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N.M.R. and X-ray diffraction of the 7,7′-disodiumcromoglycate-water lyomesophases

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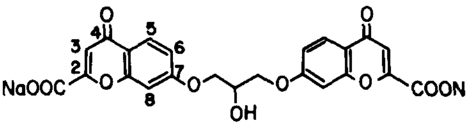
Aqueous solutions of 7,7′-disodiumcromoglycate (7,7′-DSCG) form a variety of mesophases, whose natures depend on concentration and temperature. We have used optical microscopy, N.M.R. (of ^{2}H, ^{17}O and ^{23}Na) and X-ray techniques to construct a phase diagram for this system and to characterize the various mesophases. In the concentration range 3 to 25 wt % 7,7′-DSCG four different mesophases are found. On cooling the isotropic solution an opaque gel phase is first obtained, followed on further cooling by a birefringent glassy liquid. At concentrations below 14 wt % it is nematic, while at higher concentrations it appears to be a different, more ordered, phase. At lower temperatures a hexagonal phase is formed which finally solidifies on cooling to −15°C. The N.M.R. and X-ray characteristics of these mesophases are discussed.

1. Introduction

Conventional lyotropic liquid crystals are formed from amphiphilic compounds and polar solvents in appropriate ratios. Typical amphiphiles like soaps, detergents and phospholipids consist of long, rod-shaped molecules with well-segregated hydrophilic and lipophilic regions [1]. In recent years several lyotropic-forming compounds have been discovered whose molecular structures are quite different from the common amphiphiles. Examples are diethylammoniumflufenamate [2], several drugs derived from chromones [3] including 5,5′-disodiumcromoglycate (5,5′-DSCG) [4, 5], as well as a number of water-soluble reactive dyes [6]. These compounds consist of an aromatic core to which several hydrophilic groups are attached, but no well-defined segregation between hydrophilic and hydrophobic regions in the molecules can be identified. Here we add another member to this list of unconventional lyotropics. This is 7,7′-disodiumcromoglycate (7,7′-DSCG), an isomer of 5,5′-DSCG. We present N.M.R., X-ray and optical microscopy studies of its mesophases which have a number of unusual characteristics.

The phase diagram of the 7,7′-DSCG-water system was constructed mainly on the basis of deuterium N.M.R. of solutions using D_2O as solvent. These results and related measurements on ^{17}O and ^{23}Na N.M.R. are described in §3. Although this system exhibits similar phases to those observed in some of the chromone compounds, it does not conform to the general pattern observed in the latter; in particular 7,7′-DSCG possesses a high-temperature gel-like phase that has apparently not been observed before. Section 3 also contains results on deuterium N.M.R. of specifically



labelled 7,7′-DSCG molecules which provide information on the ordering of the amphiphilic molecules in the various phases. In §4 X-ray data are presented and discussed in terms of possible structures of the phases, and a short summary is given in §5. The experimental details are summarized in the following section.

2. Experimental

2.1. *Material*

7,7′-DSCG was kindly provided as a white, slightly hydrated powder from Fisons Ltd. The degree of hydration was estimated as five to six water molecules per 7,7′-DSCG. Doubly deuteriated 7,7′-DSCG, at the 3,3′ positions, was prepared by exchange with D_2O as described in the last paper of [5] for the 5,5′-DSCG homologue.

Solutions were prepared gravimetrically by dissolving the desired amount of 7,7′-DSCG in distilled water. The concentrations are given in wt %, i.e. 100 × (weight of 7,7′-DSCG)/(weight of solvent water + weight of solute). For ^{2}H and ^{17}O measurements of the water component, D_2O ($>$ 99 at. %) or water enriched to 5 at. % oxygen-17 was used, respectively. The ^{23}Na and deuterium N.M.R. of the labelled 7,7′-DSCG were made on solutions in H_2O.

2.2. *N.M.R.*

N.M.R. measurements using a Bruker CXP300 superconducting spectrometer operating at 46·07, 40·68 and 79·39 MHz for deuterium, oxygen-17 and sodium-23, respectively. Some deuterium measurements which required sample rotation [7] were made on a WH90 spectrometer which employs an electromagnet and operates at 13·8 MHz. Most spectra were recorded using the single pulse excitation method; however for the deuterium spectra of the labelled 7,7′-DSCG the quadrupole echo method was used. The experimental conditions are given in the appropriate figure captions.

2.3. *Optical microscopy*

Optical microscopy observations were made using a Zeiss Universal polarizing microscope. The temperature was controlled with a Mettler FP5 hot stage. The accuracy of the temperature reading was ± 1°C. For these studies samples sealed in rectangular glass tubes (2 × 0·1 mm) were used.

2.4. *X-ray*

X-ray measurements were made using a low angle diffraction camera operating with Cu Kα radiation (average wavelength 1·54 Å) which was collimated by a series of slits and height limiters and monochromated first by a Ni filter followed by a single Franks mirror [8]. The distance from the specimen to the detector was 46 cm. The X-rays were generated by a Philips fine focus sealed tube operating at 40 kV and 30–34 mA. A semi-transparent beam stop permitted the main beam intensity to be monitored. The scattering profile was recorded using a delay line linear detector, the output of which was stored in 256 channels in a Z-80 microprocessor. Typical scan times were between 1 and 2 hours.

3. Optical microscopy and N.M.R. results

We have studied the optical microscopy, N.M.R. and X-ray characteristics of the 7,7′-DSCG-water system at concentrations up to 25 wt % and temperatures from − 10 to 100°C. As a general introduction to the experimental observation we present in figure 1 the phase diagram of this system as determined from polarizing microscopy and deuterium N.M.R. The high temperature phase, I, corresponds to the isotropic solution which is colourless, transparent, fluid, and of course, does not show birefringence. On cooling solutions containing more than about 3 wt % 7,7′-DSCG a sudden transition occurs in which the sample becomes opaque and gel-like; this phase is indicated as R in figure 1. Under a polarizing microscope (cf. figure 2) it shows birefringence, and X-ray as well as deuterium N.M.R. of labelled DSCG indicates a high degree of molecular ordering. Oddly enough, the ^{2}H and ^{17}O N.M.R. of the water component, as well as the ^{23}Na N.M.R. in this phase, exhibits single peak spectra, implying that the aqueous continuum in it is mobile and disordered.

On further cooling, another discontinuous transition takes place which is manifested by the appearance of a glassy viscous liquid. The transition is quite sharp, with a

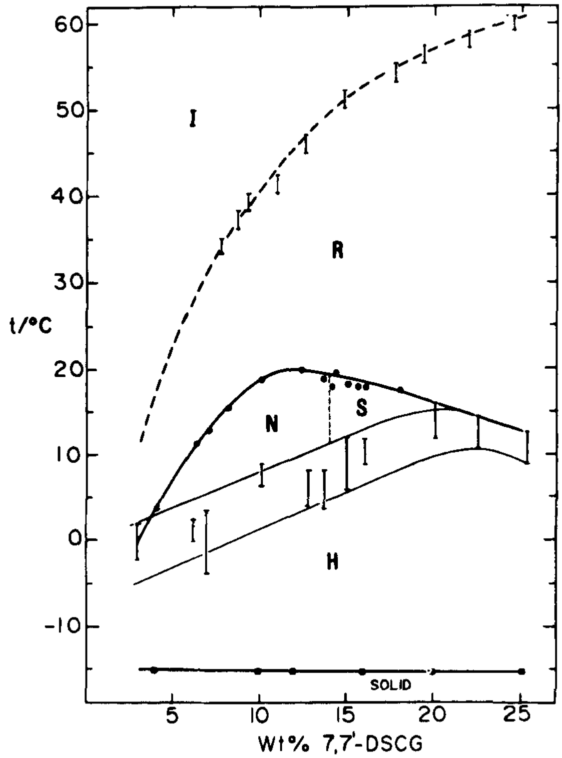


Figure 1. The phase diagram of the 7,7′-DSCG-water system as constructed from polarizing microscopy and N.M.R. measurements. The circles or bars correspond to experimental observation. I is the regular isotropic liquid, R is a gel-like opaque phase, N and S are glassy viscous liquids and H is a low temperature mesophase. The band between N/S and H is a biphasic region.

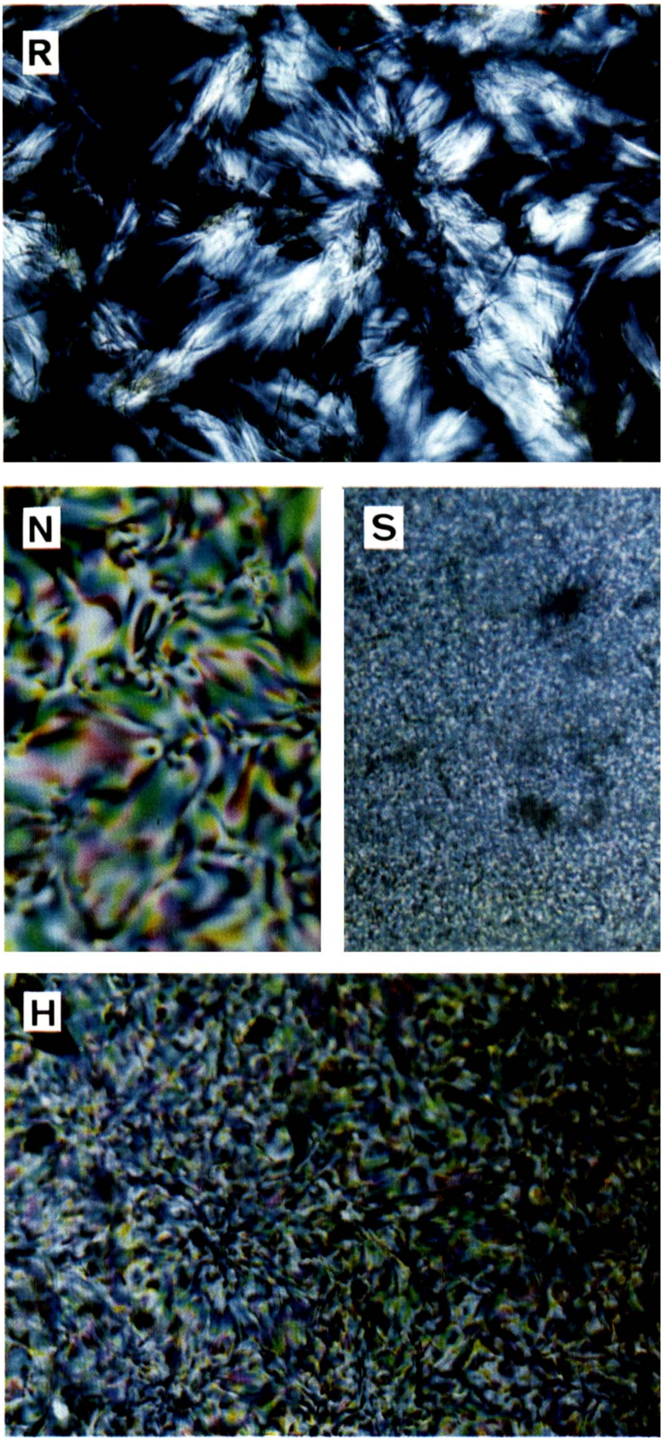


Figure 2. Polarizing microscopy pictures of the four mesophases of 7,7′-DSCG as indicated in figure 1.

biphasic region of less than 1°C. Under an optical microscope this liquid appears in two forms (see figure 2). In solutions containing less than about 14 wt % DSCG, schlieren textures of typical nematic liquid crystals show up, while at higher concentrations features typical of more highly ordered mesophases are observed. We refer to these phases as N and S, respectively. The boundary between these two phases is not well defined. It may involve a gradual change of N to S or perhaps a wide biphasic region. The deuterium and oxygen-17 N.M.R. of the solvent water as well as the sodium-23 signal for these phases exhibits quadrupole splittings as would be expected from aligned liquid-crystalline samples [5]. Further cooling results in discontinuous changes of the domain pattern (see figure 2) caused by a transition to another ordered mesophase which, from X-ray measurements, appears to be hexagonal and so it is labelled H. It may be related to the phase designated as M in the chromonic lyomesophases [3]. Finally, on cooling the H mesophase to below − 15°C the sample solidifies.

3.1. *N.M.R. of the water ^2H and ^{17}O and of ^{23}Na*

Typical deuterium spectra in the mesophase region are presented in figure 3 for three concentrations of DSCG as indicated in the figure. The upper trace in each column corresponds to the gel-like phase R. Despite the fact that it is birefringent and, as shown later, gives well-defined X-ray diffraction, the deuterium spectrum of D_2O in this phase consists of a single peak. Its line width is, however, strongly dependent

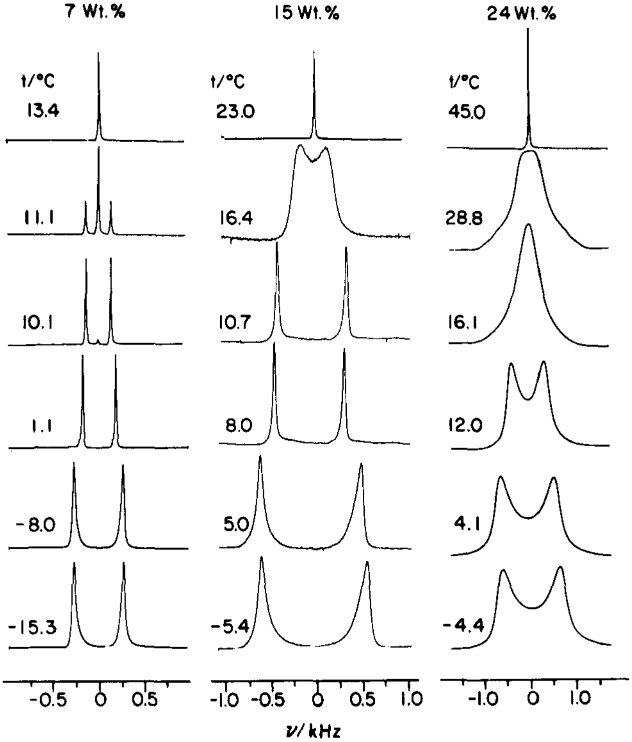


Figure 3. Deuterium N.M.R. spectra (at 46 MHz) of solutions containing the indicated concentrations of 7,7'-DSCG in D_2O as a function of temperature. The top trace in each column corresponds to phase R, the next three traces to N or S, and the bottom two to H. The spectra were recorded using single pulses followed by Fourier transformation.

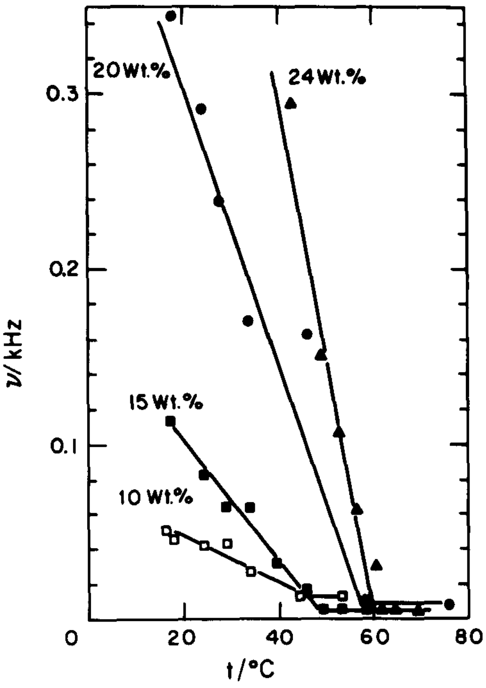


Figure 4. The full line width at half maximum intensity of the deuterium signal in the R and I phases of solutions containing the indicated amounts of 7,7′-DSCG in D_2O.

on the temperature and on the DSCG concentration. Plots of the full width at half maximum intensity versus temperature for various concentrations of DSCG are shown in figure 4. It may be seen that at the higher concentrations, close to the lower transition temperature, this width has increased to more than 300 Hz, while in the high temperature range in all solutions it approaches a common value of about 10 Hz.

On cooling from R to the N or S phases the deuterium spectrum transforms to a doublet with quite narrow components for the more dilute solutions (7 and 15 wt % in figure 3), and somewhat broader peaks in the more concentrated ones. The same doublet structure remains on further cooling into the H phase. Such spectra are typical of deuterium in ordered mesophases, and the observed splittings provide a measure for the degree of ordering of the water molecules [9]. These splittings are plotted in figure 5 as a function of temperature for a number of solutions. A common feature of these plots is the presence of a low and usually also a high temperature plateau with an intermediate slope between them. We associate the low temperature plateau with the H phase, and the narrower high temperature plateau with either N or S, depending on the concentration of the solution. The slope region between the two plateaus apparently corresponds to a biphasic mixture consisting of H and either N or S. The fact that a gradual change in the splitting is observed in this region rather than a superposition of two doublets, as expected for a first-order transition, may be attributed to the smallness of the liquid-crystalline domains. If these domains are sufficiently small, fast water diffusion would result in a single doublet spectrum with an average quadrupolar splitting. This average will gradually change on going from the N or S phases to the H phase as observed experimentally. From the X-ray results, to be discussed later, a lower limit of 500 to 1000 Å for the domain size can be

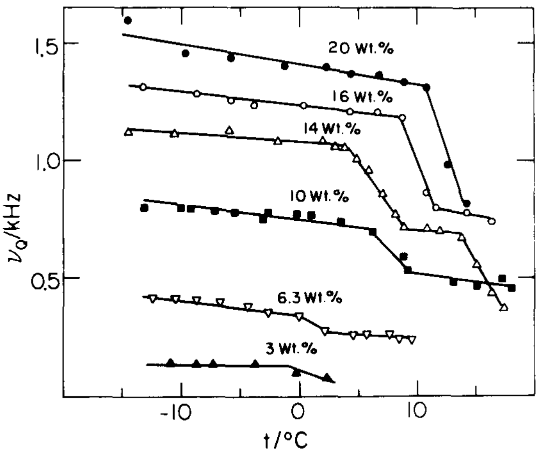


Figure 5. Plots of the splitting of the doublet components in the deuterium N.M.R. spectra of D_2O solutions containing the indicated amounts of 7,7′-DSCG, as a function of temperature.

estimated, but the actual size is not known, and could be considerably higher. Note that in the 14 wt % solution there is a second, high temperature, slope; this may be related to the fact that this solution corresponds to the boundary between N and S.

As the H phase is cooled further the doublet components gradually broaden until at around − 15°C they undergo a sudden spreading out due to solidification.

The deuterium spectra of the solvent D_2O could also be used to show that the sign of the anisotropic magnetic susceptibility, $\Delta\chi$, of the N, S and H phases is negative, i.e. they prefer to align with the director perpendicular to the magnetic field [1]. An example of such an experiment [7] is shown in figure 6 for the N and H phases in a

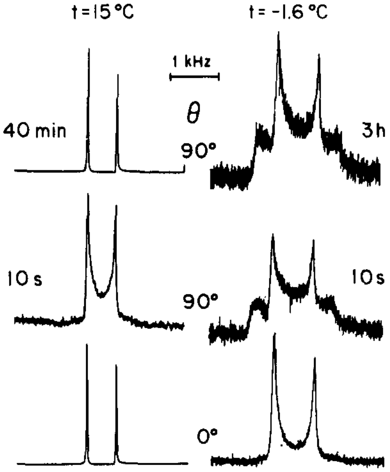


Figure 6. Deuterium N.M.R. spectra in solutions containing 10 wt % 7,7′-DSCG in D_2O. The bottom traces were obtained after allowing the solution to cool from the isotropic liquid to the indicated temperatures within the magnetic field. The middle traces were obtained immediately after rotating the sample by 90° about an axis perpendicular to the field direction. The upper traces were taken sometime later as indicated. The experiments were done on a Bruker WH90 at 13·8 MHz.

10 wt % solution of DSCG in D_2O. The bottom traces in this figure were obtained after cooling the sample within the magnetic field to the temperatures indicated. The samples were then rotated by 90° about an axis perpendicular to the magnetic field and spectra were immediately recorded again (the middle trace in each column). The upper traces were recorded several minutes or hours after rotating the sample. It may be seen that in the nematic phase (15°C) the sample is almost completely realigned within several seconds although the 10 s spectrum shows some residual intensity at frequencies outside the doublet components. The same solution at − 1·6°C (H phase) exhibits after a 90° rotation a pattern typical of a planar distribution of domains, with an overall splitting twice as large as that of the original doublet. This spectrum did not change even after several hours. These results indicate that both phases are uniaxial and align perpendicular to the field direction ($\Delta\chi < 0$). The S phase behaved similarly to the nematic phase; however, the rate of realignment after the 90° rotation was much slower.

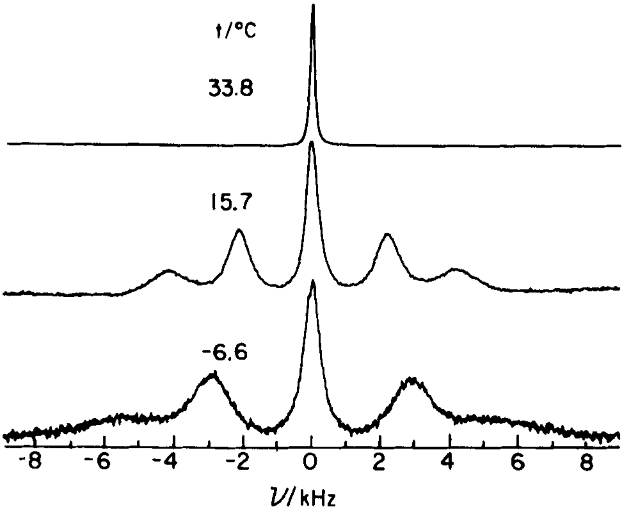


Figure 7. Oxygen-17 N.M.R. spectra (40·68 MHz) in a 12·9 wt % solution of 7,7′-DSCG in water enriched to 5 wt % ^{17}O. The spectra from top to bottom correspond to the R, N and H phases.

The behaviour of the ^{17}O spectrum is quite similar to that described for the water deuterons. Oxygen-17 has a spin $I = 5/2$ and therefore in an ordered mesophase it exhibits a five line hyperfine spectrum. Examples of such spectra are shown in figure 7 and quadrupole splittings versus temperature for a number of concentrations are plotted in figure 8. As for the deuterium results there is no splitting in the R phase, while the splitting pattern in the other phases has two plateaus with an intermediate slope.

From the splitting of the solvent deuterium and oxygen-17 nuclei the ordering matrix, S, for the water molecules in the various liquid-crystalline mesophases can be determined [9]. Using the coordinate system and definitions of the first paper of [5] we find that $|S_{xx} - S_{yy}|$ varies between 0·003 and 0·017 and $|S_{zz}|$ between 0·07 and 0·1. The latter figures are however associated with a large uncertainty, since they multiply a small geometrical factor [10]. The range of the ordering matrix is very similar to that determined for the 5,5′-DSCG mesophases.

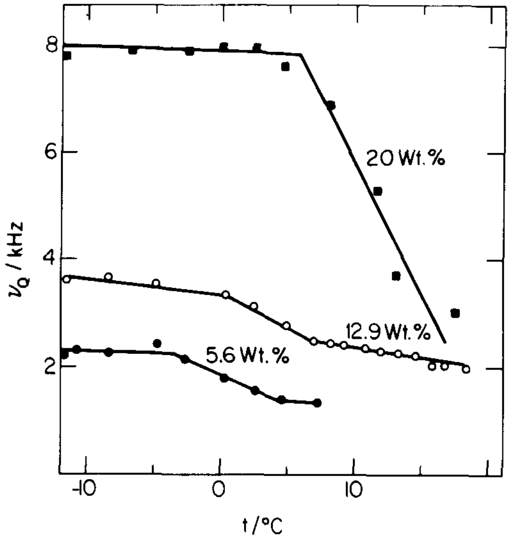


Figure 8. Plots of the oxygen-17 quadrupole splittings as a function of temperature for three solutions containing the indicated concentrations of 7,7'-DSCG in water enriched with ^{17}O.

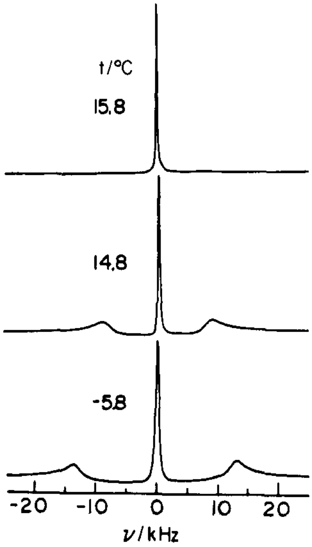


Figure 9. ^{23}Na N.M.R. spectra (79·39 MHz) in a 12·6 wt % solution of 7,7'-DSCG in water. The three traces correspond, from top to bottom, to the R, N and H phases.

Finally we refer to the results for the ^{23}Na N.M.R. ($I = 3/2$); examples of spectra are shown in figure 9 and plots of quadrupole splittings versus temperature are summarized in figure 10 for various concentrations of 7,7'-DSCG. A peculiar phenomenon exhibited by these results is the absence of a concentration dependence for the splitting and the lack of a discontinuity or change in slope on going from N or S to H.

The phase diagram in figure 1 is based on the optical and N.M.R. results which we have described. The boundary between I and R (the dashed line) was drawn from

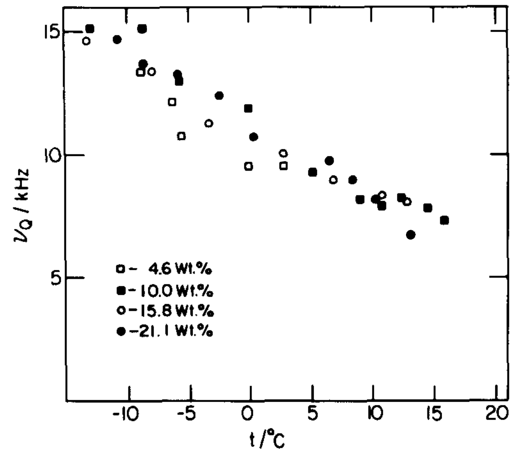


Figure 10. The sodium-23 quadrupole splitting in four different aqueous solutions of 7,7′-DSCG as a function of temperature.

the first observation of birefringence on cooling the isotropic solution, while the transition to N or S was determined from the appearance of a splitting in the deuterium (as well as the ^{17}O and ^{23}Na) spectrum. The transition to H was associated with the slope regions between the plateaus in figure 5. This biphasic region is indicated by the wide band in figure 1 between H and the N/S phases.

3.2. *Deuterium N.M.R. of 7,7′-DSCG-3,3′-d_2*

Additional deuterium N.M.R. measurements were made using specifically labelled 7,7′-DSCG. Examples of spectra of solutions containing 10 and 16 wt % 7,7′-DSCG labelled at the 3,3′ positions are shown in figure 11. The signal-to-noise ratio in these experiments is considerably poorer than for the solutions in D_2O, because of their wider frequency range and the lower deuterium content. Within the R mesophase the spectra exhibit a doublet of about 130 kHz splitting. On cooling to N and S the spectrum transforms to a doublet of about half the splitting and in the intermediate bisphasic region the spectra consist of a superposition of the two doublets, as would be expected for a first-order transition. In all spectra an intense central peak is also observed which is due to natural abundance deuterium in the solvent water (it is truncated in the traces shown in figure 11). On further cooling to phase H the spectrum of DSCG broadens beyond detection. The temperature dependence of the quadrupole splittings of the 3,3′ deuterons are plotted in figure 12 versus temperature for the various solutions studied. Within the experimental scatter of the results the splittings are essentially independent of concentration and within the mesophases are also independent of temperature, but they do decrease by a factor of two on going from H to N or S.

In discussing the results of the R phase where the 3,3′ deuterons exhibit a splitting of 130 kHz we note that this is about half the maximum splitting of a deuteron in a rigid C–D bond. If the doublet observed in this phase were due to an ordered liquid-crystalline sample it would be difficult to rationalize the absence of quadrupole splittings for the ^{23}Na and the water ^{2}H and ^{17}O nuclei. The quality of the 3,3′ deuteron spectra is however not sufficient to rule out the possibility that they represent the perpendicular features of a powder pattern due to a disordered rigid system. The R

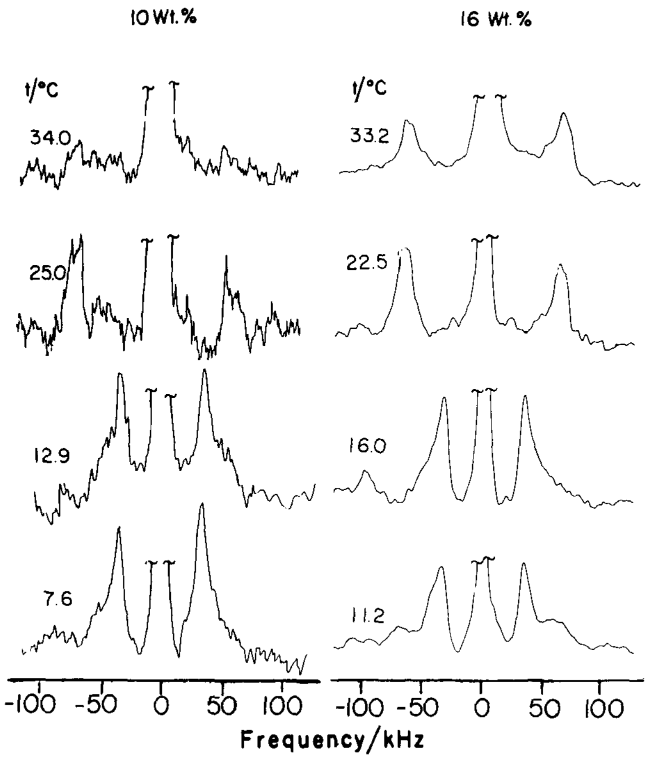


Figure 11. Deuterium N.M.R. spectra (at 46·07 MHz) of two solutions containing 7,7′-DSCG-3,3′d_2 in H_2O at different temperatures. The spectra were recorded using the quadrupole echo pulse sequence using the following parameters: $\pi/2$ pulse widths, 4-6 μs; interval between $\pi/2$ pulses, 30 μs; cycle time, 0·1 s; sweep width, 500 kHz; line broadening parameter, 2 kHz; number of scans, about 100 000. The central truncated peak corresponds to natural abundance deuterium in normal water. Its splitting is removed by the large line broadening parameter. The upper two spectra correspond to N and S phases and the lower two to the H phase.

phase could then be visualized as consisting of highly ordered micelles or a gel-like network, through which water molecules and sodium ions can freely diffuse. If these domains are sufficiently small and not aligned by the magnetic field the fast diffusion will average out the quadrupole splitting of the solvent molecules and free ions, resulting in an effective isotropic spectrum, as observed for the water ^2H and ^{17}O nuclei and for the ^{23}Na in the R phase.

The spectra in the N and S liquid crystalline phases are also of low quality but here we know from the solvent N.M.R. that the samples are well aligned in a direction perpendicular to the magnetic field. Since only a single spectrum is observed for both the 3 and 3′ deuterons we may assume that the two aromatic parts of the 7,7′-DSCG molecule are coplanar and in analogy with the 5,5′-isomer they are stacked on top of each other to form columnar micellar units. The quadrupole splitting of the 3,3′ deuterons is then given by

$$\begin{aligned}\Delta\nu &= 3/2(e^2qQ/h)S\,1/2(3\cos^2\alpha - 1)\,1/2(3\cos^2\theta - 1),\\ &= 3/8(e^2qQ/h)S,\end{aligned}$$

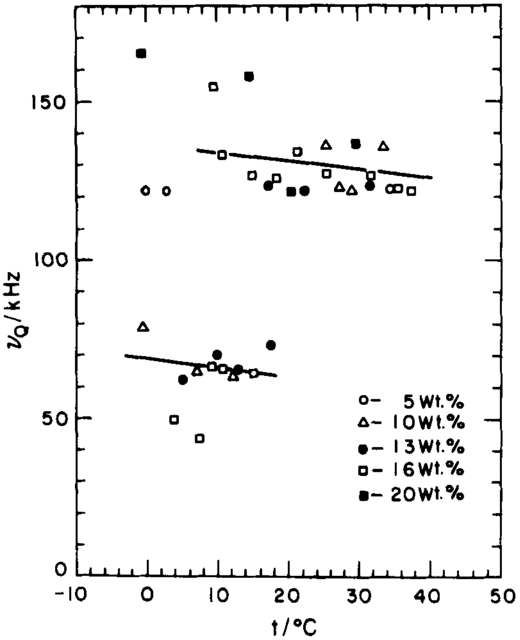


Figure 12. Plots of the deuterium splittings as a function of temperature in five different solutions of 7,7′-DSCG-3,3′d_2 in normal water.

where α is the angle between the C–D bond and the micellar axis, θ is the angle between the director and the magnetic field, and S is the product of the order parameter of the DSCG molecules in the micelles and that of the micelles themselves. In our case $\alpha = \theta = \pi/2$, taking the quadrupole interaction of deuterium in the C–D bond e^2qQ/h to be 183 kHz, and $\Delta\nu = 65$ kHz from figure 11, yields $S \approx 1{\cdot}0$. This indicates essentially complete ordering of the micelles although free rotation of the molecular planes are allowed in this model.

4. X-ray diffraction

The X-ray diffraction results on the 7,7′-DSCG lyomesophases are consistent with the phase diagram from N.M.R. and optical microscopy. In particular they confirm the presence of four distinct phases as indicated in figure 1. Typical diffraction patterns for two solutions containing 10 wt % and 16 wt % 7,7′-DSCG are shown in figure 13. We first discuss the results for the 10 wt % solution.

In the high temperature R phase two sharp diffraction peaks are clearly seen corresponding to d values at 27°C of 51·2 Å and 25·1 Å. A third very weak and broad peak at 32·1 Å (indicated by the arrow in figure 13) is barely discernible on the shoulder of the inner peak. The peak positions are temperature dependent but the ratio of the spacings are fairly constant. The three lines have spacings $1 : 1/\sqrt{2} : 1/2$, and can be indexed in terms of a two-dimensional square lattice corresponding to the 1,0 : 1,1 : 2,0 reflections. This assignment should be considered tentative, but the sharpness of the two strong peaks is a strong indication that the phase is highly regular. A plot summarizing the observed dependence of the d spacing on temperature is given in figure 14. In the R phase these spacings decrease with increasing temperature reaching, for the 1,0 direction, a minimum of about 40 Å near the clearing temperature.

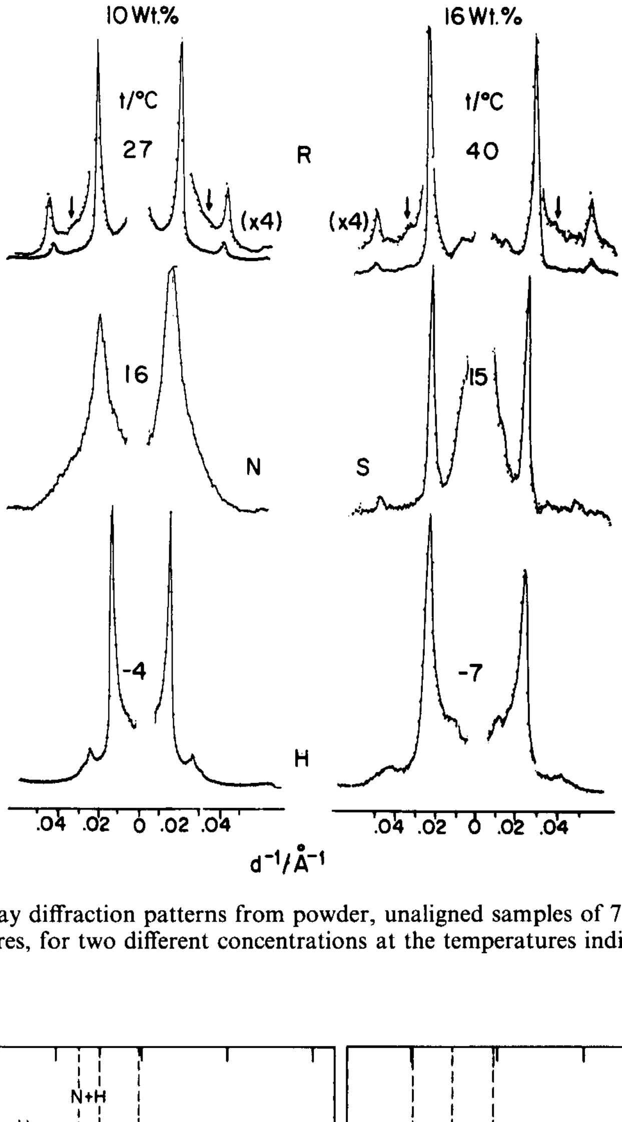


Figure 13. X-ray diffraction patterns from powder, unaligned samples of 7,7′-DSCG-water mixtures, for two different concentrations at the temperatures indicated.

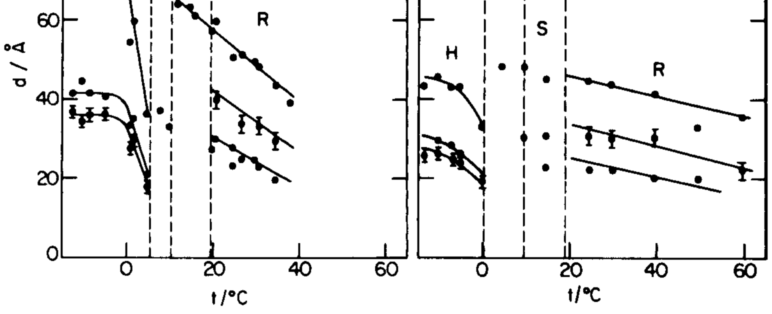


Figure 14. The variation with temperature of the spacings of the X-ray diffraction peaks in the two 7,7′-DSCG-water mixtures depicted in figure 13.

In the N phase only a single broad peak is observed, as would be expected for a nematic liquid [11]. Its position appears to be an extension of the 1,0 diffraction peak of the R phase and it continues to increase on cooling, reaching approximately 70 Å at the transition to H. At this point the diffraction pattern changes again and becomes more structured. It now consists of a weak outer shoulder and two inner peaks. The pattern of three spacings are approximately in a ratio $1 : 1/\sqrt{3} : 1/2$ and can therefore be indexed in terms of a two-dimensional hexagonal lattice corresponding to the 1,0 : 1,1 : 2,0 planes. Just below the transition from the N phase these spacings correspond to a lattice constant of about 46 Å; however on cooling they increase steeply and then level off at approximately 80 Å.

The diffraction patterns of the 16 wt % solution are quite similar to those described except that here the intermediate mesophase exhibits sharper reflections, indicating that it is not nematic but rather a more highly ordered phase. This confirms the assignment of two different phases, N and S below and above 14 wt % DSCG. The diffraction pattern in phase H is similar to that of the more dilute solutions but the shoulder and the outer peak are much broader and therefore very poorly resolved. Another difference from the 10 wt % solution is the occurrence of an additional broad diffraction at very low angles. Its exact position cannot be determined since it falls within, or close to the edges, of the beam stop; however its spacing is of the order of 100 Å. It is possible that it reflects ordering in the direction perpendicular to the two-dimensional lattice.

These X-ray diffraction results were obtained from unaligned samples. To substantiate the magnetic field alignment experiments performed by N.M.R. we also performed a number of X-ray measurements on aligned samples. The measurements were made on the H phase because it could be transferred from the magnetic field to the X-ray diffractometer without loosing the alignment. The samples were contained in circular 1·5 mm quartz capillaries and the alignment was affected by allowing the sample to cool from the isotropic liquid to about −5°C. The X-ray measurements were performed at 0°C. Three measurements were made, all on a 10 wt % solution aligned in a 7 T superconducting magnet; one sample was aligned with the field along the long axis of the capillary, while the two others were aligned with the magnetic field in two directions perpendicular to the capillary axis. The results of the three experiments are shown in figure 15. It gives a schematic diagram of the experimental set-up in which the X-ray beam is along Z and the resulting diffraction intensities are recorded on a two-dimensional XY position sensitive detector [12]. They all correspond to the 75 Å spacing which was indentified with the 1,0 reflection. For a magnetic field along $Y(X)$ two arc-shaped sets of intensity contours, centred on the vertical $\pm Y(\pm X)$ axis are observed, while for a field along Z, homogeneous circular contours are obtained. These results are consistent with those of the N.M.R. experiments which indicate a perpendicular alignment of the directors with respect to the magnetic field. The discussion of these X-ray results is based on the analysis of Bamford and Tompa [13] for thin film samples. Applying their formalism to the present case the relation

$$\sin\chi = \operatorname{tg}\theta \operatorname{tg}\phi$$

applies, where ϕ gives the orientation of the unique axes of the hexagonal domains in the ZX (ZY) plane, measured from the X (Y) axis, θ is the Bragg angle, and χ is the reflection angle in the XY plane of the detector measured from the Y (X) axis. Thus for random alignment of domains in a plane perpendicular to the magnetic field we would expect for $B \parallel Z$ a homogeneous distribution of intensities in the XY plane

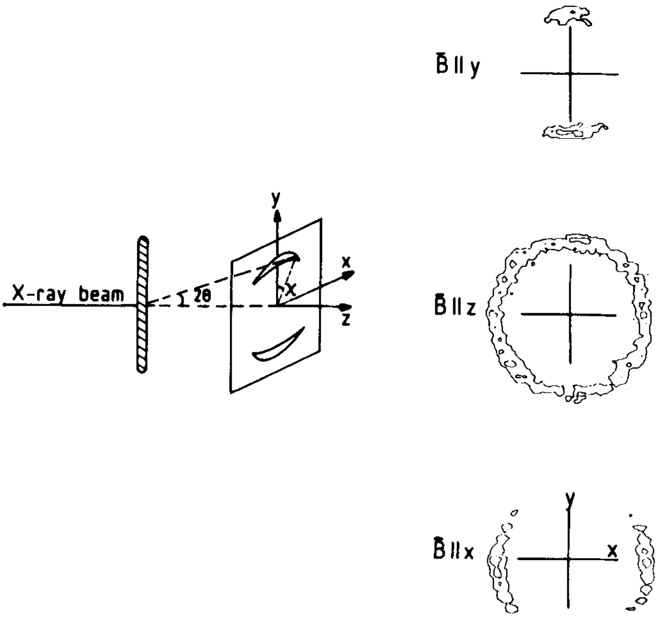


Figure 15. The geometry of the X-ray diffraction experimental set-up (left), and the diffraction patterns (right) obtained from three aligned samples of 7,7′-DSCG (10 wt %) at 0°C (H phase). The samples were contained in circular 1·5 mm quartz capillaries and aligned by cooling them from the isotropic liquid within a magnetic field (7 T) oriented as indicated in the figure.

while for $B \parallel X$ ($B \parallel Y$) two arcs centred around the $\pm X$ ($\pm Y$) axis, as is roughly observed experimentally. For a perfect planar distribution the span of these arcs is expected to be quite narrow. From Bamford and Tompa's equation the intensity profile, as a function of the angle χ, is calculated to be

$$h(\chi) \sim \frac{1}{d\chi/d\phi} = \frac{\operatorname{tg}\theta\cos\chi}{\operatorname{tg}^2\theta + \sin^2\chi}.$$

For small scattering angles this profile corresponds to sharp lorentzian-like curves with full width at half maximum intensity of approximately 2θ. The experiments indicated in figure 15 correspond to $\theta = 0{\cdot}57°$ but the spread in χ is much larger than the expected range due, most probably, to imperfect planar alignment. The main features expected for a uniaxial phase with negative $\Delta\chi$ are however clearly exhibited by the results of figure 15.

The X-ray experiments reported refer to the low angle diffraction region of up to $\theta \approx \pm 3°$, corresponding to d spacings larger than 14 Å. In a few cases wider angles were scanned, but under the prevailing experimental conditions no additional peaks in particular around $\theta = 13°$, corresponding to $d = 3{\cdot}4$ Å, were observed. The presence of such a peak, which is often found in highly ordered mesophases and corresponds to the molecular stacking repeat distance, cannot however be ruled out before more experimental data in this region is obtained.

5. Summary

The 7,7′-DSCG-water system exhibits a variety of mesophases with different optical textures, diffraction patterns and orientation characteristics. The high temperature

R phase appears to be a gel in which the DSCG molecules form a relatively rigid, but sparse structural network, through which water molecules and sodium ions can move freely. This phase does not align in a magnetic field; it is birefringent and the X-ray results suggest that it is tetragonal. The stability of its molecular network originates most probably from electrostatic forces between sodium ions and pairs of carboxyl groups of neighbouring molecules [14].

On cooling, several liquid-crystalline phases are formed in which aggregates of DSCG molecules play the role of the basic units. These aggregates appear to have a rod-like structure in which layers consisting of several DSCG molecules (perhaps in the form of a ring) are stacked on top of each other to form columns. The spacing between these columns is different in the different mesophases and changes with temperature and composition. In the more dilute solutions (< 14 wt %) the average distance between the columns is large (~ 60 Å) resulting in a nematic phase (N), as evidenced by the optical, X-ray and N.M.R. results. However at higher concentrations the closer packing of the aggregates results in a more highly ordered and a considerably more viscous phase (S). Once aligned, for example by a magnetic field, this phase does not subsequently realign if the sample is rotated in the field. Finally when either the N or S phases are cooled to below 0°C another liquid-crystalline phase (H) is formed, which from the X-ray results is identified as an hexagonal phase.

The three liquid-crystalline phases (N, S, H) are characterized by high orientational order and negative anisotropic magnetic susceptibility, i.e. they prefer a perpendicular alignment of the director to a magnetic field. This is consistent with the proposed structure of the aggregates, since this will cause the planes of the DSCG molecules to lie parallel to the magnetic field which is the more stable situation for unsaturated molecules. The essential concentration independence of the orientational order of the DSCG aggregates (cf. figure 12) also explains the fact that the ^{23}Na splitting is independent of DSCG concentration (cf. figure 10). The latter is a weighted average of the splittings in the various sodium sites, in particular bound sodium within the micelles and free ions in the bulk water. If the distribution between the sites is independent of the DSCG concentration we would expect a constant ^{23}Na splitting, as found experimentally.

To conclude we find it quite remarkable that molecules like the DSCG isomers with a molecular structure so different from the normal rod-like amphiphiles exhibit lyotropic mesophases with such a variety of structures. It is very likely that many other innocent-looking molecules will be found to exhibit such mesomorphic properties [15].

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[10] In the equation for ν_Q in this paper the first term multiplying ($S_{xx} - S_{yy}$) should read $\sin^2\beta\cos 2\gamma$ (and not $\sin^2\beta\cos 2\alpha$).

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