding a value for the stacking free energy change α of 6.8 ± 0.8 (in units of the Boltzmann constant times the temperature).

TABLE 2 Results from Phase and Absorption Investigations for Five Chromonic Liquid Crystals

Compound	Liquid crystal concentration (wt%)	α
Disodium Cromoglycate	11	6.8 ± 0.8
Sunset Yellow FCF [6]	24	7.2 ± 0.1
Bordeaux Dye [17]	6	9.2 ± 0.4
Acid Red 266 [21]	1	11.7 ± 0.4
Blue 27 [7]	6	12.0 ± 0.5

infinite number of molecules. This relationship can be combined with the distributions of aggregate size one obtains from isodesmic aggregation to predict how the absorption coefficient depends on dye volume fraction (or dye concentration). The only unknown parameters are α and a_∞. Figure 3 shows data for the compound disodium cromoglycate along with a fit of the theory to the data, yielding a value for α of 6.8 ± 0.8. Notice that the concentrations in Figure 2 are quite small, well below the lowest concentration at which the liquid crystal phase forms.

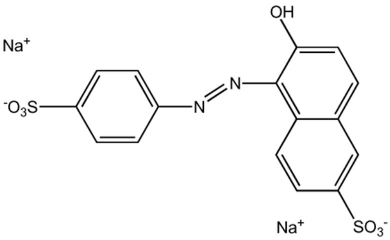
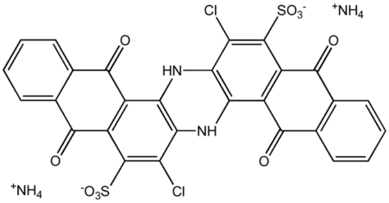
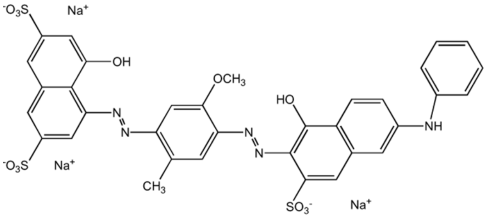
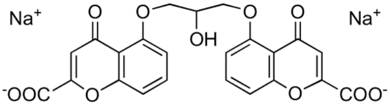
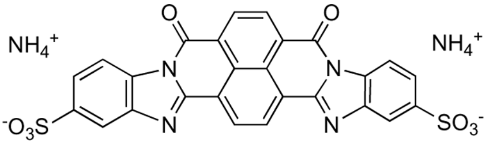
When this procedure is performed for absorption data on a number of compounds, the results in Table 2 are obtained.

An appreciation of the estimate of α obtained from the x-ray data on Bordeaux dye is now possible. Recall that α was estimated to be about 10 by analyzing the x-ray peak for a sample of Bordeaux dye in the liquid crystal phase. Table 2 shows that analysis of the Bordeaux dye absorption spectra at much lower concentration yields a value of 9.2. This rough agreement between estimates of the driving force for aggregation from very different concentrations using very different techniques also occurs for some other systems [13], indicating that it could be an indication that these measurements of α describe an important feature of the aggregation process.

V. TENTATIVE CONCLUSIONS

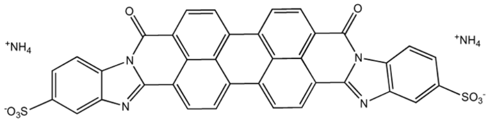
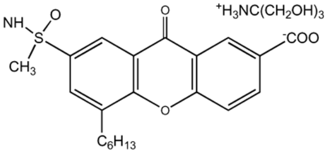
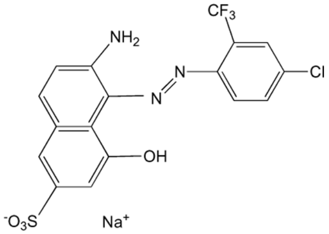
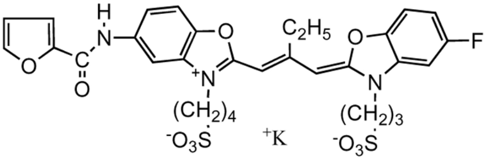
What can be learned from accumulating results on several chromonic liquid crystals? Perhaps the most intriguing observation is that the ratios of cross-sectional area to molecular area fall close to very small integers for the majority of the systems. Thus it is tempting to conclude that the aggregate structures of many chromonic systems are very simple, consisting of one or two molecules in a cross-section. Is there anything about the molecular structure of these compounds that makes such a conclusion plausible? If one looks at the location of the charged groups that make the dye soluble in water (see Table 3),

TABLE 3 Structures for Nine Molecules that Form Chromonic Liquid Crystals

Compound	Area/molecular area	Molecular structure
Sunset Yellow FCF	1.0	
Blue 27	1.0	
Direct Blue 67	1.1	
Disodium Cromoglycate	1.8	
Bordeaux Dye	1.9	

(*Continued*)

TABLE 3 Continued

Compound	Area/molecular area	Molecular structure
Violet 20	2.2	
Xanthone Dye	3.3	
Acid Red 266	6.0	
Cyanine Dye	6.3	

one notices that they are located on opposite sides of the molecule for the molecules that have one molecule per aggregate cross-section and on the same side of the molecule for the molecules that have two molecules per aggregate cross-section. Thus one tentative conclusion is that when the charged groups occur on opposite sides of the molecule, there is no arrangement of more than one molecule that can keep the charged groups apart. On the other hand, if the charged groups are on the same side of the molecule, two molecules can be arranged in the same layer with the charged groups far away from each other. The compounds with three or more molecules per aggregate cross-section have more complicated structures, making even tentative conclusions difficult.

Table 2 seems to indicate that there is no relationship between the stacking free energy change and aggregate structure. However, if one looks at the two pairs of molecules with the same number of molecules per cross-section, a definite connection is seen, namely the higher α is, the lower the concentration at which the liquid crystal phase is stable at room temperature. Thus a second tentative conclusion is that for identical aggregate structures, the value of the stacking free energy change determines the phase diagram.

A great deal remains to be learned about chromonic liquid crystals. But as this analysis reveals, some trends are starting to become evident. It is the hope that these trends will help guide researchers as they continue to examine the aggregate structure and aggregation properties of chromonic liquid crystals.

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