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Mesomorphism in the System Disodium Chromoglycate–Water

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Abstract—The system has been studied by a combination of polarization microscopy, using a hot stage, and X-ray diffraction analysis. The sequence of condensed phases occurring at room temperature with increasing concentration of disodium chromoglycate (DSCG) is: (i) a mesophase N; (ii) a mesophase M; (iii) crystalline solid solutions SS. A variety of evidence has shown that the molecule of DSCG retains an essentially planar configuration throughout the system.

The mesomorphic phases are optically negative, indicating a parallel, or approximately parallel, arrangement of the molecular planes. (A parallel arrangement of these planes in the SS solid solutions had been previously indicated by a preliminary X-ray analysis, which pointed to there being only one molecule in the unit cell; and in conformity with such an arrangement the crystals were found to be optically negative.) The transformations between the N and M phases and between the M and SS phases take place pseudomorphically, and on reversal the original textures are recovered.

The N phase appears to be genuinely nematic in structure, in contrast to other cases of lyotropic systems showing nematic-like textures that have been reported, but which are believed to be deformed lamellar phases. The M phase gives X-ray reflections corresponding to a " middle " structure, of the M_1 type, i.e., one in which the DSCG is clustered into rods separated by a water continuum, and with the polar —COONa groups occupying the surfaces of the rods. Considerations based on calculations of the diameter of the rods indicate that some water is associated with the DSCG molecules within the rods.

1. Introduction

The work described concerns the phases formed on the addition of water to disodium chromoglycate (DSCG), and in particular the mesophases which appear in the system. The work forms part of a wider investigation into the properties of DSCG which is being carried out by McCrone Research Associates for the Pharmaceutical Division of Fisons Ltd.⁽¹⁾ The compound is used in the treatment of asthma and bears the trade name " INTAL ".

DSCG ($C_{23}H_{14}O_{11}Na_2$) has the structural formula shown in Fig. 1. Its crystals readily take up water to form a series of interstitial solid solutions with a limiting composition of about 9 molecules of water to 1 of DSCG. Under dehydrating conditions at ambient temperatures the last traces of this water are very firmly held and cannot be removed by phosphorus pentoxide. A recent X-ray structure analysis finds that the crystals are triclinic, though with all the interaxial angles near to 90°, and confirms that there is one molecule in the unit cell (H. Geddes, University of Leeds; publication pending). The structure indicated by this new work, while essentially planar, differs from that suggested by Cox, Woodard, and McCrone on the basis of their preliminary study⁽¹⁾ mainly in that the two ring systems are not side by side but have their planes rotated through about 180° with respect to one another, and thus point in opposite directions. The intake of water to form the solid solutions causes an expansion of the unit cell mainly in the direction of its longest spacing.

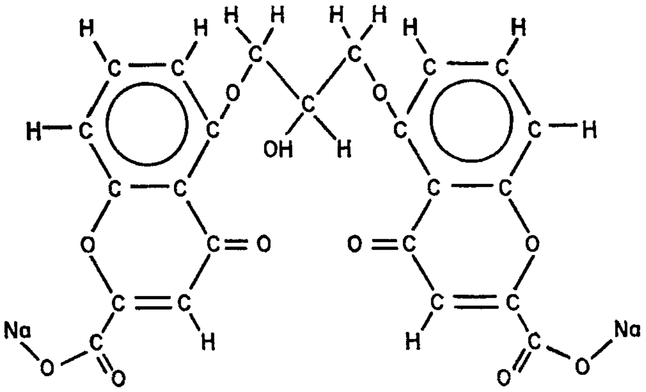

Figure 1. Structural formula of disodium chromoglycate.

Figure 2 shows the temperature-composition diagram for the system. It was obtained prior to the present work by a combination of hot-stage observations and solubility determinations.(1) With increasing concentration of DSCG the sequence of condensed phases occurring at room temperature is as follows: (i) the mesophase *N*; (ii) the mesophase *M*; (iii) the crystalline solid solutions (*SS*) mentioned above. Neither of the mesophases has a congruent melting point, i.e., exhibits a maximum in its solubility curve, but mixtures of appropriate compositions undergo peritectic-type transformations with change of temperature. Thus a mixture of composition corresponding to arrow *C* (Fig. 2) and consisting entirely of *M* and *N* phases undergoes transformation into isotropic solution and *M* alone at 42°, the composition of this solution meanwhile remaining constant at *D*. A mixture corresponding to arrow *E* and consisting entirely of *M* phase undergoes transformation first into *M* plus isotropic solution, and then at 73° the *M* phase is progressively replaced by solid solutions *SS*, the composition of the isotropic solution meanwhile remaining constant at *F* until this transformation is complete.

In view of the possibilities of free rotation around the single bonds between the two ring systems in the DSCG molecule it was perhaps to be expected that the essentially co-planar conformation existing in the *SS* phase would not be retained in the presence of higher concentrations of water, and especially in isotropic solutions. However, recent determinations of the anisotropy of light scattering of dilute solutions (0.3–3%) of DSCG and of their magnetic birefringence, made by J. V. Champion and G. H. Meeten,(2) have indicated that the ring systems are still approximately co-planar under these conditions. It is highly probable that the co-planar conformation owes its stability to the formation of hydrogen bonds. The hydroxyl, carbonyl, and carboxyl groups in conjunction with associated water molecules offer many possibilities of such bonding. The tenacity with which *SS* crystals retain the last traces of water under dehydrating conditions (see above) is also in harmony with the idea that water plays an important part in determining the configuration of the molecule.

DSCG is to be classed as an amphiphile though one of an unusual type, and the fact that it forms mesophases with water is to be

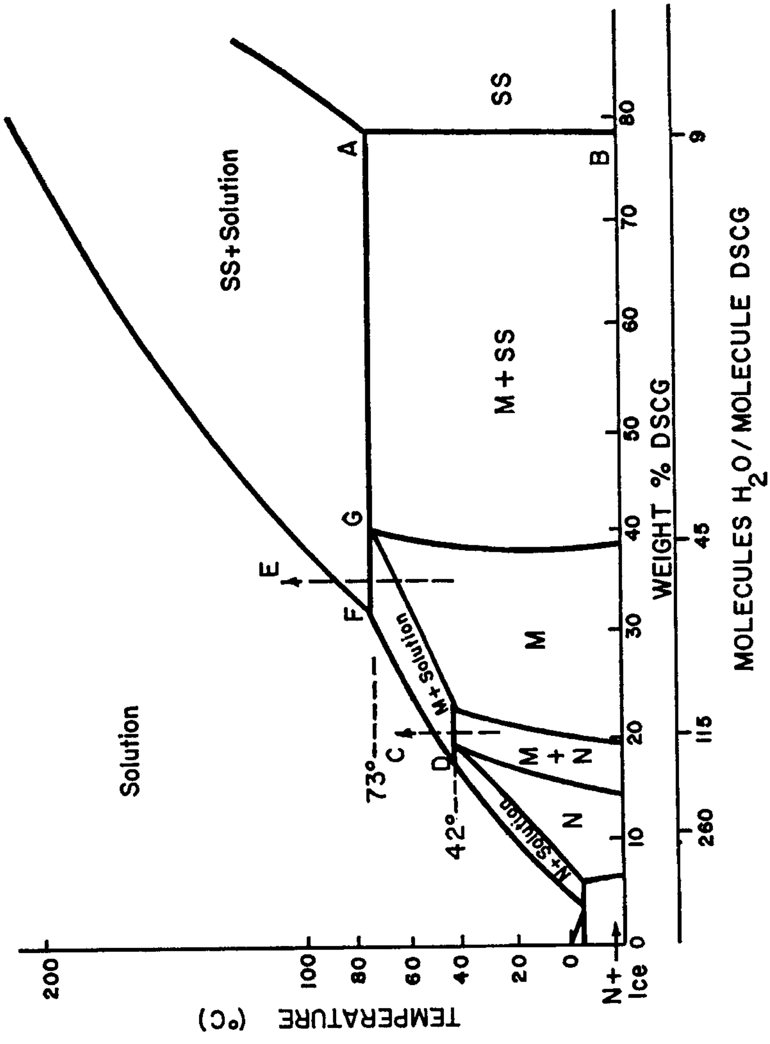

Figure 2. Temperature–composition diagram for the DSCG/water system.

attributed to this character. The two ionizable —COONa groups are the same as the polar groups in the sodium soaps and they are strongly hydrophilic. The rest of the molecule can be regarded as lipophilic as a whole with some modification of this property due to the presence of the —OH and —C=O groups and their presumed association with water. Some parallels with the mesomorphic behaviour of the soaps, and in particular the disoaps, were to be expected, but on the other hand the very considerable difference between the constitution of the lipophilic part of the molecule and that of the long-chain structures of these compounds made it likely that a close similarity in behaviour would not be found, as has indeed proved to be the case.

2. The Microscopy of the Mesophases

THE *N* PHASE

The phase can be studied under the polarizing microscope at room temperature by mounting an approximately 10% mixture of DSCG in water between the slide and cover slip. The mixture will consist either of the *N* phase alone, or of this phase plus some solution, depending on the precise composition and temperature (see Fig. 2). It is very fluid and spreads readily into a thin film. Alternatively, a more concentrated mixture may be pressed out between a slide and cover slip, taking less material than is necessary to occupy the whole area of the slip, and the surrounding space then filled with water. The *N* phase will form in the zone of contact with the water.

Between crossed polars the mesophase presents a texture consisting of a multitude of sinuous dark lines and bands, and there is a complete absence of any rectilinear features in the pattern (Fig. 3). In some areas between the bands, polarization colours are shown in white light (usually first order white in thin films), while in others the medium shows a bluish tint in thin films, and here darkness can be produced by rotating either the polarizer or the analyzer (more completely in monochromatic light), indicating that in these areas the medium has a structural twist. On rotating the stage, or the polars in unison, some parts of the dark lines and bands sweep into other positions, showing that they are areas in which the medium is in extinction owing to their vibration directions being parallel to

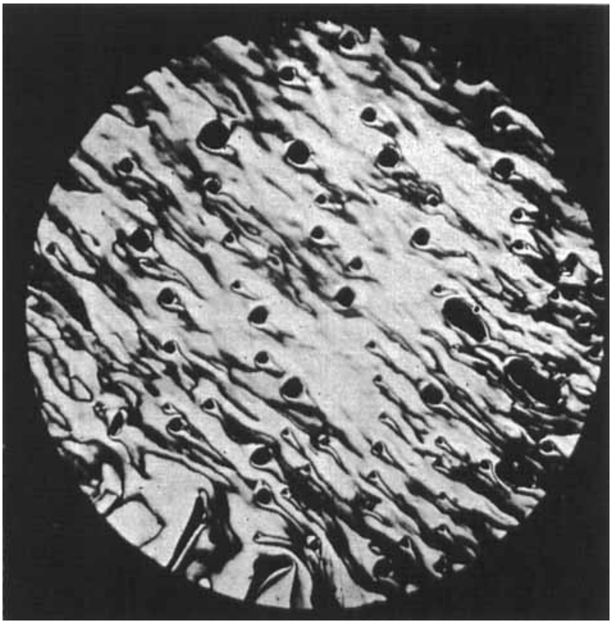

Figure 3. *N* phase, crossed polars.

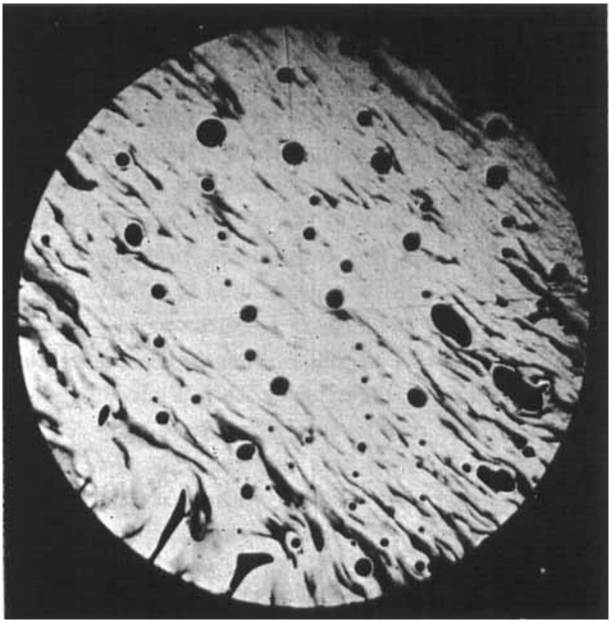

Figure 4. *N* phase, with crossed circular polarizers.

those of the polars. In many cases this sweeping movement is pivoted on a fixed point, like the movement of the isogyres in a biaxial interference figure. Other parts of the lines and bands are unaffected by the rotation and must be areas in which the optic axis of the medium is perpendicular to the plane of the preparation, thus giving isotropic behaviour in parallel light. These latter areas can be seen in isolation by using crossed circular polarizers (Fig. 4), since this optical system suppresses all extinction effects that are due to coincidence between the vibration directions of the medium and the polars.

The sinuous texture of the *N* phase, the presence in it of areas showing optical rotation, and the sweeping motion of some of the extinction bands around fixed points recall a texture sometimes shown by the nematic phases of single mesomorphic compounds in thin films, and termed by G. Friedel " plages à noyeaux " (nucleated domains).(3) Such phases are optically positive because they are based on parallel arrangements of elongated molecules. The sign of the *N* phase (determined on the interference figures given by regions that were suitably oriented and sufficiently uniform†) is, however, negative. This sign is to be expected for a structure in which planar molecules are arranged with their planes parallel, or approximately parallel, to one another, and which is nematic in the sense that the distribution of the centres of the molecules is random and that they have freedom to move past each other in directions parallel to these planes. Precisely what role the water would play in such a structure is, however, not clear at present.

Observations made on the transformation between the *N* and *M* phases, and having some bearing on the problem of the structure of the former, will be described below after the structure of the *M* phase has been discussed.

THE *M* PHASE

Evidence for the structure of this phase was first gained from a

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† The figures usually obtained were optic normal ones (optic axis parallel to the plane of the preparation), on which the direction of the optic axis could be deduced as being that in which the polarization colours fell from the centre outwards, or for thinner films, in which the isogyres entered the field on rotating the stage.

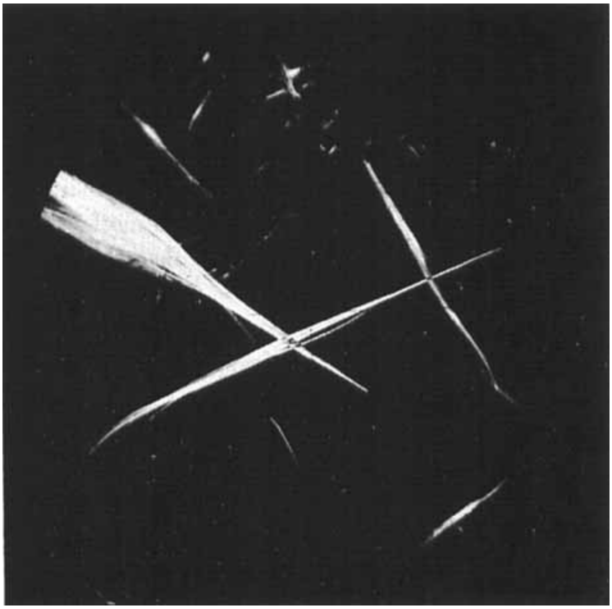


Figure 5. Solid solution crystals (*SS*).

microscopical study of the transformation between it and the solid solution phase *SS* around the peritectic point at 73° (*F*, Fig. 2), using a hot stage. A mixture of composition *E* (Fig. 2) at a temperature just above 73° consists of solution and crystals of *SS* of composition *A* or near to *A*. The fine needles are often clustered into bundles (Fig. 5). On lowering the temperature of the stage to just below 73° the replacement of *SS* by phase *M* of composition *G* begins. This takes place in two ways: (i) the *SS* needles transform pseudomorphically with some increase in width but usually no increase in length,‡ (ii) additional *M* is deposited from solution. This stage is shown in Fig. 6 in which the pseudomorphs can be seen surrounded by rodlets of *M* from solution, many of which are curved. This additional production of *M* is necessary to maintain the composition of the solution constant at *F* during the transformation as required by the

‡ Curved growths have occasionally appeared at the ends of the pseudomorphs but these are thought to be deposits from solution as in (ii), for which the pseudomorphs have acted as nuclei.

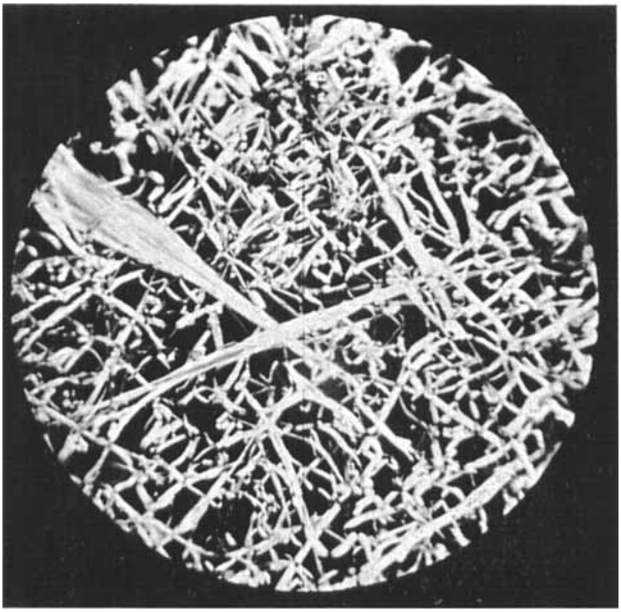


Figure 6. Same field as Fig. 5 after slight cooling below 73 °C; *M* phase.

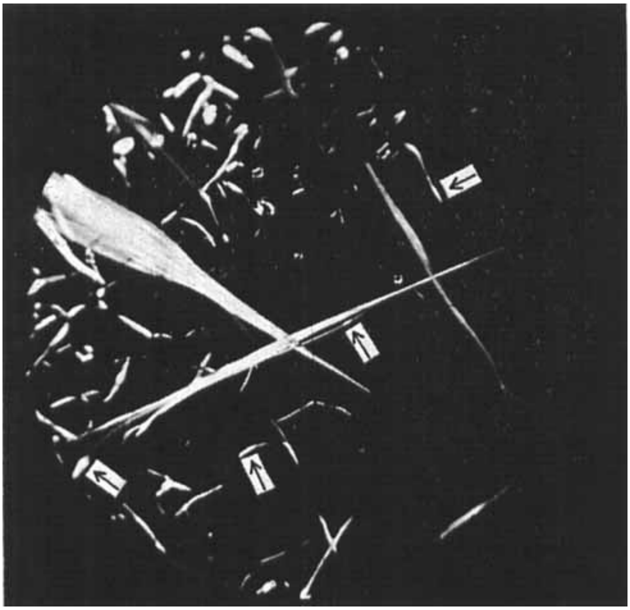


Figure 7. Same field as Fig. 6 after warming. The arrows indicate areas where *M* phase has not yet transformed to the *SS* phase.

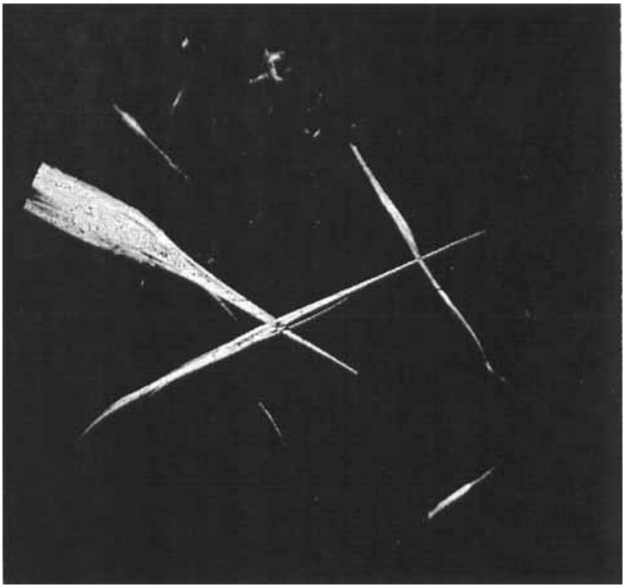


Figure 8. Same field as Fig. 7. Transformation to *SS* phase complete.

Phase Rule, since the *M* phase contains much more water per molecule of DSCG than does *SS*. On raising the temperature the reverse transformation occurs, the *M* deposited from solution dissolving and the pseudomorphs changing back to *SS* needles. The near completion of this stage is shown in Fig. 7, in which the arrows point to places on the long needles at which there is thickening owing to the presence of *M* phase which is as yet untransformed. When the transformation is complete the *SS* needles in their original positions and without any apparent alterations in shape are regained (Fig. 8: compare this with Fig. 5). This remarkable pseudomorphic transformation can be repeated a number of times on the same specimen without destroying the pattern of the *SS* needles.

In *SS* crystals containing about $5H_2O$ the α-axis (the " fast " axis) of the indicatrix makes the small angle of 13° with the axis of elongation of the needles.⁽¹⁾ The negative optical sign shows that the planes of the molecules must be at least approximately normal to the α-axis and thus to the axis of elongation of the crystals. Complete crystallographic data for *SS* in equilibrium with *M* at 73°, i.e., containing $9H_2O$ (*A*, Fig. 2) are not available, but there is no reason to suppose that the orientation of the molecules in such crystals is very different from that just stated, since observations made during the transformation experiments, in which the *SS* needles were lying in random orientations around the axis of elongation, showed that their "fast" vibration direction was uniformly parallel or nearly parallel to this axis. In any case the exact orientation of the molecules is not important for the considerations which follow.

The *M* pseudomorphs also have a " fast " length, and observations on interference figures given by optically homogeneous regions[†] show that this direction is also the optic axis, so that the optical sign is negative. This, taken in conjunction with the fact that the pseudomorphs are formed without an increase in length with respect to the parent *SS* needles (see above), indicates that the molecular planes are substantially normal to the axis of elongation of the pseudomorphs as as well as to that of the needles.

The smooth and reversible nature of the transformations between the *SS* phase and *M* phase suggests that they take place with the

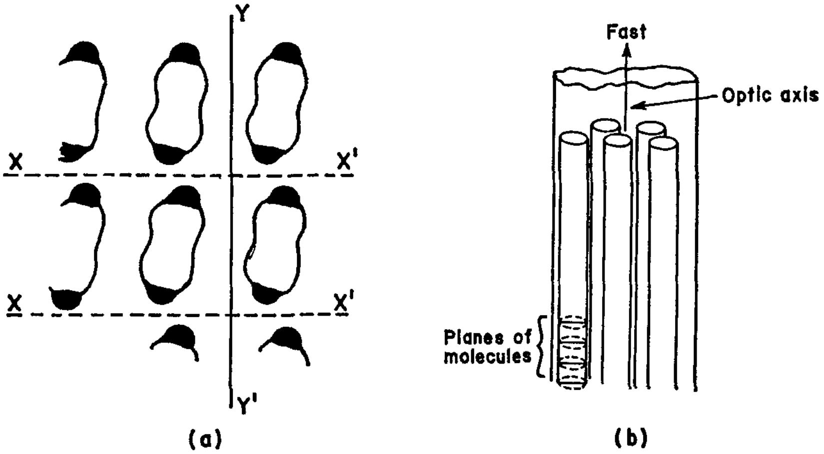


Figure 9. (a) Structure of cross section of an *SS* needle, schematic. (b) Optical orientation and structure of an *M* pseudomorph.

[†] The pseudomorphs commonly show transverse striations which are narrow sections slightly misoriented from the main direction of the structure. Areas in which these occur are avoided in obtaining interference figures.

minimum disturbance of the molecules. Consider first a structure for the *M* phase which might be proposed on the basis of the fact that DSCG has, like a disoap, two terminal polar groups. The arrangement of the molecules in the cross section of an *SS* needle must be essentially as shown in Fig. 9(a), in which the molecules are represented schematically with the –COONa polar groups as heavy black " knobs ". (The recent X-ray evidence points to the molecules being tilted in the approximately rectangular unit cell as in the figure, and as might be expected from general packing considerations.)

If now the transformation consisted of intrusion of water along the planes XX′, a lamellar structure would result in which the layers of DSCG molecules were bounded on both sides by their polar groups in contact with the water. Further, if at the same time, the DSCG molecules gained the freedom to turn into random orientations around the direction normal to the layers (YY′), or alternatively, if the separate layers by a rotation in their own planes achieved a random orientation around this direction, then uniaxiality and a lamellar

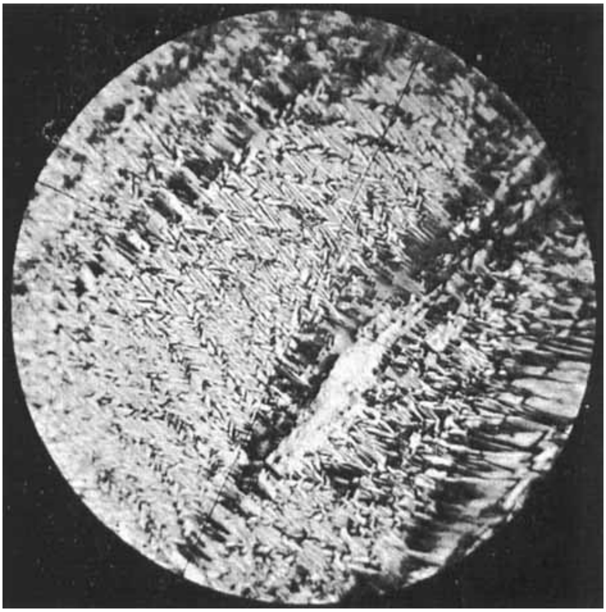


Figure 10. Herringbone texture developed by the *M* phase.

" *G* " type of phase (using the nomenclature of P. A. Winsor⁽⁴⁾) would result. But such a structure must be ruled out because (i) it would be optically positive, (ii) the optic axis would lie at right angles to the long axis of the pseudomorph, and (iii) X-ray diffraction spacings (see later) would bear the ratio 1: 1/2: 1/3: 1/4, and all these consequences are contrary to what is found.

The optic orientation and optical sign of the pseudomorphs are consistent with a " middle " phase type of structure in which the molecules are grouped into rods of indefinite length and parallel to the optic axis, and with the average orientation of the molecular planes at right angles to the axes of the rods (Fig. 9(b)). The formation of this structure from the *SS* needles can be imagined as involving the DSCG molecules in little more than simple rotations in their own planes. X-ray diffraction results to be described below support this structure. Moreover, the following microscopically-observed textures given by the *M* phase provide further support to this conclusion. Figure 10 shows a zig-zag or herringbone texture

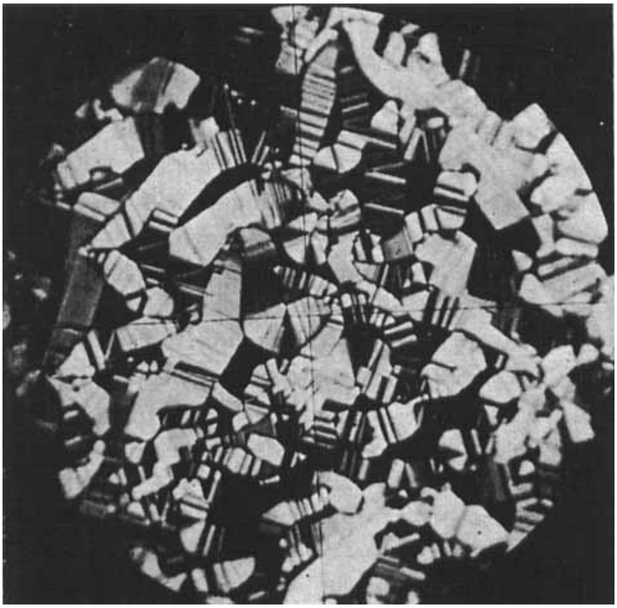


Figure 11. Striated bands and spherulites formed by the *M* phase.

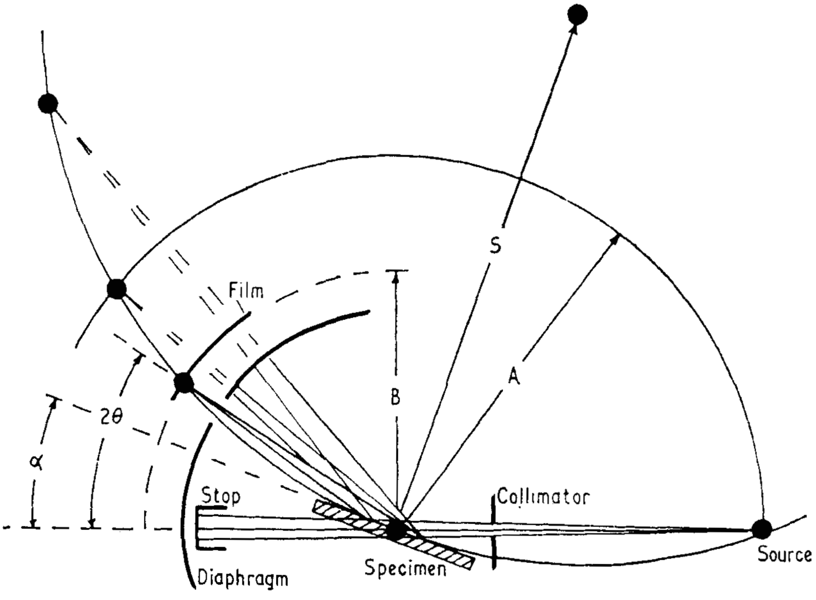
frequently developed by the *M* phase when formed by the loss of water around the edges of a film of *N* phase between a slide and cover slip on standing. Figure 11 shows a confused texture of striated bands and spherulites which develop when the *M* phase, resulting from the transformation of *SS* crystals as in Fig. 6, is allowed to cool slowly to room temperature. The zig-zag and striated appearances in these textures are due to adjacent narrow strips in the structures having slightly different extinction positions. Both these textures are commonly shown by certain middle phases of other amphiphile-water systems, and the zig-zag alternation of extinction directions has been discussed by J. Rogers and P. A. Winsor.⁽⁵⁾

THE TRANSFORMATION BETWEEN THE *N* AND *M* PHASES

A study of this transformation in both directions, made by changing the temperature of appropriate mixtures through the peritectic point at 42° (Fig. 2) has shown that it too is pseudomorphic. Observations may conveniently be made near the junction between the *N* and *M* phases in a thin film, originally consisting of *N* only, which has undergone peripheral evaporation as described above. (Figure 13 in Ref. 1 gives a good illustration of such a two-phase region.) The composition of any part of the preparation which is near the junction must be near to that indicated by arrow *C* in Fig. 2. An area of the *N* phase which is in this region and which is sufficiently optically uniform to give a recognizable interference figure (usually an optic normal one) is selected, and the direction of the optic axis noted. On raising the temperature slowly through 42°, partial melting first occurs at a large number of closely-spaced points giving the preparation a stippled appearance, and this is followed by transformation to the *M* phase. This shows a fine zig-zag texture (Fig. 10), but it is usually sufficiently optically uniform to give a recognizable optic normal figure with the direction of the optic axis the same as that of the original *N* phase. On lowering the temperature the latter phase is recovered in its original orientation. Apart from the development of the zig-zag texture in the *M* phase which indicates that some kinking has occurred to allow this more highly ordered phase to occupy the available space (see Rogers and Winsor⁽⁵⁾), no dimensional changes are observed during the transformation.

3. X-Ray Study of the Mesophases

X-ray diffraction data for the *M* phase were first obtained with a Guinier-type camera with an asymmetrically cut bent quartz crystal monochromator to isolate the cobalt Kα radiation. The sample was contained between two sheets of 6 μm Mylar film and held in a rotating holder. The sample thickness was nominally 0.25 mm. The specimen holder surface was at an angle of 60° to the incident beam. A single, sharp, intense, low-angle diffraction line was obtained and a broad line from 3.42–3.48 Å. The position of the sharp, low-angle line varied with the concentration of DSCG; the position of the broad line was invariant. The penalty of using crystal reflected radiation (i.e., strictly monochromatic) was that long exposures were necessary.



Diffraction geometry of the Brentano arrangement

$$\operatorname{Tan} \alpha = \frac{A \sin 2\theta}{B + A \cos 2\theta}\,;\ \sin \alpha = \frac{A}{2S}$$

where α = angle between the incident beam and the specimen plane, A = distance between the source and specimen axis, B = radius of the Brentano circle, S = radius of the Seeman-Bohlin circle.

Figure 12. Basic geometry of Nelson diffractometer.

As preferred orientation of the liquid crystals might well be present in the thin specimen layer, it was necessary to determine if other diagnostic lines existed. This required the use of a different diffraction geometry from the asymmetric transmission-type used above. These investigations were facilitated by using a new diffractometer designed by Dr. J. B. Nelson.⁽⁶⁾ The basic geometry of this diffractometer is shown in Fig. 12. It uses the asymmetric para-

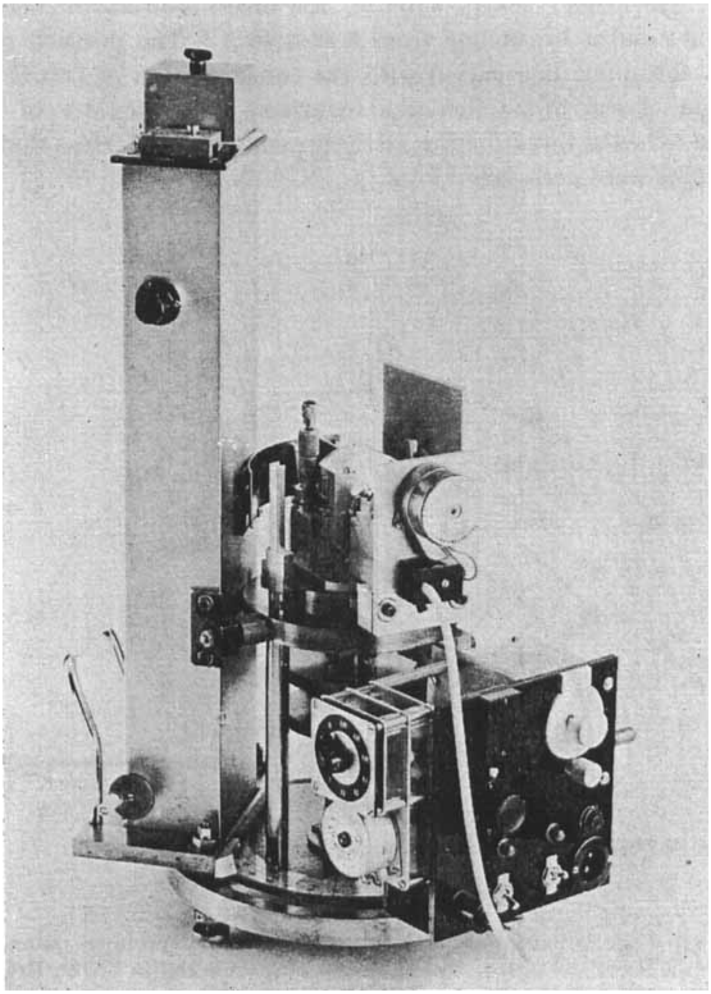


Figure 13. Nelson diffractometer with film cassette in position.

focusing geometry of Brentano(7) and the use of the oscillating diaphragm ensured that diffraction lines were recorded only when the parafocusing condition was fulfilled. In addition to using the diffractometer (Fig. 13) in the reflection mode with a flat, rotatable specimen holder shown in Fig. 14, the value of a transmission rotating specimen holder and a stationary reflection specimen holder which could be turned through 180°, were also assessed. Both of these sample holders enable the scattering patterns to be recorded on both sides of the direct beam position and thereby permit accurate pattern measurements to be made without the use of calibration specimens.

The diffraction patterns were recorded on film held in a curved configuration inside a light-tight cassette. This had the advantage that the diffraction data from the calibrating specimens, the direct beam and the experimental samples were all recorded on a single piece of film (Fig. 15) and precise calibration marks, such as the direct beam position, could be ascertained. When it was found that

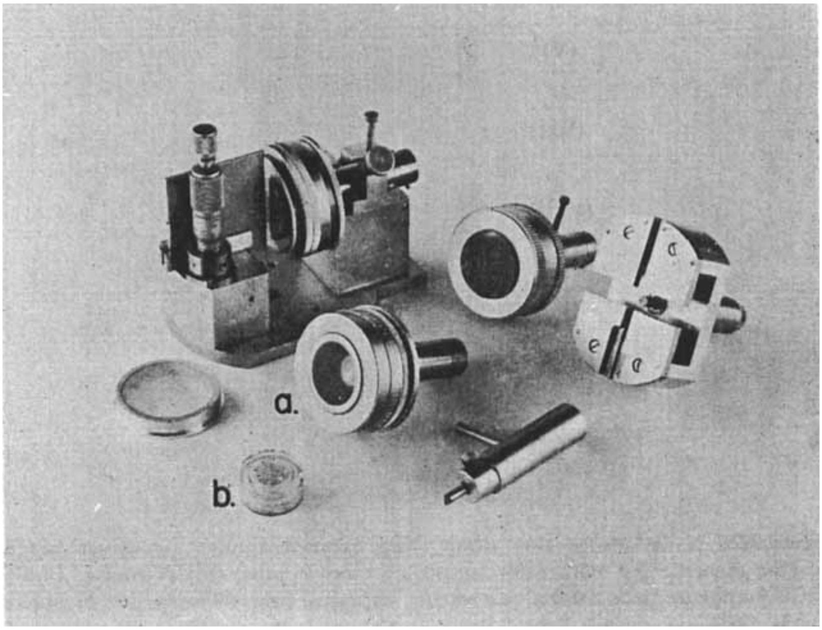


Figure 14. Specimen holders for Nelson diffractometer. (a) The rotatable specimen holder, (b) the inserted holder.

the direct beam position could be readily and accurately found by calibration with zinc stearate powder in the reflection holder which recorded on one side of the beam position only, it was decided not to use the other methods, on account of their longer exposure times.

The specimens were enclosed in a rotatable reflection holder with

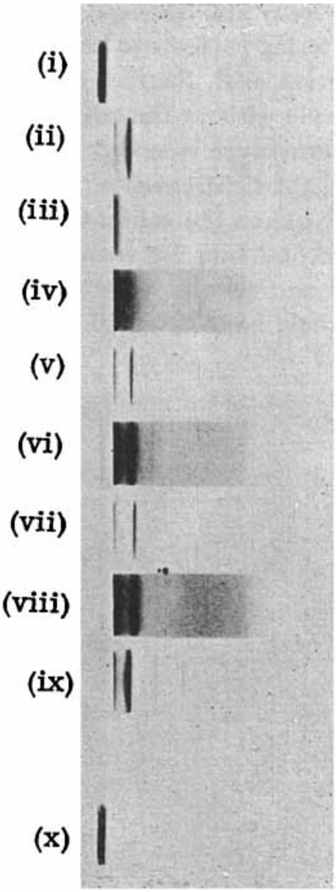


Figure 15. X-ray diffraction film. The exposures are: (i) direct beam, (ii) zinc stearate for calibration, exposure time 9 mins, (iii) *N* phase, 13.6% DSCG, exposure time 9 mins, (iv) as (iii), exposure time 60 mins, (v) *M* phase, 20.0% DSCG, exposure time 9 mins, (vi) as (v), exposure time 60 mins, (vii) *M* phase, 23.8% DSCG, exposure time 9 mins, (viii) as (vii), exposure time 60 mins, (ix) as (ii), (x) direct beam. The two faint lines are indicated by dots in exposure number (viii).

2 μm thick polycarbonate film which gave a very low background scattering. It was found that this specimen-supporting film was necessary in order to record any weak specimen diffraction lines which might be superimposed on the X-ray scattering of the intramolecular DSCG or water patterns. The liquid crystal specimens themselves were spread in a thin layer on this polycarbonate film and a small inserted holder (Fig. 14), full of the same liquid crystal composition, was also enclosed to prevent the thin layer of liquid crystals from drying out. The polycarbonate film was slightly permeable to water and in 48 h the liquid crystal film had noticeably dried. It was therefore essential to use short recording exposure times.

The diffraction patterns given by the diffractometer were recorded with iron-filtered cobalt radiation. With the reflection-type parafocusing Nelson diffractometer, two exceedingly faint but sharp lines, designated d_2 and d_3 in the table below were observed, in addition to the intense, sharp lines, designated d_1, already seen in the Guinier-type transmission camera patterns. The failure to observe this very faint pair of lines with the strictly monochromatic Guinier-type camera probably arises from the existence of preferred orientation of the M phase in both types of specimen holder. In order to measure the intense low-angle lines precisely and to record the weak pair of lines, it was necessary to use two exposures, one of 9 min for the former and 60 min for the latter. Over this period no water loss from the specimens was detected. The compositions of the liquid crystals were determined on a separate sample by drying to constant weight at 150 °C.

As this observation of the weak pair of lines was associated with filtered rather than crystal reflected monochromatic radiation, it was necessary to establish whether the faint lines were indeed arising from the Kα reflections of cobalt or from radiations characteristic of elemental impurities in the X-ray anode focal area. The dangerous lack of attention in structural studies to the presence of target impurities was pointed out many years ago(8) but many authors still continue to be neglectful. The procedure recommended in that paper was followed again. As no target impurities were found, the faint lines did indeed represent true structural features.

The diffraction data for seven M-phase liquid crystal compositions, recorded at 18–20 °C, is shown in Table 1.

TABLE 1 Recorded X-Ray Diffraction Data for M-Phase Liquid Crystals

wt./wt.% DSCG	w	d_1(Å)	d_2(Å)	d_3(Å)
20.0	21.9	36.8	21.9	19.0
20.8	22.9	35.6	21.2	18.2
23.9	26.6	33.6	19.7	16.9
27.6	31.4	31.7	18.3	15.9
31.9	37.0	29.3	16.9	14.7
36.5	43.7	26.7	15.7	—
38.1	45.7	26.0	—	—

w is number of grams of DSCG in 100 cc of liquid crystals.

As already mentioned, a broad line from 3.42–3.48 Å was also recorded. The position of this broad line did not change with composition and was present when the N-phase liquid crystals were X-rayed but not when a 6% solution was X-rayed. This broad line is considered to result from some preferred inter- or intramolecular distance. Its absence in solution may be evidence that it results from an intermolecular spacing in the liquid crystals but it is possible that, at the increased dilution in the solution, it is not detectable. If it is associated with an intermolecular spacing, it means that this preferred distance exists in both the M and N phases.

As shown in Table 2, the three diffraction lines which have been recorded for most concentrations of the M-phase liquid crystals,

TABLE 2 X-ray Diffraction Data for M-Phase Liquid Crystals Showing Relationship of d_1, d_2 and d_3

d_1(Å)	$\sqrt{3}d_2$(Å)	$\sqrt{4}d_3$(Å)	$\bar{d}_1$	d_p
36.8	37.9	38.0	37.6	43.3
35.6	36.7	36.4	36.2	41.7
33.6	34.0	33.8	33.8	39.0
31.7	31.7	31.8	31.7	36.8
29.3	29.2	29.4	29.3	33.8
26.7	27.2	—	26.9	31.0
26.0	—	—	26.0	30.0

d_p is $2d_1/\sqrt{3}$, the spacing between rod centres (see below).
$\bar{d}_1$ is the mean of d_1, $\sqrt{3}d_2$ and $\sqrt{4}d_3$.

have the ratio of $1 : 1/\sqrt{3} : 1/\sqrt{4}$ to each other. This is indicative of the hexagonal arrangement of rods constituting the structure of middle phases in lyotropic liquid crystal systems.(4,9)

When the values of $\bar{d}_1$ shown in Table 2 were plotted against $1/\sqrt{w}$, where w was the number of grams of DSCG in 100 cc of liquid crystals, a straight line was obtained. Bernal and Fankuchen,(10) in their classical paper on viruses, stated that a consequence of this simple relationship between volume concentration and $\bar{d}_1$ is that the rods in the hexagonal array in these systems distribute themselves so as to fill the available space as uniformly as possible. A further implication is that with the changes in concentration, the rods do not change significantly in their composition but only separate in directions normal to their axes.

In the *M* phase, if the rods are assumed to be cylinders with circular cross-section, then it is possible to calculate the cylinder diameter from the formula(13):

$$d_c = d_p(2\sqrt{3}\phi/\pi)^{1/2}$$

where d_c is the diameter of the cylinders
d_p is the distance between the cylinder centres, $2d_1/\sqrt{3}$
ϕ is $[1 + \bar{V}_w/\bar{V}_a(1 - C)/C]^{-1}$
$\bar{V}_w$ is partial specific volume of water
$\bar{V}_a$ is partial specific volume of amphiphile
C is weight concentration of amphiphile.

The density of liquid crystals with a composition of 19.7% DSCG, was determined by the density bottle method. This was the highest concentration of DSCG which was sufficiently fluid to permit the use of this method. The density was determined as 1.094 g/cc and from this value a reasonable estimate of the partial specific volume of DSCG was made.

The cylinder diameters in Table 3 have been calculated from the above formula.

The calculated cylinder diameter was constant and had a mean value of 16.0 Å. These calculations were based on a model having DSCG cylinders in a continuum of water, with the polar —COONa groups on the outside of the cylinders, and assumed complete separation of the DSCG and the water. Such a structure is designated an M_1 type of middle phase in the nomenclature of P. A. Winsor.(4)

The constancy of the calculated diameter suggested that the model was essentially correct.

TABLE 3 Cylinder Diameters Based on a Model with Complete Separation of Water and DSCG

Weight % DSCG	$\bar{d}_1$(Å)	d_p(Å)	d_c(Å)
20.0	37.6	43.3	16.0
20.8	36.2	41.7	15.7
23.9	33.8	39.0	15.9
27.6	31.7	36.8	16.2
31.9	29.3	33.8	16.2
36.5	26.9	31.0	16.1
38.1	26.0	30.0	16.0

d_p is the distance between the cylinder centres.

d_c is the cylinder diameter.

The N phase of composition 13.6 wt.% of DSCG was also analyzed. A broad and weak diffraction maximum occurred at a low angle and the band at 3.42–3.48 Å was also recorded. The low angle diffraction maximum was only recorded with the conditions used for the d_2 and d_3 lines of the M phase. No sharp diffraction lines were recorded for the N phase. When interpreted using the Bragg equation, the centre of this broad low angle line occurred at 44.5 Å. This value continued the steady increase of d_1 with decreasing DSCG concentration. Clunie *et al.*(11) have noticed a steady change in the "*d*" spacing of sharp first order diffraction lines across liquid crystal phase boundaries. However, in the present case, there is no justification for using the Bragg equation to interpret such a single broad diffraction line. Klug and Alexander,(12) among many others, have pointed out that it is unwise to assume that Bragg-type diffraction scattering is responsible for such a broad low-angle line. Nevertheless, it is likely that this line results from some statistically preferred, but unknown, distance between the DSCG molecules in the N phase.

4. Discussion

THE *M* PHASE

The X-ray diffraction data have been used to calculate(13) the cylinder diameters for a model with water cylinders in a DSCG matrix (M_2 type of structure(4)) although such a structure is difficult to visualize with Geddes's conformation of DSCG. The results show a decreasing cylinder diameter with increasing DSCG concentration, in contrast to the constant diameter obtained for the M_1 model (above). While this constancy does not prove that the M_1 model is correct, it does suggest that it is the more probable alternative. There is another reason for preferring the M_1 model. According to theoretical reasons put forward by Winsor,(4) the plane layers of polar groups in a " *G* " lamellar phase should on the addition of more water tend to become convex towards the water region, leading to the formation of an M_1 phase. As indicated earlier in this paper we do not think that a *G* phase occurs in the DSCG-water system, but similar considerations would seem to apply to the plane layers of polar groups in contact with water molecules in the *SS* solid solutions.

Although the above evidence points to an M_1 structure, the cylinder diameter calculated from the X-ray data may be too low. The number of molecules per unit length has been calculated by the method used by Luzzati(13) and it is 0.420 or 1 molecule/2.38 Å if the molecules are stacked one upon the other. The unit cell dimension is approximately 3.9 Å in the direction of crystal elongation, which, judging from the pseudomorphic transformation between *SS* and *M* phase, is also the rod axis direction in the *M* phase. From a study of a model of the molecular conformation found by Geddes, it can be seen that this dimension could be reduced from 3.9 Å to 2.4 Å in passing from the crystal to the *M* phase if the two ring systems were to become more closely co-planar. Although such a change is possible, there is an alternative explanation as is shown below.

The usual model for the cylinder diameter calculation (as used above) assumes complete separation of the water and amphiphile. This is a reasonable model when considering a chain molecule with a hydrophilic head but its direct application to the present middle phase formed with an essentially planar molecule can be questioned. The crystals (*SS*) take up 9–10 molecules of water at 20 °C before the structure collapses and *M* phase liquid crystals are formed. As this amount of water is closely associated with the DSCG molecule in the crystalline state, it does not seem logical to use a model for the *M* phase which assumes complete separation of water and DSCG, especially since hydrogen bonding with water may be necessary to hold the molecules in an approximately planar configuration in the mesophases. (Recent work(2) has shown that this molecule does not possess free rotation at the bridge, even in dilute solution, but is still approximately planar.) We have therefore repeated the cylinder diameter calculations for two conditions: first, assuming 10 molecules of water/molecule of DSCG in the cylinders, i,e.. approximately the amount of water in the crystals (*SS*) when they collapse to the *M* phase; secondly, working back from the maximum possible cylinder diameter. The latter has been derived from the hexagonal spacing which corresponds to the most concentrated *M* phase and assumes that the cylinders have circular cross section and do not overlap. The cylinder diameter with the 10 molecules of water/molecule of DSCG within the cylinder is 20.4 Å. For a cylinder diameter of 28.0 Å, close to 30 Å, the last entry for d_p in Table 2, the number of molecules of water/molecule of DSCG within the cylinder is 33. The calculated number of molecules of DSCG/unit length of the cylinder is not changed when some water is treated as being within the cylinders and the cylinder diameter is re-calculated. However, with this model, the DSCG molecules do have a larger volume in which to distribute themselves and achieve the calculated value of 0.42 molecules/unit length. Consequently, less change in molecular conformation would be necessary during the transformation between the crystals and the *M* phase. It is not possible at this time to determine absolutely the most probable number of molecules of water/molecule of DSCG which are to be considered within the cylinder diameter, but we believe from the above that it may well lie in the range 10–30 molecules of water and will not vary with concentration. To preserve the amphiphilic character of the molecule, it seems likely that the water will be associated with the carbonyl and carboxyl groups. For any fixed ratio of water to DSCG within the cylinders, the cylinder diameter is constant. The linear relationship between d_1 and $1/\sqrt{w}$ strongly suggests that the additional water associated with decreasing DSCG concentration goes between the rods and the composition of the rods remains constant.

THE *N* PHASE

Nematic-like textures have been observed in some other amphiphile-water systems. For example, in the aqueous glyceride systems studied by K. Larsson(14) they are shown by submicroscopic dispersions of droplets of a lamellar phase in water, produced by the vigorous stirring or agitation of coarser dispersions of the droplets which appear spontaneously within certain ranges of temperature and composition. The droplets are believed to be drawn out into threads in the finer dispersions. Also a streaky texture (so-called " schlieren " texture) has been observed in certain *C*- and *F*-type smectic phases when prepared between specially cleaned glass surfaces,(15) though it is not clear how such a texture can be related to the stratified structure generally held to be a characteristic property of all smectic phases. The texture shown by the *N* phase of DSCG-water mixtures, however, appears regularly and spontaneously whenever the appropriate range of composition and temperature is entered, and without any special treatment of the medium itself or of the glass surfaces confining it. It seems highly unlikely therefore that it can be of any kind of modified lamellar or smectic phase as in the cases just cited. A more detailed optical study of it would probably throw some additional light on the structure.

Champion and Meeten(2) have shown that DSCG forms into agglomerates in 1% solution and, as the concentration is increased, this tendency increases and the agglomerates form more rapidly. Some association into planar micelles in the *N* phase is therefore probable. The fact that the transformation between the *M* and *N* phases proceeds so smoothly and reversibly, and without a change in optic orientation, suggests that in the direction $M \rightarrow N$ a break-up of the rods takes place by simple translations and rotations of the planar molecules, mainly in their own planes, leading to the nematic type of structure.

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