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T. K. Attwood[a]; J. E. Lydon[a]; C. Hall[b]; G. J. T. Tiddy[b]
[a] Astbury Department of Biophysics, University of Leeds, Leeds, England [b] Unilever Research, Port Sunlight Laboratory, Merseyside, England

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The distinction between chromonic and amphiphilic lyotropic mesophases

by T. K. ATTWOOD and J. E. LYDON
Astbury Department of Biophysics, University of Leeds, Leeds LS2 9JT, England
C. HALL and G. J. T. TIDDY
Unilever Research, Port Sunlight Laboratory, Bebington, Wirral, Merseyside L63 3JW, England

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Optical microscopy, X-ray diffraction and NMR spectroscopy have been used to examine whether the hexagonal phases of representative chromonic and amphiphilic mesogens are miscible. The systems studied were octaoxyethyleneglycol dodecylether with either disodium cromoglycate or 5-*n*-hexyl-7-(5-methylsulphonimidoyl) xanthone-2-carboxylic acid. The results clearly demonstrate that the hexagonal phases of these two systems are not miscible, although miscibility does occur in the isotropic solution. These observations suggest that chromonic mesophases are a new breed of lyotropic liquid crystals.

1. Introduction

1.1. *Lyotropic mesophases*

The most frequently encountered types of lyotropic mesophase are those formed by surfactant/water mixtures. There are, however, other kinds of lyotropic mesophase: rigid polymers can form liquid crystal phases in both aqueous and non-aqueous solvents [1] and a third category, which has received much attention, is that formed by rigid, polarizable polyaromatic compounds in water. This last type of mesophase, which has been termed chromonic [2], was first characterized for anti-asthmatic/anti-allergic drugs. Some ionic dyes [3, 4] share this property also. Indeed, it would appear that such phases are widespread and have been repeatedly encountered in the past [5–8] but that their nature had not been generally appreciated. Thus the aqueous mesophases of the substituted phenanthrene and naphthalene sulphonic acids reported in 1915 by Sandquist [5] and in 1927 by Balaban and King [6] are probably of this kind. There are two well characterized chromonic phases. Both consist of columns of molecules stacked in an untilted fashion. In the M phase the columns lie in a hexagonal array, whereas in the more dilute nematic N phase these columns are separated by so much water that the hexagonal ordering is lost and only the parallel alignment of the columns is retained (see figure 1). From the point of view of their chemical nature, lyotropic mesophases can be divided into three separate groups, based on the very distinct structural elements that comprise the phases. The three groups are amphiphilic, chromonic and polymeric phases. Their properties are compared in table 1.

The miscibility criterion [9] has proved to be exceptionally valuable for the characterization of thermotropic smectic and discotic phases. The basic concept is that if two mesophases of different compounds exhibit an uninterrupted mixed liquid

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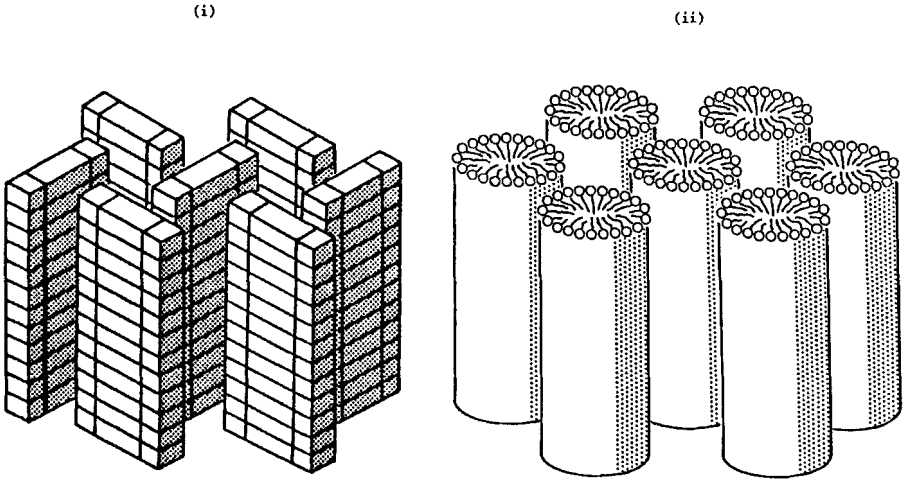

Figure 1. The structural distinction between the hexagonal H_1 phase of conventional amphiphiles and the hexagonal M phase of chromonic systems. (i) In the M phase of chromic systems, the molecules are stacked into columns rather than micelles. The driving force causing the molecular aggregation arises from enhanced dispersion forces between the aromatic rings and there is no requirement either for a division of the molecule into a hydrophilic head and a hydrophobic tail or for any flexibility within the molecule. The hexagonal symmetry arises from the hexatic, dynamic herringbone structure (in a fashion similar to that visualized for the structure within each layer of the thermotropic smectic B phase). (ii) In the H_1 phase the hexagonal array results from the packing of cylindrical micelles of more or less circular cross-section. The driving force causing the aggregation of molecules into these micelles results from the segregation of hydrophobic and hydrophilic regions. There must, therefore, be a clear distinction between the hydrophilic head and the hydrophobic tail of each molecule. Furthermore, in order to fill the awkward space in the interior of the micelles, the hydrophobic parts of the molecules need to be in a fluid state.

crystal phase across a phase diagram, then these two mesophases are of the same type. It is important to stress that the converse does not hold: that two phases do not mix is not necessarily evidence that they are of a different type. This investigation was carried out to determine whether amphiphilic and chromonic phases are miscible. Before the investigation, we did not know what result to expect. On the one hand, because of their completely disparate chemical natures it appeared to be inevitable that the two systems would prove to be immiscible. Conversely, on the other hand, it could have been argued that because both mesophases consist of elongated assemblies dispersed in a water continuum, and in arrays with the same symmetry, they ought to be able to mix in all proportions. From the latter viewpoint it is difficult to see how the chemical differences of the molecular assemblies can be transmitted through the 20 to 30 Å of water separating them in such a way as to make the mixed system mesogenically unviable.

The miscibility approach is not routinely applied to the characterization of lyotropic phases. However, conventional hexagonal (H_1) phases are in general miscible, provided that their temperature ranges, water activities and chemical natures (ionic type) are not grossly incompatible. Moreover, it has been our experience that, in at least some instances, chromonic phases of different drugs are unquestionably miscible, indicating a close qualitative similarity of structure. Purely geometric considerations would appear to rule out the miscibility of phases with grossly dissimilar structures

Table 1. Properties of different chemical classes of lyotropic mesophases.

	Amphiphilic	Chromonic	Polymeric
Molecular structure	Molecules with distinct hydrophilic and hydrophobic parts (usually flexible alkyl chains)	Planar polyaromatic molecules bearing hydrophilic substituents	Linear rigid polymers
(Typical compounds)	(Soaps, Detergents)	(Drugs, dyes)	(Biological polymers including cellulose actin and nucleic acids)
Surface properties	Highly surface active	No special surface activity	Can be surface active
Type of molecular aggregation	Micellar aggregates form only above a critical concentration, due to the hydrophobic effect. Micelles can be spherical, cylindrical, disc-shaped or extended double lamellae	No critical concentration; gradual aggregation process at low concentrations. Molecules usually stack forming untilted columns	None
Thermal behaviour	Exhibit a Krafft temperature	No Krafft temperature	No Krafft temperature
Mesophase type	Cubic, hexagonal (H_1), lamellar and/or inverse phases; micellar nematic phases	Nematic (N) and hexagonal (M) phases well established (layer structures also suggested)	Nematic arrays only
X-ray diffraction patterns	Characteristic diffuse 4·5 Å reflections arising from the aggregation of fluid alkyl chains	Characteristic strong, sharp 3·4 Å reflections arising from the stacking of aromatic molecules	No general characteristic features

(for example systems consisting of rods and those consisting of lamellae) but they would not prohibit the miscibility of phases with generally similar structures, such as cylindrical micelles of the hexagonal phase with the polymer mesophase. In such situations, however, energetic interactions may prevent mixing, especially because the entropy of mixing is small [10]. If there are repulsive interactions between micelles and polymer molecules, this would tend to lead to the production of two coexisting mesophases. On the other hand, if there are attractive interactions, these could result in the binding of aggregates to the polymer, disrupting both mesophases and giving either an isotropic solution or causing the precipitation of another phase. We would expect, therefore, polymer systems to be generally immiscible with those of other classes of lyotropic mesophases. The most likely case where miscibility might occur appears to be for mixtures of the hexagonal phases of amphiphiles and chromonic systems: the molecular aggregates have similar dimensions and the mesophases form at comparable volume fractions in water. We report here the first investigation of such mixed systems.

We had assumed that the closer the similarity in the physical parameters of the two mesophases, the greater the likelihood that they would be miscible. Hence we endeavoured to select an amphiphile system showing an H_1 phase at room temperature and having a water content (and therefore activity) more or less compatible with that of the chosen chromonic M phases. With this in mind, we chose for investigation ternary systems involving the non-ionic surfactant octaethyleneglycol dodecylether [11], ($C_{12}EO_8$; $CH_3(CH_2)_{11}O(CH_2CH_2O)_8H$) and the anti-asthmatic drugs disodium cromoglycate (SCG) and the anti-allergic drug (5-*n*-hexyl-7-(5-methylsulphoniumidoyl) xanthone-2-carboxylic acid (HMSXC, sodium salt) shown in figure 2. A non-ionic surfactant was chosen so that there would be no electrostatic repulsions between the two types of aggregates. Cationic surfactants were not considered suitable because it was known that attempts to mix cationic and anionic amphiphile hexagonal phases result in lamellar phases or insoluble precipitates. SCG was an obvious choice, being the most studied non-amphiphilic mesogen to date. HMSXC, on the other hand, was chosen by virtue of its being the only chromonic drug known to possess a significant

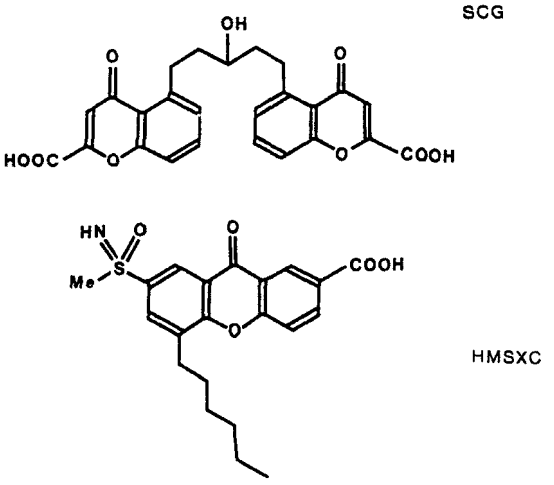

Figure 2. Molecular structures of the chromonic drugs SCG and HMSXC. The sodium salts were used in this study.

alkyl chain component (C_6). We wished to establish to what extent this hydrophobic element played an analogous role to those of amphiphilic molecules in promoting chromonic phases or whether such a mixture could induce the drug to participate in micelle formation in the conventional manner.

2. Experimental

2.1. *Materials*

The amphiphile $C_{12}EO_8$ was obtained from Nikkol Chemicals (Tokyo). The drugs SCG and HMSXC were obtained from Fisons and Roussel, respectively. Heavy water (^2H_2O) was supplied by BDH Ltd. All materials were used as supplied.

2.2. *Optical microscopy*

Microscope studies were carried out either with a Vickers polarizing microscope equipped with a Mettler FP52 heating stage with a FP5 control unit or a Reichert Thermopan microscope and Koffler hot stage. Samples were mixed thoroughly and equilibrated in sealed glass tubes for several weeks prior to examination between slide and cover slip. The micrographs were taken using a Zeiss Ultraphot or a Reichert camera attachment.

2.3. *X-ray diffraction*

Diffraction studies were carried out with a camera designed to obtain fibre diffraction patterns, with a speciment to film distance of 60 mm. Samples were contained in 0·2 mm diameter Lindemann glass tube capillaries. Exposure times were of the order of two or three days and were all made at ambient temperatures, nickel filtered CuK_a radiation was used. In view of the somewhat lengthy exposure times, the samples were checked optically following each diffraction run to ensure that no phase changes had taken place.

2.4. *Nuclear magnetic resonance spectroscopy*

The NMR spectra were recorded using a Bruker CPX-300 spectrometer operating at 46·07 MHz and 79·39 MHz for ^2H and ^{23}Na resonances, respectively.

3. Results

A series of SCG/$C_{12}EO_8$ and HMSXC/$C_{12}EO_8$ samples was prepared having the compositions given in figure 3. The phases present were determined by optical microscopy, low-angle X-ray diffraction and NMR spectroscopy. We considered that the combination of these three techniques would enable the various mesophases to be identified with some degree of certainty.

3.1. *Optical microscopy*

Examination of the samples by optical microscopy gave the results listed in table 2. The numbers listed for each mesophase are the melting temperatures of the phase regions (to form an isotropic solution). With the SCG/$C_{12}EO_8$ system, samples at the extremes of the composition range showed the familiar textures characteristic of the two pure mesophase types. The remainder of the samples, however, had a

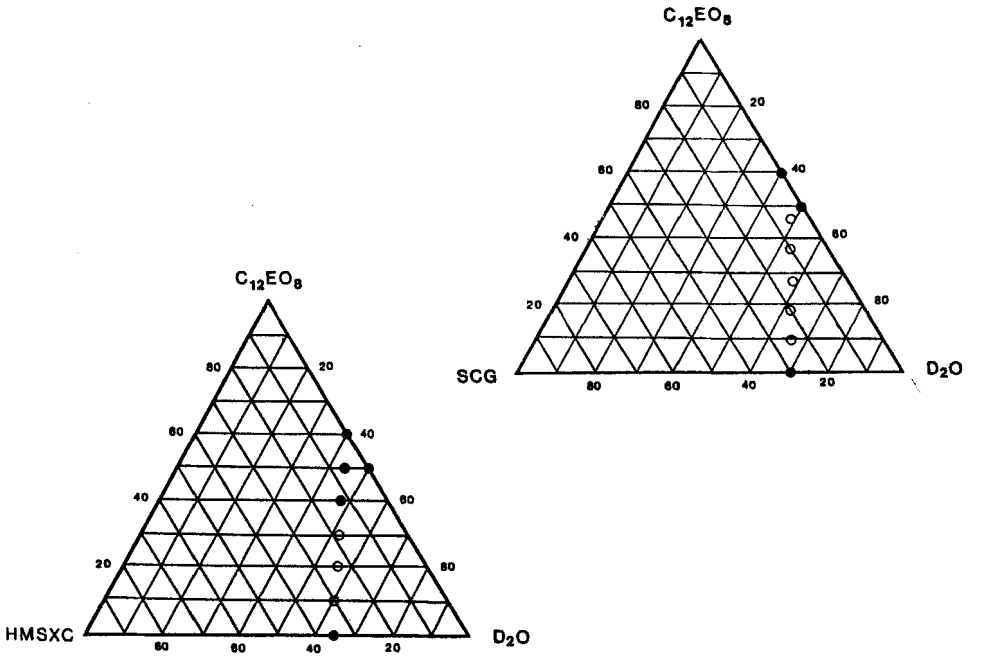

Figure 3. Ternary phase diagram showing the compositions (wt %) of the samples used for the study of the mixed amphiphile/chromonic systems. Optical textures of some of these mixtures are shown in figure 4. The solid circles represent one phase regions and the open circles represent multi-phase regions.

Table 2. Transition temperatures (mesophase–isotropic) for the two mixed systems as observed by optical microscopy.

$C_{12}EO_8$/wt %	SCG/wt %	$T_{MI(L_1)}$/°C	$T_{H_1L_1}$/°C
50	0	–	57
45·8	5	54	44
36·7	10	68	46–8
27·5	15	67	46–8
18·3	20	67–8	46–8
9·2	25	66	44
0	30	60	–
$C_{12}EO_8$/wt %	HMSCX/wt %	$T_{MI(L_1)}$/°C	$T_{H_1L_1}$/°C
60	0	–	53
50	6	–	42
40	12	–	48
30	18†	37	27
20	24†	50	29
10	30†	62	–
0	36	92	–

† Isotropic solution phase also present at 25°C.

curdled appearance, where domains of the two separate components could be readily distinguished by their disparate birefringences. When pressure was applied to the cover slip, the samples distorted in a manner indicating structural inhomogeneity, with isolated rafts of one component flowing within the continuum of the other.

Raising and lowering the temperature appeared to cause a deterioration rather than an improvement of the texture.

On heating, the two components melted independently to give isotropic liquids. Both transitions occurred over fairly narrow temperature ranges and, in contrast to the mesophases, the isotropic solutions appeared to be completely miscible. The transition temperatures are listed in table 2, which shows that where we have two coexisting mesophases, they melt independently at fairly constant temperatures. This is good evidence that the water activities in each phase are approximately invariant in the two phase region, since both of the pure mesophases have melting points that are sensitive to composition. The single liquid observed above the M melting temperature reforms the two distinct mesophases on cooling.

There was no sign of any isotropic liquid phase at room temperature. Nor was there any evidence of H_1/M miscibility at high SCG/$C_{12}EO_8$ concentrations (i.e. in regions of the sample where ^2H_2O evaporation had occurred).

The HMSXC/$C_{12}EO_8$/H_2O system showed a broadly similar pattern of phase behaviour, with no indication of miscibility of the mesophases but with complete miscibility of the isotropic liquids. In samples near the middle of the composition range, the isotropic L_1 phase appeared also and we take this to be a further indication of the incompatibility of the two types of mesophase. Typical optical micrographs for several samples of this series are reproduced in figure 4. The photographs show regions of M + L_1 for two samples and H_1 + M for a third. The only significant difference between these observations and those for the SCG/$C_{12}EO_8$/water system lies in the amount of chromonic drug that can be dissolved in the amphiphile H_1 phase. As shown in figure 4 (V), at least 12 per cent of HMSXC can be incorporated before a separate M phase is formed. The converse situation, however, does not occur and the $C_{12}EO_8$ is no more soluble in the M phase of HMSXC than it is in the M phase of SCG. As with the SCG mixtures, there was no indication of the H_1 and M phases becoming miscible at lower water concentrations (i.e. at the edges of the cover slip where evaporation had occurred).

3.2. *X-ray diffraction*

Diffraction patterns of the pure mesophases are presented in figure 5. As might have been expected, these patterns are similar, in as much as each shows a set of sharp inner reflections corresponding to the various repeat distances of a hexagonal lattice (and bearing the ratios $1 : 1/\sqrt{3} : 1/\sqrt{4}$). Beyond this, however, the pictures are quite different, the surfactant H_1 phase shows a diffuse ring at 4·5 Å arising from the lateral separation of the fluid alkyl chains within its constituent micelles, whilst the chromonic M phases show short 3·4 Å arcs corresponding to the stacking repeat distance of aromatic molecules along the length of the columns.

The diffraction patterns of the mixed mesophases were also obtained and a representative example is shown schematically in figure 5 (III). The result is a superposition of the patterns of the two separate pure components, and contains both the strong sharp 3·4 Å arcs of the chromonic columns and the diffuse 4·5 Å rings of the micellar interiors, together with the two distinct sets of hexagonal spacings. (Note that although the intensities of these reflections were dependent on the relative amounts of the two components, their positions were found to be virtually invariant with composition.) Thus the diffraction results indicate that, in a mixed sample, the regions of the amphiphile H_1 phase and the chromonic M phase behave independently, with no tendency for materials from either phase to be incorporated into the other to any large extent.

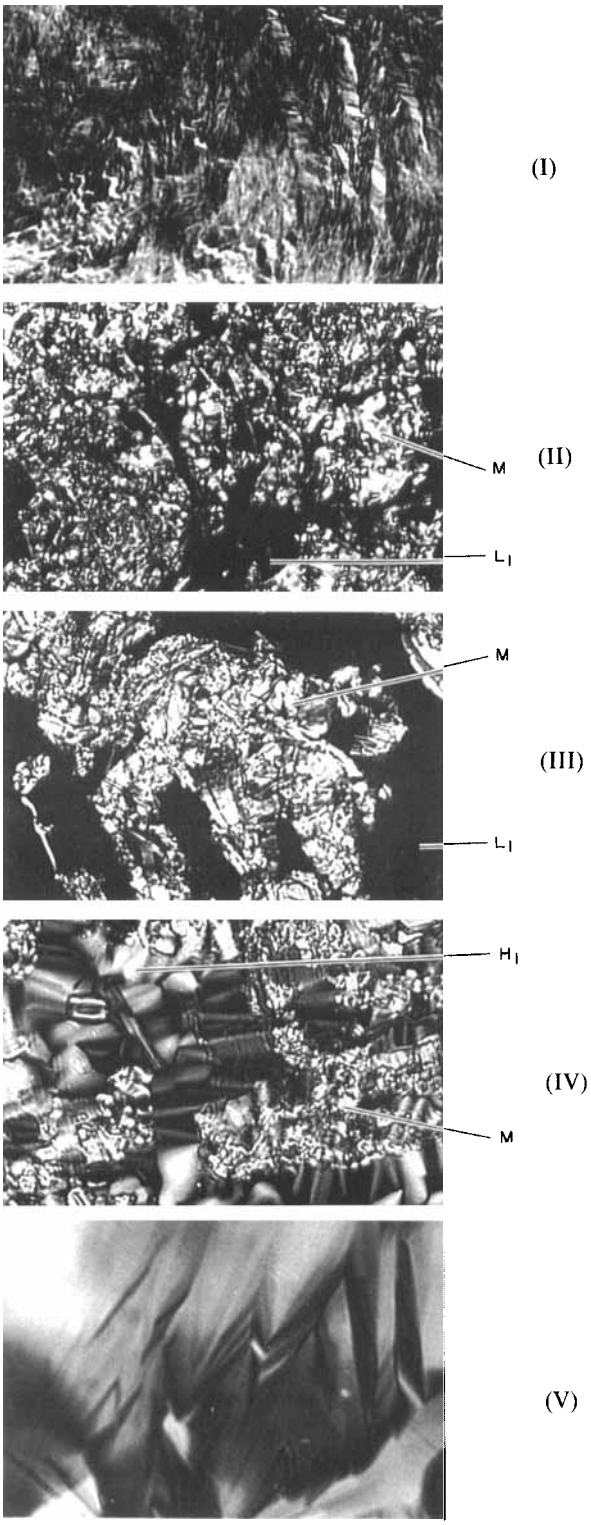

Figure 4.

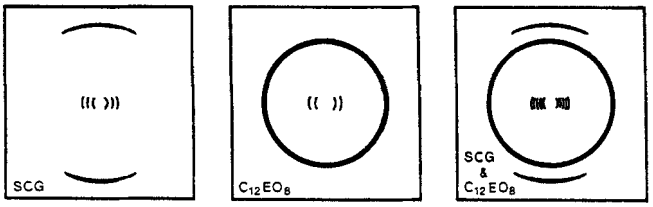

Figure 5. Drawings of the X-ray diffraction patterns of the hexagonal phases of (i) the SCG/water system, (ii) the $C_{12}EO_8$/water system and (iii) of a 1 : 1 mixed sample. (i) The chromonic M phase of SCG (30 per cent at room temperature). This drawing shows the sharp axial 3·4 Å reflection arising from the layer stacking and the sharp equatorial reflections arising from the hexagonal lattice with centre to centre distance of 32 Å. (ii) The hexagonal H_1 phase of $C_{12}EO_8$ (50 per cent at room temperature). The sharp inner equatorial reflections correspond to a hexagonal lattice with centre-to-centre distance of 45 Å. The outer diffuse ring at a spacing of 4·5 Å is characteristic of the semi-fluid nature of the alkyl chains. (iii) The mixed SCG/$C_{12}EO_8$/water system (15 : 27·5 : 57·5). This diffraction pattern shows the sharp 3·4 Å arcs of the chromonic M phase plus the rather more diffuse 4·5 Å ring of the amphiphile H_1 phase. Both sets of sharp inner equatorial reflections are present. The diffaction pattern is, therefore, more or less a combination of those of the separate mesophases showing that the two hexagonal lattices coexist and there there is no indication of any significant mixing at the molecular level.

3.3. *NMR spectra*

For the SCG/$C_{12}EO_8$ mixtures, both ^2H and ^{23}Na spectra were recorded from powder samples. The ^2H spectra contained a broad singlet due to the chromonic M phase, overlapping with a powder quadrupole doublet from the $C_{12}EO_8$ phase. The latter has a quadrupole splitting (W) of 300–400 Hz, which is in good agreement with the published data [12] for $C_{12}EO_8$ alone. The presence of a broad single peak for the M phase, rather than a powder doublet, is presumably due to the rapid diffusion of water between small M domains with different orientations. The measured linewidths ($Wn_{1/2} \approx 700$ Hz) are consistent with the previously reported W values of Goldfarb *et al.* [13].

Sodium-23 (spin quantum number $I = 3/2$) usually gives a powder doublet spectrum superimposed on a sharp central line in mesophases. In SCG-rich mixtures, the ^{23}Na spectrum showed a single broad band from the outer two resonances of the M phase. For the other samples, with 5 and 10 per cent SCG, an additional outer doublet appeared superimposed on the broad outer line (W = 3·5–4·0 kHz). We assign this doublet to the small concentration of SCG present in the H_1 phase. The central resonance was sharp in all of the spectra. Thus both the ^2H and the ^{23}Na data demonstrate the coexistence of the M and H_1 phases.

For the mixtures containing HMSXC, only ^2H NMR spectra were recorded. A single broad peak was obtained for the pure HMSXC M phase ($Wn_{1/2} \approx 500$ Hz) whilst the spectra of samples which contained the L_1 phase were dominated by an

Figure 4. Optical textures of the HMSXC/$C_{12}EO_8$/^2H_2O system (× 200, crossed polars, taken at room temperature). The mixed samples are numbered according to the compositions shown in figure 3. (I) Single chromonic M phase 36 per cent HMSXC; (II) 10 per cent $C_{12}EO_8$, 30 per cent HMSXC; (III) 20 per cent $C_{12}EO_8$, 24 per cent HMSXC; (IV) 30 per cent $C_{12}EO_8$, 18 per cent HMSXC; (V) Single amphiphile H_1 phase 40 per cent $C_{12}EO_8$, 12 per cent HMSXC.

intense, sharp single peak. A barely resolvable doublet (W = 120 Hz, $Wn_{1/2}$ = 300 Hz) was obtained for the 40/12 sample (with no central line), whilst the 50/6 mixture gave a powder doublet spectrum (W = 352 Hz, cf. 60 per cent $C_{12}EO_8$, 554 Hz) [12]. The phase equilibria of the various samples indicated by the NMR spectra concur therefore with the inferences from the optical studies. The coexistence of the M and H_1 phases together with L_1 over the central region of the composition range, and the absence of L_1 and M_1 phases in the $C_{12}EO_8$-rich samples is confirmed.

4. Discussion

All of the data from the various techniques on both of these systems show unequivocally that the H_1 and M phases are immiscible. Mixing of surfactants and chromonogens does, however, occur in the isotropic aqueous phases, implying that it is the incompatibility of mesophase structures rather than the chemical nature of the components that causes immiscibility. We interpret this as indicating that chromonic mesophases are a new breed of lyotropic liquid crystals. The distinction between chromonic and amphiphilic mesophases is analogous to the distinction between polar and non-polar liquids, such as water, formamide, and glycerol compared to alkanes and perfluoro carbons. All are isotropic and fluid, that is, of the same phase type. However, they have very different local structures as a result of very different intermolecular forces. The use of the terms polar or non-polar implies a particular set of physical properties such as a certain range of dielectric constants or dipole moments. Similarly, our use of the terms amphiphilic or chromonic implies the properties listed in table 1.

The presence of a length of alkyl chain on HMSXC appears to confer some amphiphilicity on the molecule, causing its solubility in the H_1 phase of $C_{12}EO_8$ to be greater than that of SCG. We can envisage the incorporation of individual HMSXC molecules into the amphiphile micelles without disruption of the aggregate structure (with the polyethylene oxide chains providing a not totally unfavourable polar environment for the aromatic part of the molecule and with the short length of alkyl chain reaching into the hydrophobic interior of the micelle). The converse situation is, however, less easy to visualize: chromonic columns are only one molecule wide and it is difficult to see how the lengthy alkyl chains of an amphiphile molecule can be inserted into the region at the centre of the column without completely disrupting the column structure and hence destroying the mesophase.

Bearing in mind the significance of alkyl chains in the formation of amphiphile mesophases it might have been expected that the C_6 chain of the HMSXC would have some importance in maintaining the structure of the chromonic mesophases of this particular compound. However, the diffraction pattern of the pure mesophase shows no indication of the 4·5 Å reflection which would indicate an assembly of alkyl chains. We conclude, therefore, that the alkyl chain of this compound has no strategic mesogenic value in the M phase and that the forces causing the aggregation of the molecules are radically different in the two classes of mesophase. These are probably due to intermolecular dispersion forces arising from charge delocalization in the aromatic rings of the chromonogens, and to the hydrophobic effect within the amphiphile micelles. Penetration of alkyl chains into the stacked aromatic rings of the chromonic aggregates or self aggregation of chromonic rings within the surfactant rod micelles leads to aggregate polydispersity and hence disruption of mesophases to form

isotropic aggregate solutions. In both cases the occurrence of hexagonal H_1 or M mesophases probably requires the presence of uniform aggregates.

It seems unlikely that any chromonic mesophases will be miscible with surfactant H_1 phases. Certainly, our study shows that H_1/M miscibility is not easy to achieve. On this basis, the H_1 phases for oxyethylene triphenylene derivatives recently reported by Boden *et al.* [14] can probably be more meaningfully reclassified as M. We would argue, therefore, that caution must be exercised in calling [15] chromonic aggregates micellar without evidence of a sharp critical micelle concentration.

The molecules of conventional amphiphiles are elongated (calamitic) whereas those of chromonic compounds are flattened (discotic). The side-by-side aggregation of amphiphile molecules in micelles, especially in the case of lamellar structures, is in a sense analogous to the formation of smectic structures by thermotropic calamitic molecules. A similar relationship exists between the discotic columnar phases and the newly defined lyotropic chromonic phases. From this viewpoint, it could be argued therefore, that the recognition of chromonic phases as lyotropic discotic phases completes the pattern of correspondence between the thermotropic and lyotropic mesophase structures.

There have been sporadic reports of lamellar phases formed by compounds such as salts of fluphenamic acid [16], whose molecular structures are of a chromonic rather than an amphiphilic nature. As far as we can judge, the proposed structure has not been unequivocally substantiated, and it is difficult to visualize the manner in which the molecules can associate to form lamellar structures. We therefore suggest tentatively that re-examination of these mesophases will show them to have structures of the chromonic type.

5. Conclusion

Investigations of two selected mixed systems suggest that the hexagonal phases formed by conventional amphiphiles are not miscible with those of chromonic phases. We expect that this will prove to be a general phenomenon, and that chromonic liquid crystals will prove to be a new breed of lyotropic mesophases. Whatever the actual arrangement of molecules within the aggregates in chromonic mesophases, their structure is very different from that of surfactant micelles. The use of the term conventional micelle in this context is misleading, since it carries a number of connotations (the elongated calamitic molecule, the distinction between hydrophobic and hydrophilic regions, the necessity for chain flexibility, the more or less radial alignment of molecules and the occurrence of critical micelle concentrations and Krafft temperatures), all of which are inappropriate to chromonic systems.

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