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Orientational Order in the Lyomesophases of the Disodiumchromoglycate-Water System by ^{2}D, ^{17}O and ^{23}Na NMR

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Deuterium, oxygen-17 and sodium-23 NMR measurements in the mesophase region of the disodiumchromoglycate (DSCG)-Water system are reported. The results indicate that, depending on the temperature and concentration of the DSCG, at least three different mesophases can exist in the system: At temperature below −4°C a relatively highly ordered smectic-like phase exist (phase III) which was not reported previously. Above −4°C two phases, labeled *N* and *M* appear. The dividing line between these two phases is at approximately 18 wt.% DSCG and depends slightly on temperature. Phase *N* which prevails on the low concentration side of the dividing line, appears to be nematic-like as manifested by the fact that it reorients in a magnetic field, while phase *M* which appears on the high concentration side of the dividing line seems to be smectic-like. There is no discontinuity in the ordering characteristics of the water solvent in the *N-M* transition region, suggesting that these two phases have similar ordered structures. These are believed to be columns of stacked highly hydrated DSCG molecules. In the *M*-phase these columns are arranged in ordered arrays, whereas in the *N*-phase they are relatively free to move within the bulk water while retaining their orientational order. The phase transition from the *N, M* phases to phase III is accompanied by a marked change in the water ordering indicating that the smectic structures in the latter phase are quite distinct from those in the *N, M* phases. Sample rotation experiments in a magnetic field show that all three phases are uniaxial and of type II (i.e. $\Delta\chi < 0$) indicating that in all the lyotropic structures the DSCG molecules prefer an orientation in which the aromatic planes lie perpendicular to the director.

INTRODUCTION

4H-1-benzopyran-2-carboxylic acid-5,5′-[(2-hydroxy-1,3-propanediyl) bis (oxy)]-bis [4-oxo] disodium salt (Registry No. 15826-37-6) (Na_2C_{23}-

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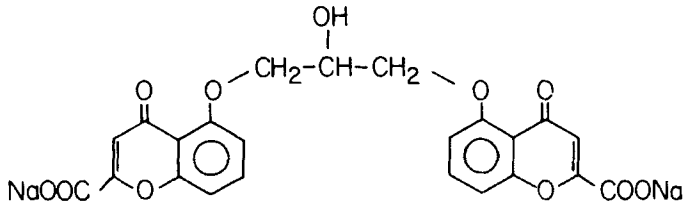
$H_{14}O_{11}$), commonly known as disodiumchromoglycate (DSCG) is distributed by Fisons Ltd. as an anti-asthmatic drug under the trade name INTAL.[1]



It is an odorless white powder with a remarkable ability for water absorption. The anhydrous crystalline solid can absorb at room temperature up to 6 water molecules per molecule of DSCG without collapse of the lattice.[2,3] At very high humidities or in aqueous solutions, the salt forms lyotropic liquid crystalline mesophases.[2,4] Based on X-ray crystallography and optical microscopy, two distinct mesophases have been identified according to the [Water]/[DSCG] ratio and the temperature. At around 20°C when the water-DSCG ratio is between ~40 and ~120 a smectic type liquid crystal, labeled *M*-phase, and resembling the soap middle phase, is formed. It consists of rods of stacked molecules which are arranged in an hexagonal array. In DSCG solutions of higher water content ([Water]/[DSCG] > 120) another phase, the *N*-phase, is formed in which the stacked rods while retaining orientational order are free to move within the bulk water. This is apparently a nematic type liquid crystal. The detailed structure of the mesophases and in particular of the stacked rods is not yet understood and is still being debated.[5,6] The most recent suggestion is that of Lydon[5] who proposed that the rods in the DSCG mesophases consist of square hollow columns in which the stacking units are made up of four DSCG molecules arranged in planes with four fold symmetry.

The ordering characteristics of mesophases can also be studied through the NMR spectra of their constituents or of dissolved probe molecules. Particularly useful information can be derived from the quadrupole splittings in the spectra of nuclei with spin $I \geqslant 1$. In the system under consideration a natural approach would be to use the NMR of ^2D in deuterated DSCG; ^2D and ^{17}O in enriched water; and ^{23}Na of the sodium cations. In the present work we report ^2D and ^{17}O NMR measurements in DSCG-Water mixtures prepared from isotopically enriched water, as well as preliminary results on ^{23}Na. The measurements were done over a wide range of concentration and temperature and provide quantitative information on the water ordering in

these systems. In addition the results indicate the existense of a new mesophase which is stable only below −4°C. The transition from both the *N* and the *M* phases to the new low temperature phase is relatively slow and it is accompanied by a discontinuity in the ordering parameters of both the water molecules and the sodium ions.

While this paper was written up a preprint of a work by Yu and Saupe[7] on the deuterium NMR in DSCG=D_2O solutions was brought to our attention. The results of the deuterium spectra in both works are in full agreement, however the measurements of Yu and Saupe were done only above zero centrigrade and thus do not provide information on the low temperature phase. On the other hand they contain data on the effect of added salt (NaCl).

EXPERIMENTAL

Materials and sample preparation

DSCG was kindly provided by Fisons Ltd. as a crystalline solid hydrate. For the computation of the solution concentrations it was assumed to be the hexahydrate, i.e. DSCG.$6H_2O$. Two kinds of heavy water were used as solvent: D_2O (Merck) containing 99.7 at.% ^2D and $D_2{}^{17}O$ (obtained from the Weizmann Institute enrichment plant) which contained 99.6 at.% ^2D and 5.0 at.% ^{17}O. For DSCG in normal H_2O doubly distilled water was used.

Samples for the ^2D and ^{17}O measurements were prepared as follows: Weighed amounts of DSCG and solvent water were placed in 5 mm NMR tubes. The samples were then sealed and kept for about 30 minutes at 40–50°C with occasional mixing until all the DSCG dissolved. For the ^{23}Na measurements solutions were prepared in 10 mm coaxial NMR tubes, containing CD_3OD as an external deuterium lock.

The composition of the solutions is given either as wt.% or as the molar ratio [DSCG]/[Water]. The wt.% is defined as (weight of DSCG.$6H_2O$) × 100/(weight of DSCG.$6H_2O$ + weight of water). The molar ratio was calculated by subtracting the six water molecules from the weight of the hydrated DSCG and adding them to the bulk solvent.

NMR Measurements

^{17}O NMR measurements were performed on a WH-270 Bruker spectrometer at 36.6 MHz using a home built probe. This probe was used together with the spectrometer's standard deuterium unit. The *rf* frequency was generated by mixing the fixed frequency from the deuterium unit with that of an external source (PTS-160 frequency synthe-

sizer) locked to the 10 MHz master clock of the spectrometer. The 36.6 MHz side band was amplified (using a 50 watt ENI, Model 350L, broad band amplifier) and fed into the *rf* coil of the probe. The oxygen-17 NMR signal was first preamplified using a low noise solid state (Aventek UTO511-2-L-7) amplifier and then mixed with the external frequency from the frequency synthesizer. The recovered signal at 41.45 MHz was fed into the IF stage of the deuterium unit and then processed in the usual way.

Deuterium measurments were performed both on the WH-270 and a WH-90 spectrometers at respectively 41.45 MHz and 13.81 MHz frequency. The latter spectrometer was used for the sample rotation experiments. Finally ^{23}Na NMR measurements were done on the WH-90 spectrometer at 23.6 MHz using a commercial variable frequency probe with deuterium lock. The temperature was controlled with a BST 100/700 unit and its absolute value was calibrated with a Fluke 2190 digital thermometer. The temperature accuracy is estimated at ±1°C.

All measurements were performed by first heating the sample to above the clearing point (40°–50°C), thoroughly shaking it to ensure complete homogeneity of the solution and then allowing it to cool within the magnetic field to the desired temperature. In the more concentrated samples, just below the clearing point where the mesophase and isotropic liquid coexist, phase separation was sometimes observed. This manifested itself in the splitting of the doublet components of the mesophase spectrum, indicating phase separation within the mesophase region. When this occurred the sample was taken out from the NMR probe, thoroughly mixed and the measurements continued.

RESULTS AND DISCUSSION

The NMR spectra of nuclei with quadrupole moments in an ordered mesophase exhibit splittings due to the time average of their quadrupole interaction.[8] In the absence of other interactions the spectrum due to a nucleus of spin I will exhibit a multiplet of $2I$ equally spaced peaks, corresponding to the various $M \rightarrow M - 1$ transitions, with relative intensities proportional to $[I(I + 1) - M(M - 1)]$. For a uniaxial liquid crystal the spacing between neighboring peaks is given (to first order in the quadrupole interaction) by:

$$\nu_Q = \frac{3e^2qQ}{2I(2I-1)h}\left(\frac{3}{2}\cos^2\theta_0 - \frac{1}{2}\right)\times$$

$$\left[S_{zz}\left(\left\langle\frac{3}{2}\cos^2\beta-\frac{1}{2}\right\rangle+\frac{1}{2}\eta\langle\sin^2\beta\cos 2\alpha\rangle\right)\right.$$

$$\left.+\frac{1}{2}(S_{xx}-S_{yy})\left(\langle\sin^2\beta\cos 2\alpha\rangle+\frac{1}{3}\eta\langle(1+\cos^2\beta)\cos 2\alpha\cos 2\gamma-2\cos\beta\sin 2\alpha\sin 2\gamma\rangle\right)\right]$$

where θ_0 is the angle between the magnetic field and the director, and α, β, γ, are Euler angles relating the principal axes of the quadrupole tensor with those of the molecular frame. The S_{ii}'s are elements of the ordering matrix and in the above equation they correspond to a molecular frame in which this matrix is diagonal.

The three nuclei studied in the present work, ^{2}D, ^{17}O and ^{23}Na possess nuclear spins of 1, 5/2 and 3/2 and accordingly in an ordered mesophase they are expected to exhibit 2, 5 and 3 peaks respectively. In Figures 1–3 are depicted examples of spectra from these nuclei in the

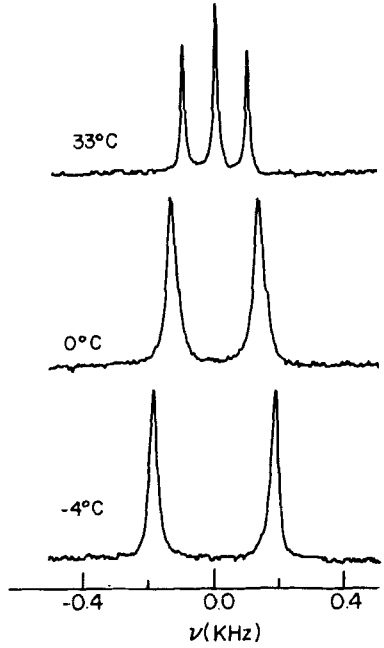


FIGURE 1 Deuterium NMR spectra in the mesophase region of a 14.8 wt.% solution of DSCG in D_2O at the temperatures indicated. The three spectra correspond to phase III (−4°C), phase N (0°C), and the biphasic region $N + I$ (33°C).

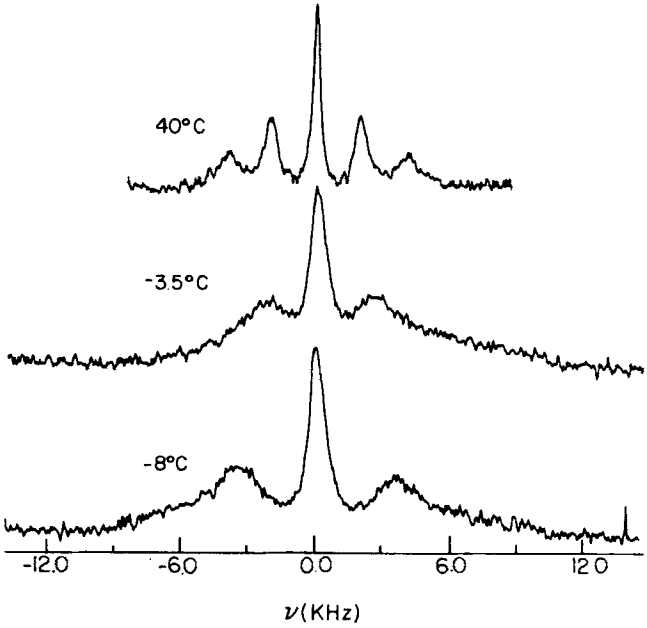


FIGURE 2 Oxygen-17 NMR spectra in the mosophase region of a 23.2 wt.% solution of DSCG in D_2O enriched to 5 at.% in ^{17}O. The three spectra correspond to phase III (−8°C) and phase *M* (−3.5°C and 40°C).

various DSCG mesophases, in order to show the quality and type of resolution obtainable in this system. The most extensive measurements were made on deuterium in D_2O solutions. We therefore start by discussing in detail the deuterium results and then turn to the ^{17}O and ^{23}Na measurements.

The ^2D NMR results and the phase diagram in the mesophase region

The water ^2D NMR spectra were measured in DSCG-Water solutions with DSCG concentrations ranging from 5 to 24 wt.% corresponding to $[D_2O]/[DSCG]$ ratios between 610 and 105. The temperature dependence of the deuterium quadrupole splitting is plotted in Figure 4 for a selection of the solutions studied. The results are completely reversible with respect to increasing and decreasing of the temperature and they are also not sensitive to the extent of deuteration of the solvent water: Note that several runs in Figure 4 (indicated by the square symbols) correspond to a 1:50 mixture of D_2O:H_2O. In general the splitting at each temperature increases with increasing DSCG concen-

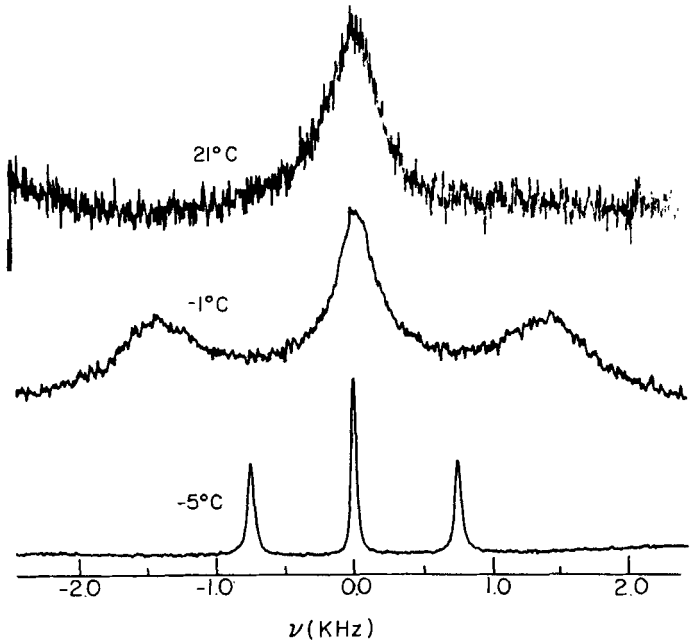


FIGURE 3 Sodium-23 NMR spectra in the mesophase region of a 10.0 wt.% solution of DSCG in H_2O. The three spectra correspond to phase III (−5°C) and phase N (−1°C and 21°C).

tration. For each solution however four regions can be identified along the temperature coordinate:

(i) At low temperatures ($<\sim -4$°C) there is a mesophase with a relatively large quadrupole splitting and narrow lines. On heating to above −4°C (depending slightly on the concentration) this phase transforms into another DSCG mesophase. The transition is accompanied by a sharp, but slow, drop in the deuterium quadrupole splitting and is observed on both heating and cooling of the solution. The kinetics of the phase transition can be followed through the continuous decrease or increase of the deuterium splitting while keeping the temperature at slightly above or below the transition point. The transformation may last between 5 and 60 minutes depending on the DSCG concentration and the presence of other solute molecules (vide infra). This low temperature mesophase, which we call phase III, was not observed previously, apparently because of the slowness of the transformation, but it has now also been confirmed by differential scanning calorimetry.[9] This phase transition can be observed in a more conspicuous way

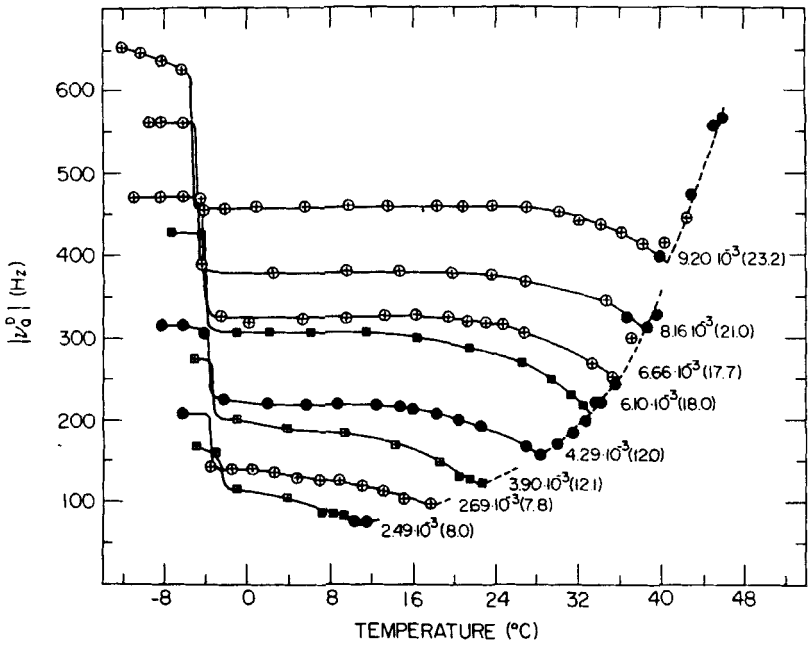


FIGURE 4 Temperature and concentration dependence of the water deuterium quadrupole splitting in the mesophase region of the DSCG-Water system. The molar ratio [DSCG]/[Water] and (*in brackets*) the corresponding wt.% of DSCG.6H_2O are indicated for each series of measurements. The spectra corresponding to data points to the right of the inverted cusp exhibit in addition to the quadrupole doublet also a singlet due to the isotropic phase (see Figure 1). The filled symbols represent experiments recorded on cooling the sample, while the empty symbols represent experiments in which the temperature was increased. The circles correspond to D_2O solutions while the squares correspond to samples in which the solvent consisted of a 1:50 ratio D_2O:H_2O.

using guest solute molecules as probes. As an example we show in Figure 5 the deuterium NMR spectra of a 2.0 wt.% solution of perdeuterated pyridine in a 14.1 wt.% DSCG=H_2O solution. This solution undergoes the phase transition at about −2°C and the presence of the guest apparently speads up the phase transformation. The spectrum of pyridine-d_5 in phase III is shown in the lower trace of the figure. The three doublets due to the three inequivalent deuterons are clearly observed. When the temperature of the solution is raised to −1.6°C and FID signals are repetitively accumulated for a period of two minutes the spectrum shown in the middle trace of the figure is obtained. It consists of a superposition of spectra taken at short time intervals during which the splittings continuously decrease. After five minutes the phase transition is complete, resulting in a sharp spectrum due to pyridine-d_5 in the high temperature mesophase (upper trace in Figure 5).

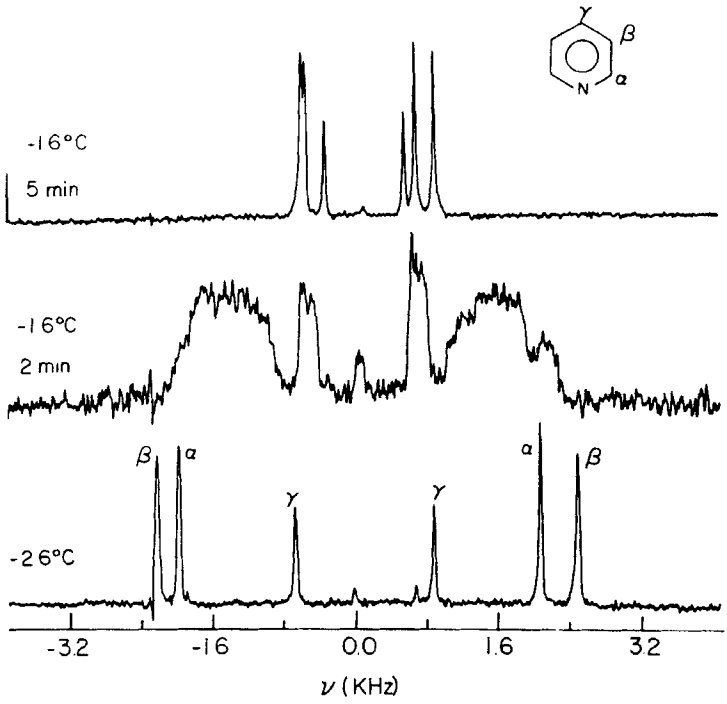


FIGURE 5 The deuterium NMR spectra of a pyridine-d_5 (2.0 wt.%) in a 14.1 wt.% solution of DSCG in H_2O in the phase III to phase *N* transition region. The bottom spectrum at −2.6°C corresponds to phase III. The middle trace is a superposition of about 250 accumulations recorded for 2 minutes after raising the sample's temperature to −1.6°C. The top spectrum was recorded five minutes later and corresponds to the pyridine-d_5 spectrum in the *N*-phase.

The fact that a single spectrum is observed during the phase transformation which continuously changes from one steady state to another is perhaps related to the domain sizes in the transition region. If these domains are sufficiently small, the self-diffusion of water or probe molecules will effectively average out the splittings in the two phases and a weighted average splitting will be observed. Hence, as the phase transformation proceeds the average splitting will continuously change from its value in one phase to that in the second phase. If, on the other hand, the domains are large we would expect to observe a superposition of two spectra whose relative intensities change continuously from 1:0 in favor of the spectrum of one phase to 0:1 in favor of the other. Clearly the phase transition between the low temperature phase III and the high temperature *N* and *M* phases fits the model of very small domains. However, the microdomains retain the original

director orientation and remerge into large domains as the phase transformation reaches completion. This follows from results of sample rotation experiments, to be described below. The spectra obtained in these experiments were characteristic of two dimensional powder domains. Once this distribution was formed in a magnetic field, it would not change on rotation of the field, a property usually associated with smectic phases. These experiments also indicated that Phase III is uniaxial and is a type II liquid crystal, i.e. it has a negative diamagnetic anisotropy.

(ii) The second region in Figure 4, corresponds to the range between about −4°C and the temperature at which the inverted cusps in the ν_Q^D vers. temperature curves occur. This region corresponds to the range previously ascribed to the *M* and/or *N* phases, and the cusps correspond to the phase transition points between these mesophases and the isotropic liquid. For all solutions the splittings at lower temperatures follow a plateau while at high temperatures they decline somewhat as the clearing point is approached. As for the low temperature phase (phase III), the splitting increases with DSCG concentration. Plots of the quadrupole splittings as a function of the [DSCG]/[Water] ratio for the two regions are shown in Figure 6. The experimental data in this figure were taken at temperatures just below (for phase III) or just above (for the *N*, *M* phases) the transition. A remarkable result which was also noticed by Yu and Saupe[7] is that the plot corresponding to the *N*-*M* region is continuous and does not indicate any discontinuity on going from the *N* to the *M* phase. According to the phase diagram of Cox, Woodard and McCrone[2] and Hartshorne and Woodard[4] this transition occurs at [DSCG]/[Water] $\cong 6 \times 10^{-3}$ i.e. at approximately the middle of the measured region in Figure 6.

Since the *N* and *M* phases are thought to be respectively nematic and smectic in nature, we sought a way to distinguish between them by studying the response of the system towards rotation in a magnetic field. It is generally observed that the director in nematic phases reorients upon rotation of the magnetic field, while in a smectic the director is locked in the sample and would not reorient.[10,11] These general comments should not be regarded as definite rules: very viscous nematics will practically not reorient or will reorient only over very long period of times, while smectics, in particular in the presence of impurities or in a multiphasic mixture, might reorient very fast.

The rotation experiments were done on samples prepared by allowing the DSCG solution to cool within the magnetic field from a temperature just below the mesophase-isotropic transition to the desired temperature. Two types of alignment may result in such a sample

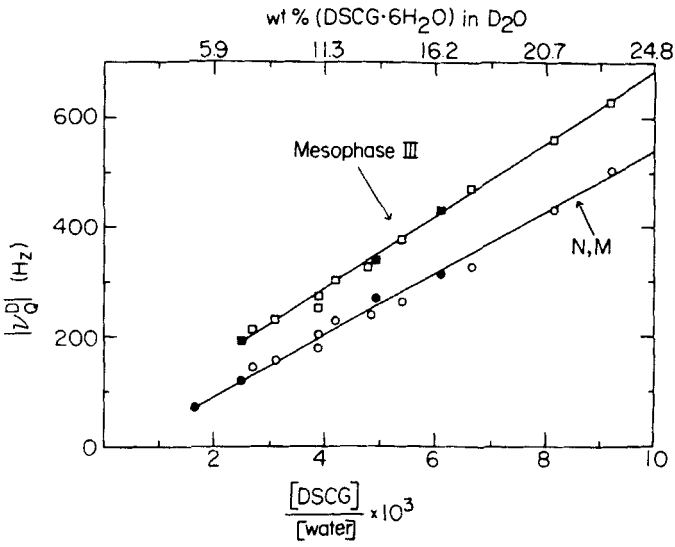


FIGURE 6 Plots of the water deuterium quadrupole splittings in the mesophase region as function of the [DSCG]/[Water] ratio. The upper and lower curves correspond respectively to phase III and the *N* or *M* phases. The experimental points were taken from the plateau regions just below (for the phase III) or just above (for the *N*, *M* phases) the III to *N*, *M* transition temperature. The empty symbols are for D_2O solvent while the filled-in symbols are for solutions containing 2% D_2O in H_2O.

according to whether the mesophase is of type I ($\Delta\chi > 0$) or of type II ($\Delta\chi < 0$). In the first case a single domain is formed in which the director is aligned parallel to the magnetic field, H, while in the second case the director aligns at right angle to the field and consequently the sample breaks up into many domains whose directors lie in the plane perpendicular to H. In both cases the deuterium spectrum will exhibit a doublet, however its spacing corresponds to $\theta_0 = 0$ in the first case and to $\pi/2$ in the second. If the sample is now rotated, say by 90° about an axis perpendicular to H and the spectrum is immediately recorded before the director had time to reorient, we would obtain for the first case a doublet of half the splitting, while in the second case a powder spectrum typical of a two dimensional distribution. The reorientation of the director can then be monitored by successive recording of the spectrum. This type of experiment can be used to (a) distinguish between type I and type II mesophases and (b) follow the reorientation rate of the director in the magnetic field and thus perhaps distinguish between nematic-like and smectic-like behavior.

We have performed sample rotation experiments on a number of DSCG solutions ranging from 8.9 to 21.0 wt.% DSCG and at different

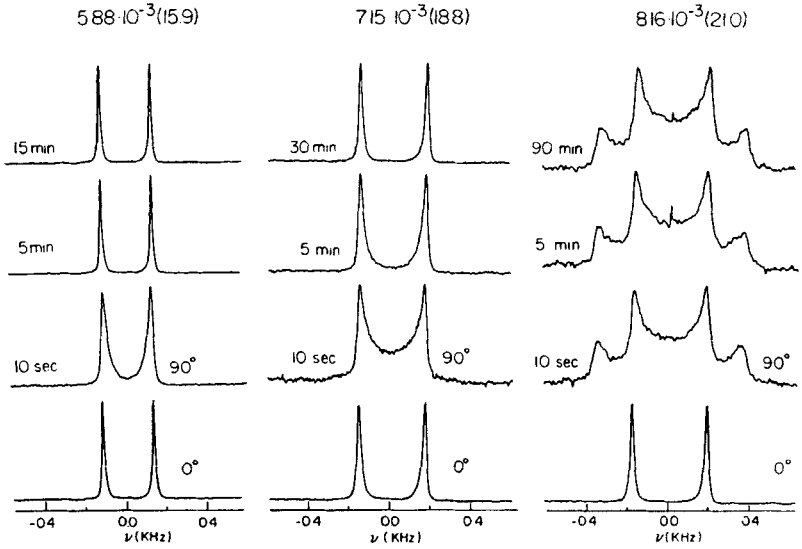


FIGURE 7 Rotation experiments using the deuterium spectra of the DSCG-D_2O system at 20°C. The mole ratio [DSCG]/[Water] and (in brackets) the corresponding concentration in wt.% DSCG.$6H_2O$ are indicated at the top of each series of spectra. In each series the bottom spectrum was obtained after cooling the DSCG solution from the isotropic to the mesophase region at 20°C. The sample was then rotated by 90° about an axis perpendicular to the magnetic field, and the spectrum immediately recorded again. This spectrum is labeled "10 sec." Spectra were then taken after 5 minutes and longer intervals as indicated. From the experiments the dividing line between the *N* and *M* phases at 20°C is set in the range 18.8 to 21.0 wt.% DSCG.

temperatures. As an example, we show in Figure 7 rotation experiments spectra for three solutions (containing 15.9, 18.8 and 21.0 wt.% DSCG) at 20°C. The bottom spectrum for each series corresponds to the original orientation of the samples; all the other spectra were recorded after rotating the sample by 90° with respect to the external field at the times indicated in the figure. It may be seen that for the 15.9 and 18.8 wt.% samples, reorientation is essentially complete after 10 seconds, while for the 21.0 wt.% sample there is no reorientation even after 90 minutes. Thus there is a clear discontinuity in the rate of reorientation in the range between 18.8 and 21.0 wt.% DSCG. We ascribe this discontinuity to the $N \rightarrow M$ transformation[4] and tentatively identify the *N* and *M* phases as respectively nematic and smectic-like.

The spectra of the 21.0 wt.% sample at 90° indicate that the *M* phase is uniaxial and of type II and we believe from the general similarities of the two phases that the *N* phase is likewise of type II.[12] We have performed several experiments of the type described above at different

temperatures from which the dividing line between the N and M phases could be estimated. It should, however, be pointed out that at $-2°C$ slow reorientation of the director was observed in all samples even at 21.0 wt.% DSCG. Apparently this temperature corresponds to a biphasic region or pretransition effects show up which make it possible for the director to reorient.

(iii) We next discuss the third region in Figure 4, ranging from the inverted cusp points to the temperature at which no signals due to the mesophase can be observed. This is a bi (or tri) phasic region, $N + I$, $M + I$, (or $N + M + I$) in which the mesophase transforms to the isotropic phase, I. The spectrum in this region consists of a superposition of a doublet due to the mesophase and a singlet due to the isotropic liquid (see Figure 1). As the temperature is raised the intensity of the latter increases at the expense of the doublet intensity. Within this region, the splitting increases with increasing temperature due to the increase in DSCG concentration in the mesophase as more water shifts into the isotropic phase.[7] The quadrupole splittings for all the solutions in this region lie on a common smooth line, since according to the phase rule the composition of the mesophase depends on only one parameter i.e. the temperature. The high temperature end of the biphasic region is not well defined because the actual temperatures at which the doublets "disappear" is determined somewhat arbitrarily.

Beyond this biphasic region the solution is isotropic (region iv) and only a single resonance line ($\nu_Q^D = 0$) is observed.

Based on the NMR characteristics described above, we set up a phase diagram of the various mesophases of the DSCG-Water system (Figure 8). In general, it is consistent with the diagram of Cox, Woodard and McCrone[2] and Hartshorne and Woodard[4] which was derived from optical microscopy and X-ray studies. The main differences are that in the latter work, phase III was apparently not observed, while by the NMR method the $N \rightarrow M$ transition is not well defined and it was not possible to determine a biphasic range including both these phases.

Oxygen-17 spectra and the orientational order parameters for solvent water

Examples of ^{17}O NMR spectra in the mesophase region are shown in Figure 2. In phase III and at low temperatures in the N and M mesophases the lines are very broad and only three out of the expected five lines are resolved. At higher temperatures the lines sharpen and all five may be discerned. In Figure 9 are plotted the ^{17}O quadrupole splittings

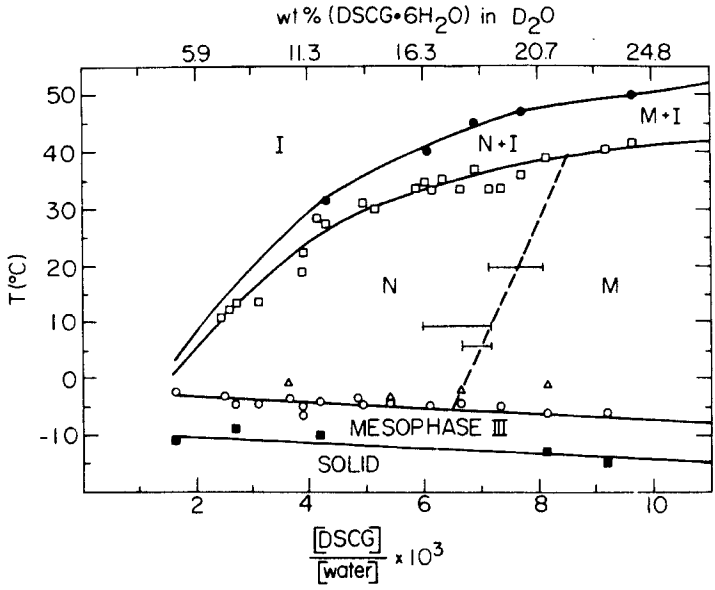


FIGURE 8 Phase diagram of the DSCG-Water system in the mesophase region based on the deuterium NMR results of the present work. The filled squares correspond to the temperature at which solidification of phase III occurs; the empty triangles and circles correspond respectively to the transformation from phase III to the *N* and/or *M* phases or vise versa; the empty squares are the *N*, *M* to *I* transition and correspond to the inverted cusps in the curves of Figure 4; the filled circles indicate the temperature at which the last trace of the doublet signals due to phases *N* or *M* have disappeared; the horizontal sticks along the dotted line represent the $N \rightarrow M$ transition as estimated from sample rotation experiments of the type shown in Figure 7.

for the three solutions studied in the present work. The general behavior is very similar to that of the deuterium spectra. In particular note the region corresponding to phase III and its transformation to phases *N* and *M*. Also, there is no discontinuity in the quadrupole splitting in the region where the $N \rightarrow M$ transformation occurs and the general behavior in the $N + I$, $M + I$ biphasic region is similar to the deuterium case.

Using the equation given in the beginning of this section and the ^{17}O and ^{2}D quadrupole splittings we can determine the orientational order of the D_2O molecules in the mesophase. For that purpose we use the coordinate system and the DOD geometry of Figure 10 together with the following quadrupole parameters[13] for the oxygen-17 and deuterium:

$$^{17}O: e^2qQ/h = 6.66 \text{ MHz}, \qquad \eta = 0.935$$
$$^{2}D: e^2qQ/h = 213 \text{ KHz}, \qquad \eta = 0.1$$

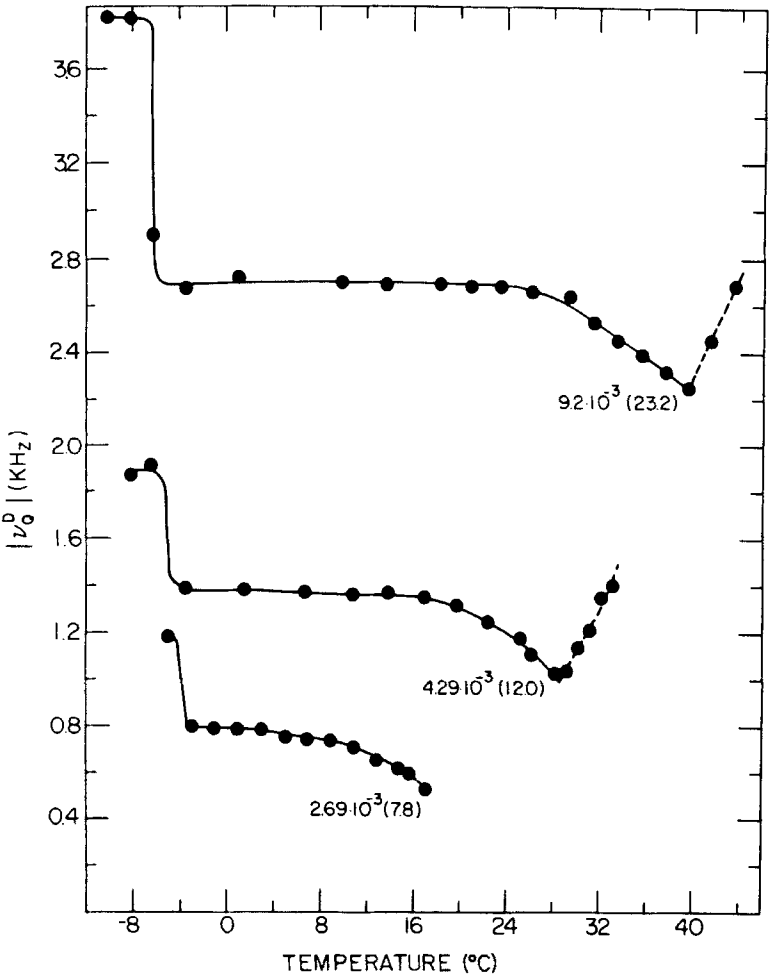


FIGURE 9 Temperature and concentration dependence of the water ^{17}O quadrupole splitting in the mesophase region of aqueous DSCG solutions. The ^{17}O abundancy was 5 at.%, and the DSCG-Water molar ratio and (in brackets) the concentration in wt.% are indicated in the figure. In the bi-phasic region, to the right of the inverted cusp the spectrum consists of a superposition of a broadened pentuplet and a sharp singlet. All spectra were recorded on cooling the sample from the isotropic phase.

Since the absolute sings of ν_Q^0 and ν_Q^D are not known, four distinct sets of solutions are possible for the ordering matrix elements S_{zz}, $S_{xx} - S_{yy}$ corresponding to whether ν_Q^D, $\nu_Q^0 > 0$; $\nu_Q^D > 0$, $\nu_Q^0 < 0$; ν_Q^D, $\nu_Q^0 < 0$ or $\nu_Q^D < 0$, $\nu_Q^0 > 0$. Examples of calculated S_{zz} and $S_{xx} - S_{yy}$ values are shown in Figure 11. These results correspond to a solution containing 23.2 wt.% DSCG. Only results for two sets of signs, viz. ν_Q^D, $\nu_Q^0 > 0$ and

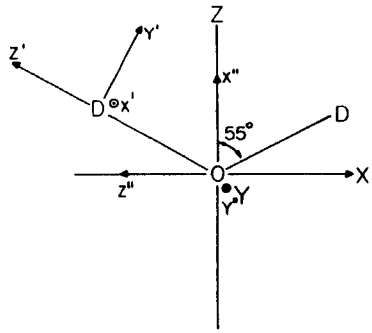


FIGURE 10 The coordinate system used to calculate the elements of the ordering matrix of the D_2O molecules. The unprimed system represents the molecular coordinate system and is used to label the S's. The singly and doubly primed systems refer to the principal direction of the quadrupole tensors of the deuterium and oxygen nuclei respectively, and were chosen to satisfy the condition $|V_{z'z'}| > |V_{y'y'}| > |V_{x'x'}|$, for the components V_{ii} of the electric field gradient tensors.

$\nu_Q^D < 0$, $\nu_Q^0 > 0$ are shown. Those for which ν_Q^D, $\nu_Q^0 < 0$ and $\nu_Q^D > 0$, $\nu_Q^0 < 0$ can be obtained by inverting the signs of the S_{zz} and $S_{xx} - S_{yy}$ in the figures. A selection of S_{ii}'s for several solutions and temperatures is given in Table I.

The observed values of the ν_Q's and thus also of the S_{ii}'s can be viewed as weighted averages between the values corresponding to the oriented water molecules bound in the ordered units (columns) of the DSCG mesophase and those for unoriented molecules in the bulk water:

$$S_{ii} = \frac{[\text{DSCG}]}{[\text{Water}]} n \int_{ii}$$

where $\int_{ii}$ and S_{ii} are respectively the orientational order parameters of the bound water and the average value actually measured, and n is the number of water molecules associated with a single DSCG molecule in the ordered units. It may be seen in Figure 11 and in Table I, that the results for the S_{ii}'s are about an order of magnitude larger for the choice $\nu_Q^D/\nu_Q^0 > 0$ compared to the choice $\nu_Q^D/\nu_Q^0 < 0$. Order of magnitude considerations suggest that the first alternative is less likely than the second: Taking[3] e.g. $n = 10$, [Water]/[DSCG] = 200 and $S_{ii} = 0.03$ gives $\int_{ii} = 0.6$. This is an unreasonably high value, and it therefore seems that the results obtained with opposite signs for ν_Q^D and ν_Q^0 are more realistic. Even for the latter case the estimated value of $\int_{ii}$ ($\sim$0.06) seems quite high considering the fact that this estimate is based on an as-

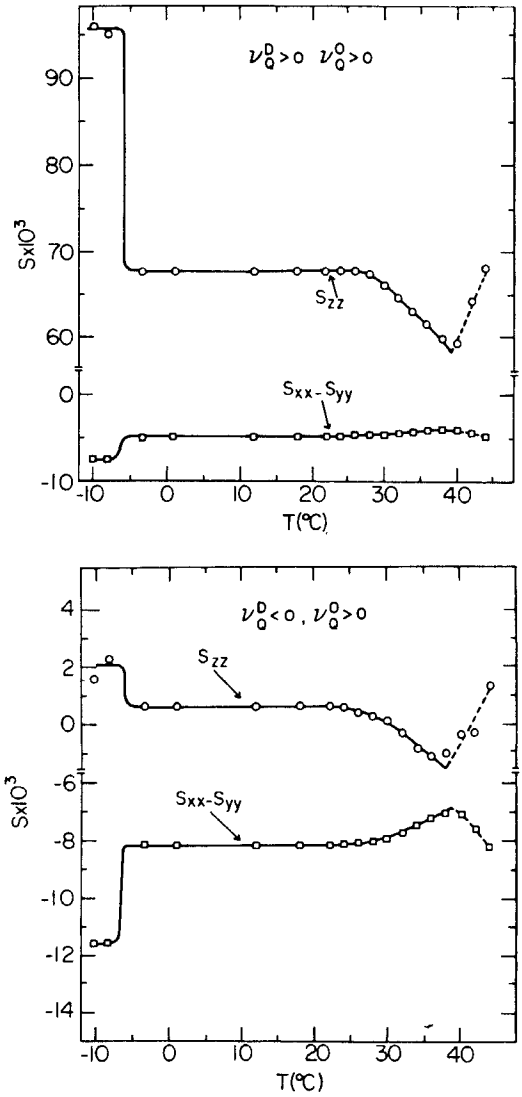


FIGURE 11 Calculated values for the ordering matrix elements S_{zz} and $S_{xx} - S_{yy}$ of the D_2O molecules in the mesophase region for a 23.2 wt.% solution of DSCG in D_2O. The points are calculated from the ^2D and ^{17}O quadrupole splittings for the corresponding solution in Figures 4 and 9. The two sets of results correspond to the choice of signs for ν_Q as indicated in the figures. The results for the set of signs ν_Q^D, $\nu_Q^O < 0$ and $\nu_Q^D > 0$, $\nu_Q^O < 0$ are obtained by inverting the signs of the ordinates in the above figures.

TABLE I

Calculated values of the ordering matrix elements,[a] S_{zz} and $S_{xx} - S_{yy}$, of the water molecules in several DSCG solutions.

DSCG wt.%	T(°C)	Phase	$\nu_Q^D, \nu_Q^0 > 0$ S_{zz}	$\nu_Q^D, \nu_Q^0 > 0$ $S_{xx} - S_{yy}$	$\nu_Q^0 < 0, \nu_Q^0 > 0$ S_{zz}	$\nu_Q^0 < 0, \nu_Q^0 > 0$ $S_{xx} - S_{yy}$
7.8	16.0	*N*	0.015	−0.0102	-4.2×10^{-5}	-1.70×10^{-3}
7.8	−2.0	*N*	0.020	−0.0140	-1.62×10^{-4}	-2.42×10^{-3}
7.8	−5.0	III	0.030	−0.0208	-2.14×10^{-4}	-3.58×10^{-3}
12.0	16.0	*N*	0.033	−0.0025	1.77×10^{-3}	-4.06×10^{-3}
12.0	−3.5	*N*	0.033	−0.0025	1.53×10^{-3}	-4.11×10^{-3}
12.0	−6.1	III	0.047	−0.0035	1.25×10^{-3}	-5.77×10^{-3}
23.2	16.0	*M*	0.068	−0.0481	6.27×10^{-4}	-8.13×10^{-3}
23.2	−3.5	*M*	0.068	−0.0481	6.27×10^{-4}	-8.13×10^{-3}
23.2	−8.1	III	0.095	−0.0069	2.24×10^{-3}	-11.55×10^{-3}

[a] The results for the opposite choices of signs for ν_Q^D and ν_Q^0 are obtained by reversing the signs for S_{zz} and $S_{xx} - S_{yy}$.

sumed hydration number $n = 10$. In the systems studied by Niederberger and Tricot[14] which contained 30–50 wt.% water, the values of S_{ii} ranged between 0.005 to 0.01. This comparison suggests that in the DSCG-Water system the DSCG molecules must be very highly ordered, with orientation parameters perhaps as high as 0.5.

NMR of sodium-23

The sodium-23 NMR was studied in the mesophase region in a series of solutions containing from 6 to 25 wt.% DSCG in H_2O. Typical spectra for a 10 wt.% solution are shown in Figure 3. The general features of the ^{23}Na results are similar to those for ^{2}D and ^{17}O: there is a sharp discontinuity in the spectrum on going from phase III to the *N* or *M* phases, and there does not seem to be discontinuous behavior in the $N \rightarrow M$ transition region. However in the details, there are several features in which the ^{23}Na results differ from those of the ^{2}D and ^{17}O. Thus, in the phase III $\rightarrow$ *N*, *M* transition there is an increase in the sodium quadrupole splitting, rather than a decrease, and within the *N*, *M* phases the linewidth increases with increasing temperature whereas in the ^{2}D and ^{17}O cases the linewidths decrease as the clearing point is approached. These observations no doubt reflect the structural characteristics of the various DSCG-Water mesophases and indicate that the sodium ions are intimately involved in their construction. However as yet not sufficient data are available to allow a quantitative interpretation.

SUMMARY AND CONCLUSIONS

It is of interest to compare the behavior of the DSCG-Water mesophases with the Lawson-Flautt type lyotropic systems which have recently been extensively investigated by Reeves and coworkers.[11] Many of these systems can be represented in terms of the following two schemes:

Hexagonal array of cylindrical micelles. Type I.	⇌ Nematic lyomesophase of cylindrical micelles. Type I.	⇌ Isotropic dispersion or solution of cylindrical micelles or constituent molecules.
Lamellar array of disclike micelles. Type II.	⇌ Nematic lyomesophase of disclike micelles. Type II.	⇌ Isotropic dispersion or solution of disclike micelles or constituent molecules.

where left to right is the direction of increasing water content. Whether a lyotropic system belongs to the upper or lower scheme depends on: (i) the shape of the micelles (cylindrical or disclike) and on (ii) the structure and diamagnetic anisotropic susceptibility of the constituent molecules. Most of the systems studied by Reeves[11] were such that for cylindrical micelles $\Delta\chi$ was negative. However more recently by introducing aromatic amphiphiles into systems forming disclike micelles, a type I lyomesophase consisting of disclike micelles was obtained.[15] This system thus corresponds to the scheme:

Lamellar array of disclike micelles. Type I.	⇌ Nematic lyomesophase of disclike micelles. Type I.	⇌ Isotropic dispersion or solution of disclike micelles of constituent molecules.

The N, M mesophases of the DSCG-Water system may be thought of as yet a fourth scheme in which M corresponds to an Hexagonal phase consisting of cylindrical micelles with $\Delta\chi < 0$ (type II) and N the corresponding nematic lyomesophase:

Hexagonal array of cylindrical micelles. Type II.	⇌ Nematic lyomesophase of cylindrical micelles. Type II.	⇌ Isotropic solution

The existence of all four possible combinations of micellar structures and signs of $\Delta\chi$ was recently also demonstrated by Boden *et al.*[16] in substituted aliphatic lyomesogens. From these observations and the above discussion it is clear that both the shape and molecular ordering in the micelles as well as the diamagnetic characteristics of the constit-

uent molecules determine the sign of $\Delta\chi$ and not just the micellar shape.

As yet very little is known about the DSCG-Water system but certain qualitative comparisons with the Lawson-Floutt systems can already be made. Perhaps the most striking phenomenon is the ability of DSCG to form a nematic lyomesophase at room temperature with a water content of over 90 wt.%. The resulting mesophase is therefore of very low viscosity and its alignment in a magnetic field is extremely rapid. Also there does not appear to be any wall effect on the director alignment in samples of several milimeter thickness. The low viscosity and good alignment of the nematic DSCG mesophase render it a potential host solvent in the study of both polar and apolar probe molecules. Such applications are in progress.

In the *N* to *M* transition region there does not appear to be any discontinuity in the water ordering parameters. This is in contrast with the behavior in the systems studied by Reeves where the corresponding transition was apparently always accompanied in a discontinuous increase in the ordering of the water molecules. This suggests that in the DSCG-Water system the micellar structure (columns of stacked DSCG molecules) is already fully developed in the *N* phase and the *N* to *M* transition corresponds predominantly to the formation of the hexagonal arrays of the *M*-phase from the dispersed units in the *N* phase. Since the water alignment depends mainly on its ordering within the columnar micelles it will not be affected by the *N* to *M* transition.

The NMR results do not provide direct information on the ordering of the DSCG molecules. It is clear however from the fact that both the *N* and *M* phases are of type II, that in their structural units the DSCG molecules are stacked with their aromatic planes perpendicular to the micellar symmetry axis. Moreover it appears that the orientational order of the DSCG molecules within the micelles is very high. This conclusion is derived from the relativley high ordering parameters determined for the water even in the dilute solutions. It would be interesting to substantiate this conclusion, and perhaps learn more about the micellar structures by direct measurements on the DSCG molecules. A natural approach would be deuterium NMR of deuterated samples.

In contrast with the *N* to *M* transition, the transformation of both these phases to phase III upon cooling the system to below −4°C is associated with a considerable change in the water order parameters, indicating that this transition is connected with a significant change in the structure of the micellar units. This perhaps also explains the slow rate of the phase III to *N*, *M* transition. The structural changes asso-

ciated with this transition can also be monitored using probe molecules dissolved in the mesophase. As we have seen in the example of pyridine (Figure 5) there is a steep discontinuous change in the ordering of this probe in the phase III to *N*, *M* transition region.

It is not known what the structure of phase III is, not even whether the columnar arrangement of molecules as in the *N*, *M* phases is preserved. In principle one would expect that the sodium ion which constitutes an essential component of the mesophase could be used to monitor the microordering within the mesophase structure. The preliminary ^{23}Na results indicate that the sodium ions indeed experience completely different environments in the two types of phases, however what these differences are cannot be deduced from the limited amount of data available. We are currently continuing the ^{23}Na NMR studies in the DSCG-Water system as well as extending them to other alkali nuclei, and we hope to report on these experiments at a later date.

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