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Structural and Orientational Characteristics of the Disodium/Cromoglycate-Water Mesophases by Deuterium NMR and X-Ray Diffraction

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Deuterium NMR and X-ray diffractometry studies of the lyomesophases of the disodium/cromoglycate-water system are reported. The deuterium NMR studies were made on three specifically labelled compounds, viz. disodium cromoglycate-6,8,6′,8′-d_4, disodium cromoglycate-3,3′-d_2 and disodium cromoglycate-10-d_1. The deuterium spectra of these species consist of doublets caused by the corresponding average quadrupolar interaction in the N and M phases; however, in phase III only the methine deuteron of disodium cromoglycate-10-d_1 could be seen. The splittings of the chromone moiety deuterons, 3,6 and 8, are essentially identical over the whole temperature and concentration range of the N and M phases, ranging between 50 and 65 kHz. The methine deuteron splitting in the M phase is similar to that of the chromone deuterons, but is considerably higher (115 to 117 kHz) in phase III.

The X-ray diffraction studies were made on a 20 wt% solution as a function of temperature between −15°C and 60°C. Two diffraction bands were observed corresponding to approximately 37 Å and 3.4 Å d-values at room temperature. Distinct changes in the diffraction pattern have been observed in the phase transition regions, Isotropic → N → M → III → solid. The results are consistent with a model in which the N and M phases consist of highly ordered cylindrical micelles of stacked disodium cromoglycate molecules whose chromone planes lie perpendicular to the cylinder axes. The 37 Å and 3.4 Å spacings are identified with respectively the intermicellar and intramicellar stacking distances, and from the NMR results the effective orientational order parameter of the micelles is calculated to be between 0.75 and 1.0 depending on the concentration.

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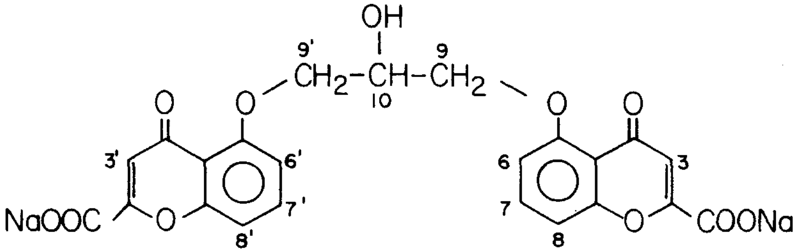
I INTRODUCTION

The disodium salt of cromoglycic acid, mixed with water, can form several lyotropic mesophases whose properties depend on the composition of the solution (see phase diagram in Figure 1).[1-3] The effect is rather unusual because the structure of the disodium cromoglycate(DSCG) molecule differs significantly from the common materials which form lyomesophases.



The latter compounds generally consist of rod-like amphiphilic molecules possessing a well defined hydrophilic end while the rest of the molecule is lipophilic. The DSCG molecules on the other hand are made up of two carboxychromone moieties linked together by an alkylene dioxy chain and thus have a distribution of polar sites in an otherwise apolar frame. A schematic phase diagram of the DSCG-Water system, including the labeling of the various mesophases, is shown in Figure 1. The structure of the N and M phases was studied previously by X-ray diffraction as a function of composition.[2] In the N phase a low angle diffraction line (~2° 2θ) corresponding to a d-value of 44.5 Å has been observed while in the M phase three lines appear in this low angle region; a relatively strong one with d-values ranging from 26 to 37 Å depending on concentration, and two weaker lines, 16 to 22 Å, and 15 to 19 Å. It was shown that the d-spacing of the strong line in this region varies linearly with the inverse square root of the DSCG concentration.[2] In both phases, a broad line appeared at higher angle (~26° 2θ) corresponding to about 3.4 Å. Based on these results it was suggested that the N and M phases consist of rod-like micelles in which the DSCG molecules are stacked on top of each other.[2,4,5] In the N phase these columns are randomly distributed in the aqueous solution retaining, however, a degree of orientational order, thus forming a lyotropic nematic phase. In the M-phase the rods are arranged in hexagonal arrays within the aqueous

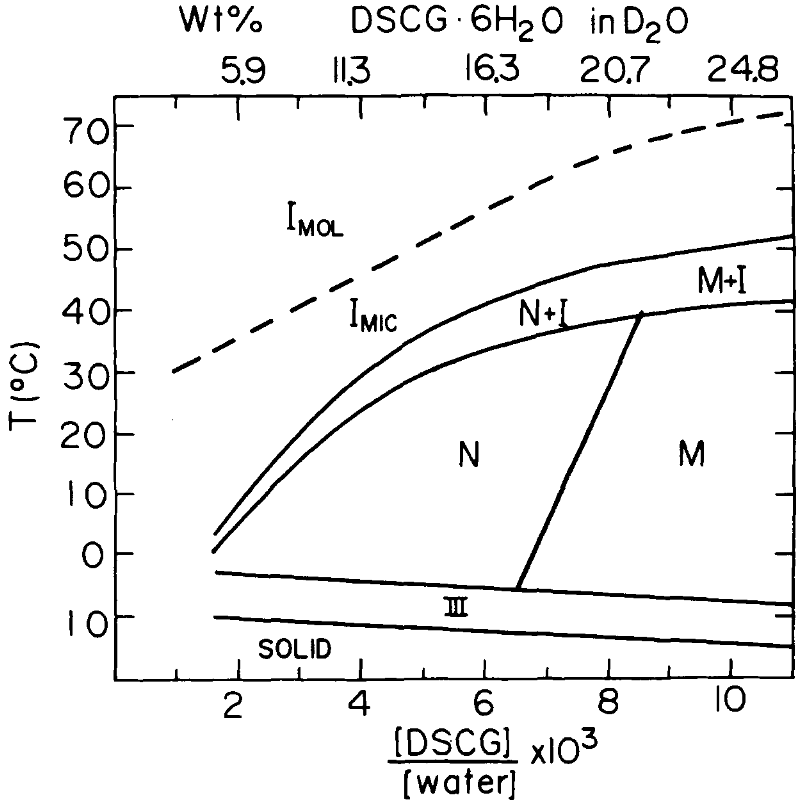


FIGURE 1 The phase diagram of the lyomesophases of the disodium cromoglycate-water system as determined by deuterium NMR in D_2O solutions (ref. 3).

medium resembling the arrangement in some columnar discotic mesophases.[6] The 3.4 Å d-spacing can thus be identified with the repeat distance of the molecules along the micellar axis, while the large d-spacings correspond to the mean distances between the centers of the rods. It was suggested that the stacking units consist of coplanar DSCG tetramers held together by sodium ion bridges, thus forming square hollow columns.[4] The structure of phase III has until now not been studied by X-rays. However, it was shown by NMR measurements that similar to the N and M phases this phase too is uniaxial and of type II i.e. possesses a negative anisotropic magnetic susceptibility ($\Delta\chi < 0$).[3] When cooled from the isotropic phase within a strong magnetic field all the phases will preferentially align with the director perpendicular to the field direction.[3]

The phase diagram of the DSCG-Water system shown in Figure 1 also contains a boundary line within the isotropic phase, which separates between a molecular solution at high temperatures and an isotropic micellar emulsion at lower temperatures. This subdivision is based on recent ^{23}Na NMR measurements in aqueous DSCG solutions.[7] Light scattering experiments in dilute DSCG solutions also indicate the formation of aggregates in the isotropic liquid.[8]

In a previous NMR study of the water ^{2}H and ^{17}O nuclei in enriched aqueous solutions of DSCG,[3] the ordering characteristics of the solvent water was studied as a function of temperature and DSCG concentration. The results indicated a relatively high degree of water ordering and suggested that the ordering of the micellar rods of the DSCG molecules must also be high even in very dilute solutions. The purpose of the present work was to check this hypothesis and to study in general the ordering characteristics of the DSCG molecules in the mesophase region. In particular, we were interested to learn about the conformation and stacking mode of the DSCG molecules within the micellar rods. To this end we have studied the deuterium NMR of several specifically deuterated DSCG molecules in the various DSCG-Water mesophases. The compounds used for the NMR study consisted of two species deuterated in the chromone rings: DSCG-6,8,6′,8′-d_4 and DSCG-3,3′-d_2, and one species labelled in the aliphatic glyceryl moiety, DSCG-10-d_1. The results are indeed remarkable in that even in the most dilute solutions which exhibit mesophases ($\sim$ 4 wt% DSCG) very high (>0.7) micellar order is observed, with the aromatic planes of the molecules oriented normal to the rods' axes.

We have also performed X-ray diffraction studies of the DSCG lyomesophases in a particular solution which as function of temperature passes through all three mesophases. In general our results confirm the previous findings by Hartshorne and Woodard.[2] However, in addition we have studied the diffraction lines from phase III and have observed small but distinct differences in the diffraction pattern during the thermotropic transitions between phases III, M and N.

In the next section (II) the synthesis of the various compounds is described, as well as the experimental procedure related to the NMR and X-ray measurements. Compounds used in this study were obtained from Fisons PLC. In section III the experimental results of both techniques are described, and finally in section IV we discuss them in terms of possible structures of the DSCG micelles.

II EXPERIMENTAL

A. Material and sample preparation

Disodium cromoglycate-6,8,6′8′-d_4 was prepared by acid catalysed exchange labelling of disodium cromoglycate[9] in concentrated deuterosulphuric acid at 85° for two days. Solvent extraction and recrystallisation of the resulting deuterated disodium cromoglycate diacid derivative from N,N-dimethylforamide followed by neutralisation with sodium hydrogen carbonate yielded disodium cromoglycate-6,8,6′,8′-d_4. The isotopic enrichments at the 6,6′ and 8,8′ positions were essentially the same; about 70% as determined by ^{1}H NMR.

Disodium cromoglycate-3,3′-d_2 was prepared by exchanging the free acid under reflux in D_2O/dioxane using Rhodium (III) chloride as catalyst.[10] The enrichment obtained after refluxing for ~12h was about 90% as determined by ^{1}H-NMR. The final product was obtained by neutralizing the recrystallized acid with $NaHCO_3$ and freeze drying.

Disodium cromoglycate-10-d_1 was prepared via the reduction of a precursor ketone.[9] Oxidation of the diethyl ester derivative of disodium cromoglycate with Jones reagent[11] followed by saponification of the resulting oxo-ester with sodium hydroxide yielded the required 10-oxo precursor. Reduction of this compound with sodium borodeuteride in sodium hydrogen carbonate solution yielded disodium cromoglycate-10-d_1. The isotropic enrichment at the 10-position was greater than 95% as determined by ^{1}H NMR.

Solutions of DSCG were prepared gravimetrically by dissolving the desired amount of the DSCG in doubly distilled water. For the NMR measurements the samples were placed in 5 mm or 10 mm o.d. tubes of ~1.5 cm length and either sealed or tightly capped before use. The concentrations of the samples were checked by comparing the doublet splitting of the HDO signal (natural abundance) with the results determined previously in D_2O solutions.[3] For the X-ray studies a 20 wt% solution of unlabelled DSCG was used. At this concentration all three mesomorphic phases, N, M, and III are accessible by changing the temperature (see Figure 1).

B. NMR measurements

The deuterium NMR measurements were performed on a Bruker CXP-300 spectrometer operating at 46.07 MHz. Two different high power probes were used; one with a 5 mm solenoid in which the r.f.

power could be adjusted to give a $\pi/2$ pulse length of 3.5 μsec. The second probe consisted of a 10 mm solenoid with a $\pi/2$ pulse of 5.7 μsec. The spectra were obtained by Fourier transformation of the second half of the quadrupole echo signal from a $[(\pi/2)_x\text{-}\tau\text{-}(\pi/2)_y\text{-}\tau\text{-}\text{echo}]_n$ phase cycle sequence.[12] The interval τ was usually 30 μ sec and the number of accumulations, *n*, ranged between 10,000 and 100,000, depending on the concentration, temperature and the desired signal to noise. The probe temperature was controlled with a BST 100/700 unit and its absolute value was calibrated periodically using a Fluke 2190A digital thermometer.

C. X-ray measurements

X-ray measurements were made using a modified vertical scanning Philips diffractometer with transmission specimen and focussing LiF (200) monochromator[13,14] adjusted for Cu Kα radiation (weighted wavelength, 1.5418 Å) in the incident beam, and a temperature controlled specimen stage. Transmission diffraction geometry was used rather than the more usual reflection geometry because of our desire to study low angles of diffraction from specimens containing volatile components (water) over a range of temperatures. At such low angles, in reflection geometry, the necessary hermetic specimen cover would need to be impossibly thin in order to transmit X-rays. In the present instrument there is some ambiguity in the zero angle calibration. Thus although the relative values of the scattering angles are quite accurate, the absolute values of the larger d-spacings may be in error by a few percent.

Intensities were recorded with a NaI(Tl) scintillation detector, appropriate preamplifier, amplifier and pulse discrimination electronic circuits, strip chart recorder, and scaler with microprocessor readout. The intensity data recorded in the microprocessor were later corrected for detection system "dead time."[15,16] The specimens were disk shaped, 0.5 mm thick, and covered at top and bottom with a 25 micron aluminum foil.

III RESULTS

In the present section we describe the results of the deuterium NMR and X-ray measurements in the DSCG-Water lyomesophases. We first describe the NMR results obtained with the various deuterated DSCG species. In the mesophase region each type of deuteron is expected to yield a doublet splitting due to its average quadrupole interaction.[17] We label the overall splitting by ν_Q and we describe its dependence on the DSCG concentration and on the temperature within the mesophase region.

A. NMR measurements

Disodium cromoglycate-6,8,6′,8′-d_4 and disodium cromoglycate-3,3′-d_2:

Examples of deuterium NMR spectra of DSCG-6,8,6′,8′-d_4 solutions at different temperatures and concentrations in the N and M mesophase regions are shown in Figure 2. All spectra exhibit a single doublet, with relatively broad components, due to both types of deuterons in the DSCG molecules, and a sharp central line due to HDO molecules in the solvent water (natural abundance). The latter signal is broadened by the apodization introduced with the fourier transformation. When a small exponential broadening is used (10 to 20 Hz) this signal too appears as a doublet. This splitting was used for calibration purposes as explained in the experimental section. The deuterium quadrupole splitting of the DSCG-6,8,6′,8′-d_4 species was studied in the N and M mesophase region in solutions containing between 4 wt% and 30 wt% DSCG. Examples of the temperature dependence of ν_Q are shown in Figure 3. There is considerable scatter in the results in particular at low temperatures where the lines become very broad. Nevertheless, they show common features for all the concentrations studied: First, upon cooling from the isotropic liquid a biphasic (I + N/M) region appears in which there is a decrease in the quadrupole splitting with decreasing temperature until a minimum is reached. Below this point the mixture converts to neat N or M (depending on the concentration). The splitting in this region first increases slightly and then reaches a plateau. The lines drawn through the experimental points in Figure 3 are intended to guide the eye and are based on the behaviour of the deuterium splitting of the solvent D_2O.[3]

The ν_Q values in the plateau region depend on the DSCG concentration and in Figure 4 this dependence is plotted as function of the [DSCG]/[water] ratio. The qualitative behaviour in respect to the temperature and concentration dependence of the deuterium DSCG quadrupole splitting is similar to that observed for solvent water,[3] although the magnitude of ν_Q is of course much smaller in the latter. Also, as for D_2O, no discontinuity in the concentration dependence of ν_Q is observed in the N to M transition region.

Upon cooling the sample within the N or M phases the linewidth of the doublet components gradually increases until about 5°C where

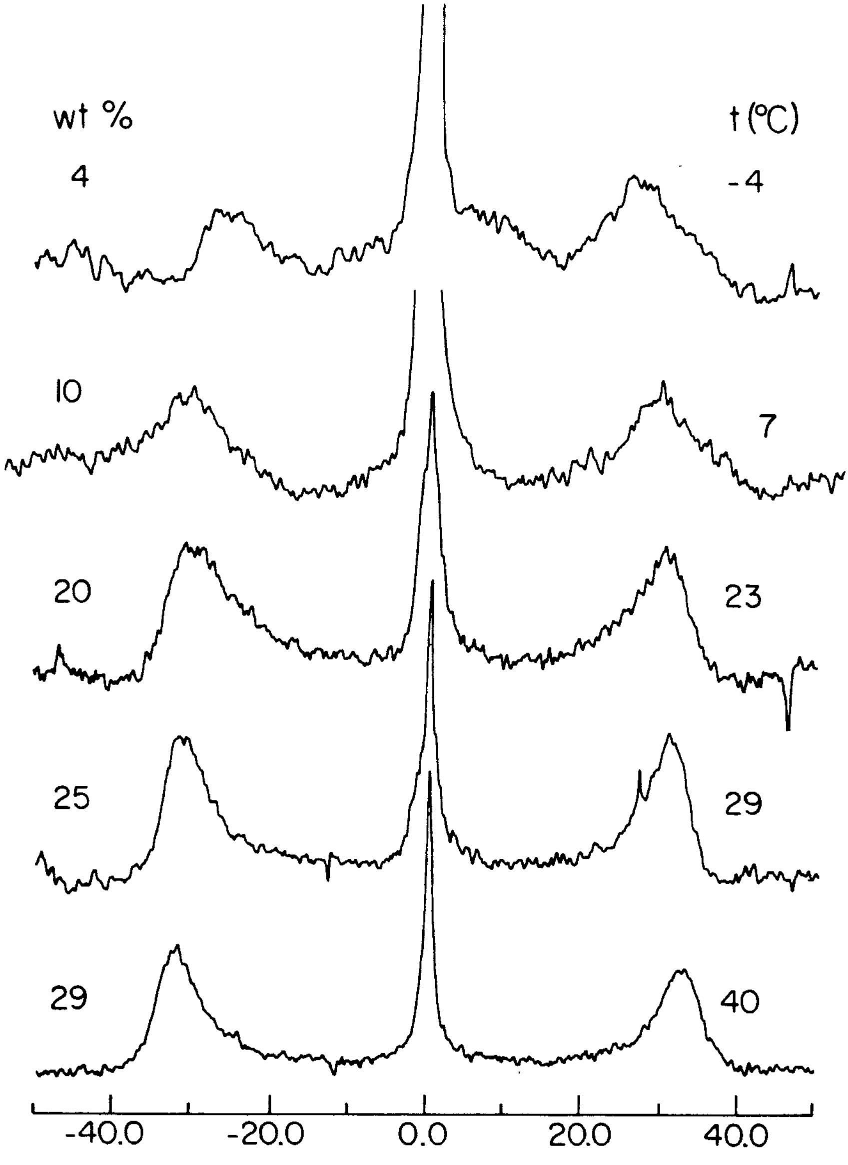


FIGURE 2 Examples of deuterium NMR spectra of disodium cromoglycate-6,8,6′,8′-d_4 in the mesophase region of the disodium cromoglycate-water system. The spectra correspond to the 'plateau' region of each solution. The concentrations in weight percent and the temperatures are given in the figure. The central peak in each trace is due to HDO (natural abundance) which is broadened by apodization. When a weaker exponential broadening is used, this line becomes a doublet.

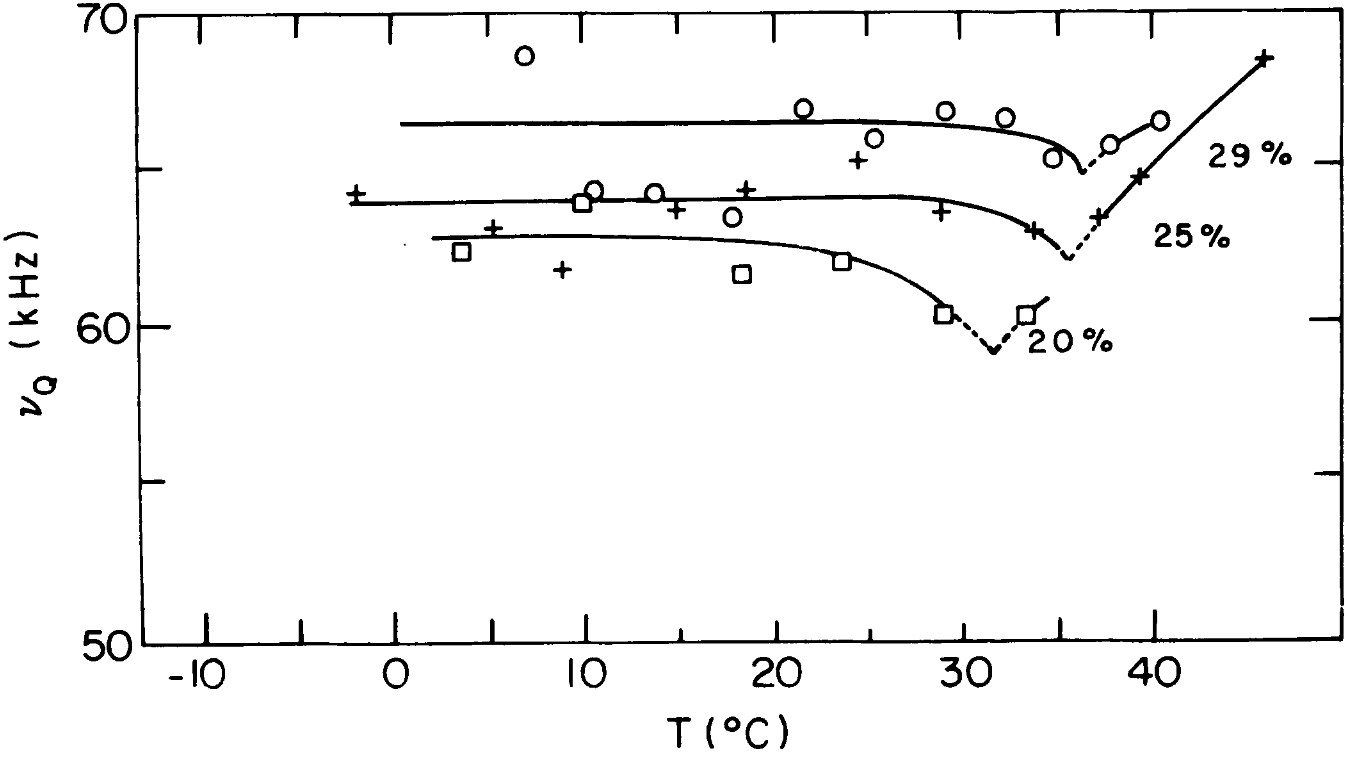


FIGURE 3 The observed quadrupole splitting ν_Q of the chromone deuterons in disodium cromoglycate-6,8,6′,8′-d_4 in the mesophase region as function of temperature for a few selected solutions as indicated in the figure.

no signal can be detected any more. Apparently, at this temperature range T_2 becomes shorter than the separation, τ, between the pulses and thus no echo signal can be formed. Likewise, after cooling further into phase III no signal may be observed.

The results for DSCG-3,3′-d_2 are very similar to those described for DSCG-6,8,6′,8′-d_4. An example of a spectrum is shown in the upper trace of Figure 5 and the results obtained for ν_Q in the plateau region for two concentrations of DSCG are indicated in Figure 4. As for DSCG-6,8,6′,8′-d_4 the signal gradually disappears upon cooling and no spectrum can be detected in phase III. An important conclusion that emerges from the above results is that all three chromone ring deuterons, 3,6 and 8, have essentially identical ν_Q values over the whole mesophase region.

Disodium cromoglycate-10-d_1:

The methine deuteron of DSCG-10-d_1 exhibits observable signals only in the M phase and in phase III. Examples of spectra are shown in the two lower traces of Figure 5. The results in the M phase behave similarly to those of the chromone ring deuterons (Figure 3), and the ν_Q values of the plateau region are indicated in Figure 4. However, unlike in the case of the chromone deuterons, the methine deuteron could also be observed in phase III even at concentrations below 10wt% (bottom trace in Figure 5); its ν_Q values in this phase are considerably larger (~115 kHz) than in the M phase (~60 kHz) and essentially independent of temperature, while the linewidths are much narrower (2 kHz vers. 5 to 10 kHz).

B. X-ray measurements

Our X-ray measurements of the DSCG mesophase agree, with some differences, with the earlier room temperature studies of this system.[2] In our instrument, the observed diffraction pattern at low angles is affected by the "wings" of the undiffracted monochromatic incident beam. Schematic sketches of the diffraction patterns in the various phases are reproduced in Figure 6. It may be seen that although the width of the undiffracted central beam of the instrument is quite small (0.08° 2θ at half maximum intensity) it contributes a very large sloping background underneath the low angle peaks. The 37 Å peak is well resolved above this background, while the 22 Å peak (not shown in Figure 6) was just barely seen, and the 19 Å peak was not observed at all. (Both the 22 Å and 19 Å peaks were reported[2] as being very weak.) The 3.4 Å peak, at 26° 2θ, is superposed upon a very broad

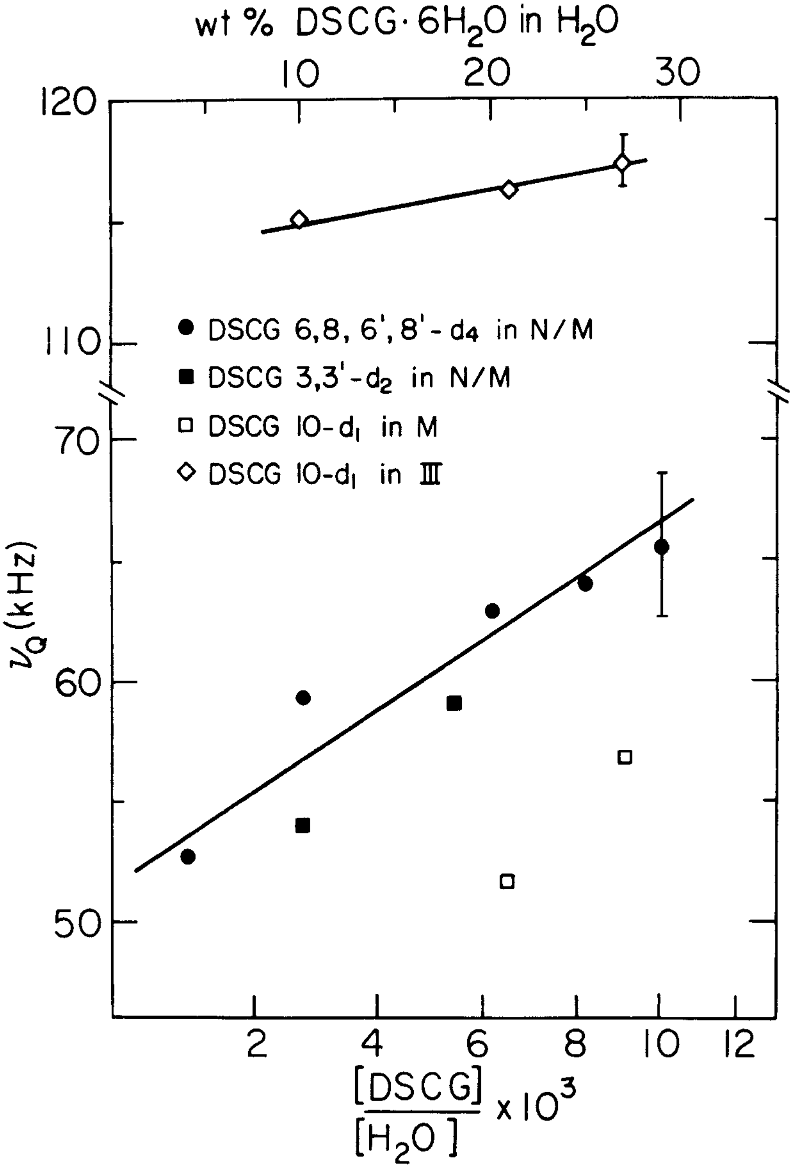


FIGURE 4 Plots of ν_Q in the plateau region versus the molar ratio [DSCG]/[Water] for several isotopic species as indicated in the figure. The results for the chromone ring deuterons correspond to the N and M phases while those for the methine are for phase III (upper curve) and M phase (lower curve).

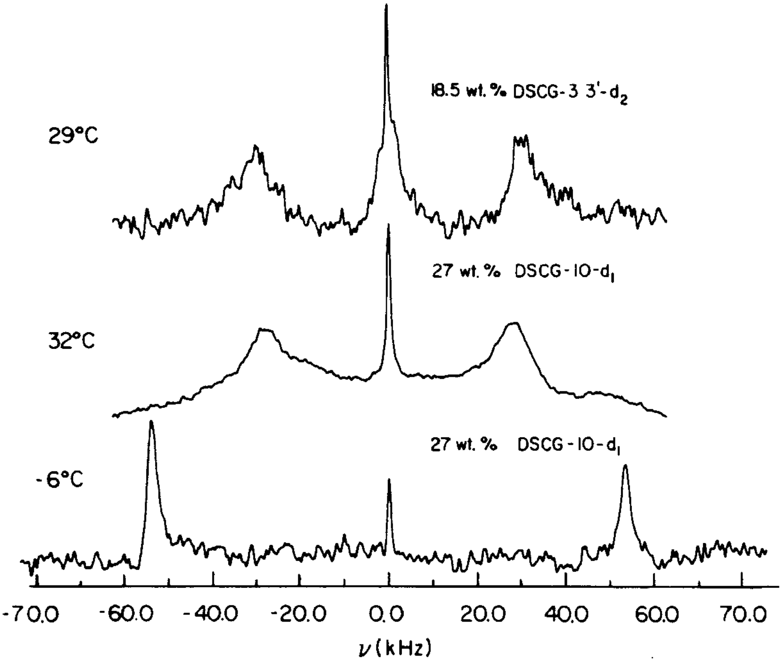


FIGURE 5 Experimental deuterium NMR spectra of deuterated disodium cromoglycate in the mesophase region. The concentration and temperatures at which the spectra were recorded are indicated in the figure. The upper trace corresponds to disodium cromoglycate-3,3'-d_2 in the M phase, while the two other traces are for disodium cromoglycate-10-d_1. They correspond respectively to the M phase (middle trace) and phase III (bottom trace). The central peaks are due to HDO.

"hump," mostly attributable to parasitic scattering from the specimen holder, as determined by measurements on an empty specimen holder.

By slowly cooling the sample from the isotropic phase within a strong magnetic field (20 KG) it was possible to prepare a partially aligned specimen, such that a preponderance of micellar axes were in the plane of the specimen disk. It so happened that there was also some in-plane preferred orientation of the director. The extent of this preferred orientation could be determined by observing the variation in the intensity of various diffraction features while rotating the specimen about its normal. The results of the measurements are shown in Figure 7. It may be seen that the net intensity of the 37 Å line varied by about a third above and below its mean value with two maxima and two minima per 360° of rotation separated by about 90° from each other. The net intensity of the 3.4 Å line varied similarly about its mean value with maxima and minima displaced by about

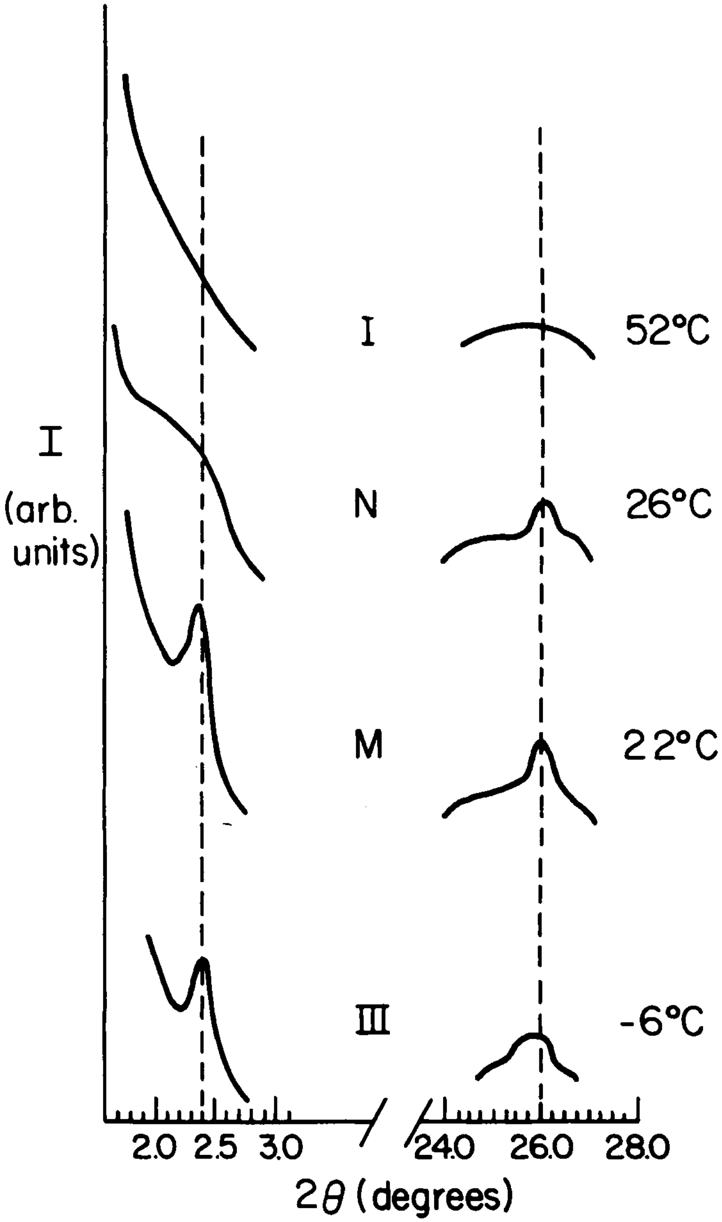


FIGURE 6 Schematic representation of the X-ray diffraction pattern around 2° and 26° 2θ observed for 20 wt% disodium cromoglycate sample in the various mesophases at the indicated temperatures.

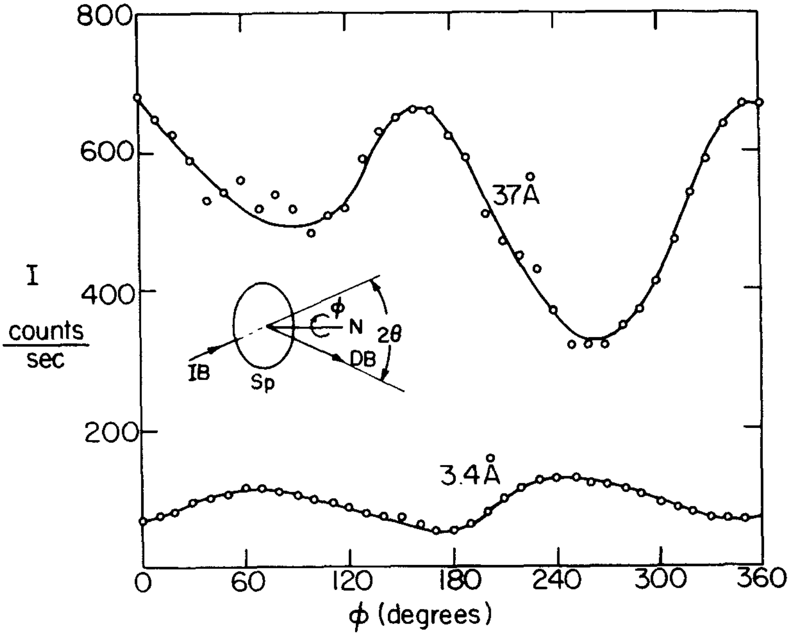


FIGURE 7 Net intensity of the 37 Å and 3.4 Å X-ray diffraction lines as function of the specimen orientation. The sample contained 20 wt% disodium cromoglycate and was aligned by cooling it from the isotropic phase within a 20 KG magnetic field to ambient temperature. The insert shows a schematic ray diagram: IB-incident beam; DB-diffracted beam; N-normal to specimen disk (also the direction of the aligning magnetic field); φ-rotation angle about the normal; 2θ-deflection of diffracted beam from incident direction.

90° from those of the low angle line. It is thus possible to conclude that the structural features of the high angle diffraction line lie perpendicular to those of the low angle line. This supports the hypothesis that the high angle diffraction arises from the periodicity of the molecular stacking along the micellar axis, and the low angle from the packing periodicity of the micelles. These results were later confirmed using a single domain DSCG sample prepared as described in ref. 18.

An experiment was then carried out in which the detector was set at 2.5° and the diffracted intensity monitored as function of temperature. At room temperature (22°C) this specimen is in the M phase (see Figure 1 for 20 wt% DSCG). As the temperature increased the diffracted intensity decreased very slightly until 26°C. At this point the intensity dropped drastically. Scanning the diffractometer over the angular region then showed a weaker and broader peak at about the same angle (2.5°). At the same time a check of the 26° (3.4 Å) line showed that while its peak intensity had decreased somewhat its position and shape remained unchanged (cf. Figure 6). We associate these changes with the transition to the N phase. Thus, although the micelles in the N-phase are no longer in a well defined two dimensional array they still retain their structural integrity.

As the temperature was further increased to over 52°C, well into the isotropic region, both the high angle and low angle lines disappeared (Figure 6), and the only observable diffraction feature was the broad "hump" mentioned previously.

Several more detailed studies of the temperature behaviour of the 37 Å and 3.4 Å lines, using the scaler and microprocessor readout, were carried out over a temperature range from −14°C to 50°C. The d-values for the low angle line obtained from one such study between −14°C and ambient for the 20 wt% solution are shown by the circles in Figure 8. Above the transition temperature to phase III, d is almost constant at 37.1 Å, while below this transition d is 35.9 Å. The high angle line broadens asymmetrically with respect to its peak position when the transition temperature is reached, becoming almost twice as broad and centered at d = 3.46 Å below the transition temperature to phase III (see Figure 6). This could be interpreted as representing the appearance of a second diffraction line (at d = 3.56 Å) in phase III, overlapping the original line (at d = 3.43 Å).

In the same study we have also observed the transition from phase III to the solid phase at temperatures below about −13°C. Seven diffraction lines (see Table I) were observed, in addition to a broad "hump" in the range 3 to 4 Å. In general, these lines are different from, and broader than those observed for solid (hydrated) DSCG at room temperature.[1] Some of them may be unresolved multiple peaks, and we have therefore not attempted to index them. The "hump" has essentially the same shape as in the mesomorphic phases.

TABLE I

Observed X-ray diffraction lines in the low temperature solid hydrate phase of 20 wt % DSCG ($t = -13$°C)

2 θ (degrees)	d (Å)	Peak intensity (arbitrary units)
4.49	19.68	10
22.62	3.93	21
24.12	3.69	10
26.70	3.34	10
33.29	2.69	2
39.70	2.27	1
43.45	2.08	1

On raising the temperature back into the region of phase III, the diffraction pattern of the solid is retained, for at least several hours.

A study was also made of the behavior of the low angle diffraction line for the same specimen as a function of temperature, ranging from below the M to N transition (22°C) up to the N to isotropic transition. The resulting d-values are plotted as triangles in Figure 8. The specimen was then realigned in a magnetic field to obtain a preferred orientation, as described above, and a third set of measurements made over the temperature range from −6°C to 43°C. These data are plotted as pluses in Figure 8. Because of the ambiguities in zero angle calibration (see experimental section) the data obtained in the second and third sets have been scaled to make $d = 37.1$ Å at 20°C, as obtained in the first data set.

In the N phase, the low angle diffraction (Figure 6) is much broader and weaker than in the M phase. In the region from 27°C to 40°C, the low angle diffraction peak is so diffuse that the steeply sloping background introduces an uncertainty of 2 or 3 Å in the values of d obtained from the data; nevertheless, the overall trends are clear. The value of d is either constant or increases very slightly up to about 30°C and then decreases linearly with temperature from about 32°C onward, so that at 48°C, very close to the transition to the isotropic phase, d has decreased by about 25%. In the temperature range from 41°C to 46°C, the low angle diffraction pattern is better defined then from 27°C to 40°C, but above 46°C the diffraction becomes quite diffuse and weak as the isotropic phase transition is approached.

The high angle peak remains relatively constant in shape and position over the M and N phases although superposed on a very broad "hump" as previously noted. Its net intensity in the N-phase decreases rather slowly, and then more rapidly at temperatures over 30°C, until it disappears at the transition to the isotropic phase.

IV DISCUSSION

In the present section we discuss the structural characteristics of the various DSCG lysomesophases that emerge from both previous and present X-ray and NMR measurements. The overall sets of results may be understood in terms of rod-like symmetric micelles as the basic structural units in all three mesophases with the following features:

1. The molecular stacking distances within the micelles in all phases is about 3.4 Å.

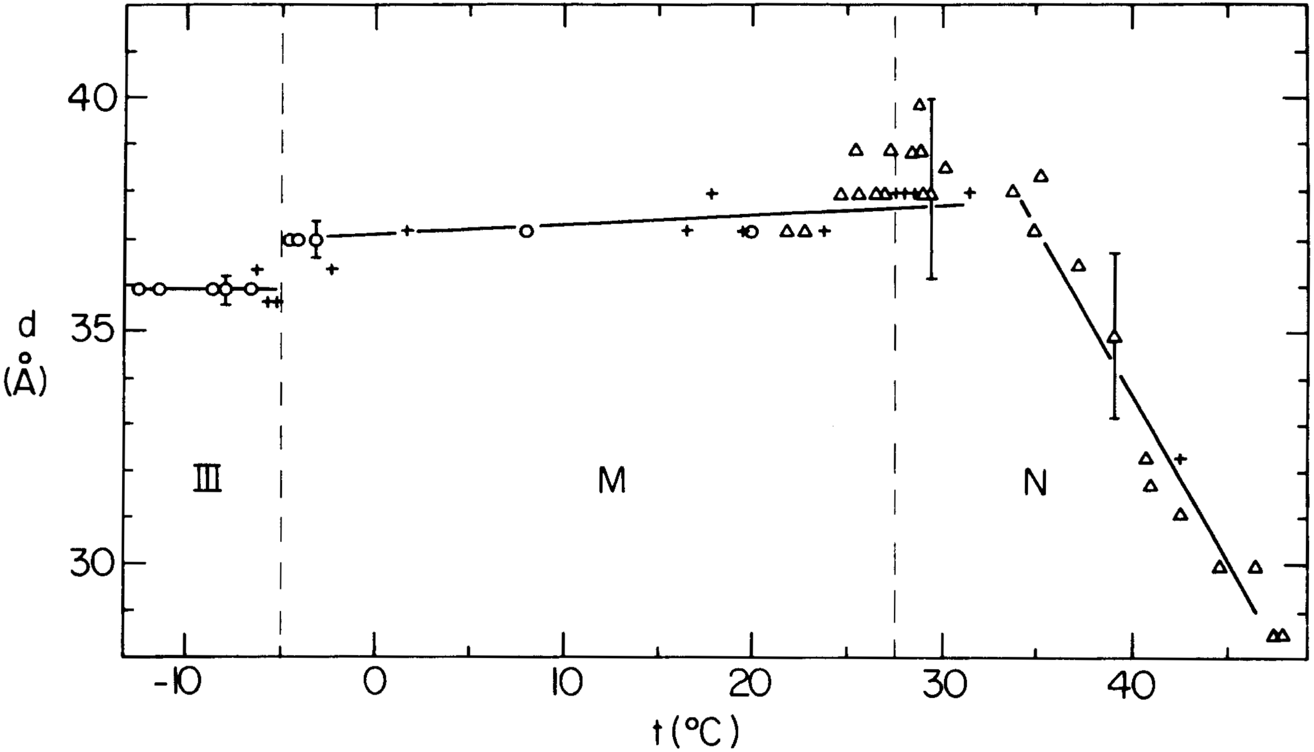


FIGURE 8 Temperature dependence of the d-spacing for the low angle diffraction peak in a 20 wt% sample of disodium cromoglycate. The symbols represent different sets of experimental runs as described in the text. The error bars represent the uncertainties of single measurements in the different regions.

2. The average distance between micelles increases linearly with the inverse square root of the DSCG concentration, is relatively independent of temperature in phases M and III and decreases with increasing temperature in phase N.

3. The N phase is apparently nematic while the M phase consists of a hexagonal columnar array. It is likely that phase III also consists of a columnar array but its symmetry is not yet established although it is known to be uniaxial.

4. The orientational order of the micelles in all mesophases is quite high depending only slightly on the temperature and the DSCG concentration.

5. Within the micelles, at least for the N and M phases, the chromone moieties lie on the average with their planes perpendicular to the micellar axes.

Perhaps the most remarkable property of the DSCG mesophases is that they may exist down to very low concentrations (4 wt%, and in the presence of salts even at lower concentrations[7]) and retain over the whole concentration range extremely high order. A quantitative estimate of the ordering can be obtained from the splittings of the chromone ring deuterons using the general theory of NMR in liquid crystals.[17]

Thus, assuming the DSCG molecules to be rigid, the average quadrupolar splitting for a particular deuteron is given by:

$$\nu^i_Q = \frac{3}{2}\left(\frac{e^2qQ}{h}\right)^i D^2_{00}(\theta_o) \sum_m \langle D^2_{mo}(\phi\theta\psi)\rangle D^2_{om}(\alpha_i\beta_i\gamma_i) \qquad (1)$$

where α_i, β_i, γ_i are Euler angles of the deuteron quadrupole tensor (assumed to be uniaxial along the CD bond direction) with respect to the molecular frame; ϕ,θ,ψ are the corresponding angles of the molecule in the frame of the liquid crystal, which is known to be uniaxial; and θ_o is the angle between the director and the magnetic field. The $D^2_{kl}(\Omega)$ are elements of the Wigner rotation matrices and the angular brackets indicate averaging over all the molecular motions. Equation 1 contains five effective motional constants $\langle D^2_{m0}(\phi\theta\psi)\rangle$ and we therefore expect that in general each of the chromone system deuterons will have a different quadrupole splitting contrary to the experimental finding which show them to be equivalent over the whole N and M mesophase region. Assuming that this equivalence is not accidental, it must indicate that the DSCG molecules aggregate into micellar clusters having overall uniaxial symmetry, with the chromone rings perpendicular to the micellar axis so that only one motional constant, i.e. $S_0 = D^2_{00}(\phi\theta\psi)$ survives the averaging process. This eliminates the γ^i dependence in Eq. 1 which now becomes

$$\nu^i_Q = \frac{3}{2}\left(\frac{e^2qQ}{h}\right)^i D^2_{00}(\theta_o)S_0D^2_{00}(\beta_i) \tag{2}$$

where β_i is the average polar angle of the CD bond with respect to the micellar symmetry axis rather than relative to a molecular axis. Since the chromone moiety is nearly planar we take for all the corresponding deuterons $\beta_i = \pi/2$, and setting $\theta_0 = \pi/2$ gives:

$$\nu^i_Q = \frac{3}{8}\left(\frac{e^2qQ}{h}\right)^i S_0 \; (i = \text{chromone deuterons}) \tag{3}$$

Now using $(e^2qQ/h)^i = 183$ kHz, the experimental results of Figure 4 yield S_0 values ranging from 0.76 in the 4 wt% solution to 0.97 in the 29 wt% solution. Although the uncertainty in these figures may be as high as 10 to 15% due to the wide spectral linewidth and the uncertainty in the quadrupole coupling constant, the results for S_0 are unusually high. This is particularly surprising since S_0 is actually a product of the micellar ordering parameter and the effective orientational parameter of the DSCG molecules within the micelles. Thus the results for S_0 are in fact only lower limits for the micellar ordering constant.

The values derived for S_0 are of the order predicted by the Onsager theory (0.85) for nematics of hard rod solutions.[19] This theory considers the onset of nematic order in such solutions to be due exclusively to steric repulsion between them, a model that may well be suitable for the DSCG mesophases. According to this theory the onset of nematic order in solutions of hard rods occurs when

$$\phi = \phi^c = 4.5\ \mathrm{D/L} \tag{4}$$

where ϕ is the volume fraction of the rods

$$\phi = 0.25\ \mathrm{C}\pi\mathrm{LD}^2 \tag{5}$$

ϕ^c is the critical value of ϕ at the isotropic-nematic transition, C is the number of rods per unit volume, and L and D are respectively their length and diameter. Comparison with the phase diagram in Figure 1 shows that at 5°C $\phi^c \simeq 0.06$ while at 30°C $\phi^c \simeq 0.15$. From

Eq. 4 it follows that the corresponding values of L/D at the phase transition concentration are 75 and 30 respectively. These results may be understood in terms of a model in which in the isotropic micellar solution there is a temperature dependent dynamic equilibrium between free DSCG molecules or small clusters of them, and larger micellar rods: At low temperatures this equilibrium will favour long rods and therefore according to Eq. 4 the nematic phase will set-in at relatively low concentrations of DSCG, while at higher temperatures the rods are shorter and therefore higher concentrations are required to stabilize the nematic phase. Assuming a diameter of 26 Å for the rods as determined by X-ray in the M phase,[2] a total rod length of ~2000 Å and ~800 Å at the transition concentration is estimated for 5°C and 30°C respectively. The same model may also be invoked to explain the effect of salts in stabilizing the DSCG mesophase.[7,20,21] Here it is the extra salt bridges which stabilize and lengthen the micellar rods.

Our results are consistent, although they do not provide a proof, with Lydon's model[4] in which the DSCG aggregates are assumed to consist of coplanar tetramers stacked on top of each other to form square hollow columnar micelles. Other structures which are consistent with the above results may also be imagined, e.g. planar trimers, or even aggregates in which the chromone moieties are parallel to each other but not necessarily coplanar. It should be noted that an X-ray single crystal study of DSCG showed that in the solid phase the chromone rings are not coplanar but are rather inclined to each other at about 53°.[22]

It is interesting to compare these conclusions with the X-ray results for the N and M phases in the 20 wt% solution. Here it was found that the d-spacing characterizing the mean distance between the micelles which in the M phase was well defined and almost independent of temperature became poorly defined at the transition to the M phase and subsequently decreased drastically with increasing temperature. It is however necessary to observe some caution in interpreting the X-ray data. There is some question as to whether the Bragg formula ($2d\sin\theta = \lambda$) is appropriate for determining the average distance between micelles in the N phase.[2,23] An alternative formula ($2d\sin\theta = 1.117\lambda$) is possibly more applicable for diffraction by rod-like entities.[23] Conceivably a weighted combination of both formulae may be necessary to explain the decrease with temperature of the effective d value in Figure 8. However, at present we have no independent justification for applying such a procedure. On the other hand at constant temperature it was found that the d-spacing increases linearly with the inverse square root of the DSCG concentration reflecting the dilution of the micelles in the two dimensional liquid crystalline array. It is remarkable that this dilution has only a minor effect on the orientational order of the micelles.

We can say much less about the structure and orientational properties of phase III. The X-ray pattern of this phase consists of low and high angle diffraction peaks similar to those seen in the N and M phases but no additional peaks were observed which would indicate higher degree of positioning ordering. The only change detected is a slight shift to lower d-values of the 37 Å peak and some broadening or perhaps a splitting of the 3.4 Å peak. The NMR results in this phase are also not very useful since the chromone deuterons could not be seen. The only signal observed in this phase is that due to the methine deuteron of the glyceryl chain. Its quadrupole splitting in phase III is significantly larger than in the corresponding M or N phases and in fact almost the maximum possible splitting of a deuteron in a C-D bond at an orientation θ_o perpendicular to the magnetic field. This must indicate that the micellar order parameter in this phase is close to unity and that the motion of the DSCG molecules has frozen-out during the phase transition into a conformation in which the C-D bond of the methine deuteron is nearly parallel to the micellar symmetry axis.

In the M phase the methine splitting is about half that in phase III even in the more concentrated solutions where the order parameter is close to unity. Thus using Eq. 2 with $e^2qQ/h = 168$ kHz yields $D^2_{00}(\beta) \simeq 0.45$. This value is consistent with an all-trans configuration of the glyceryl chain with β equal approximately 90°. Alternatively, this may result from a jump model in which the C-D bond switches between sites for which $D^2_{00}(\beta) = 1$ and 0 respectively.

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