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Liquid Crystals
Publication details, including instructions for authors and subscription information:
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Optical microscopy and deuterium N.M.R. of non-ionic amphiphiles which exhibit thermotropic and aqueous lyotropic mesophases

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To cite this Article Zimmermann, H. , Poupko, R. , Luz, Z. and Billard, J.(1989) 'Optical microscopy and deuterium N.M.R. of non-ionic amphiphiles which exhibit thermotropic and aqueous lyotropic mesophases', Liquid Crystals, 6: 2, 151 — 166
To link to this Article: DOI: 10.1080/02678298908033210
URL: http://dx.doi.org/10.1080/02678298908033210

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Liquid Crystals, 1989, Vol. 6, No. 2, 151–166

Optical microscopy and deuterium N.M.R. of non-ionic amphiphiles which exhibit thermotropic and aqueous lyotropic mesophases

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(*Received 23 January 1989; accepted 9 April 1989*)

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Tetrabenzocyclododecatetraene (I) substituted with eight methoxy-mono-, di-, and triethyleneoxide side chains exhibit the same highly ordered thermotropic mesophase, *M*. In the methoxydiethyleneoxide (I-2), and methoxytriethyleneoxide (I-3) derivatives this mesophase is also lyotropic and can sustain (at room temperature) up to 40 wt per cent water. The homologue (I-2) exhibits at higher water content another lyomesophase, M_F, which is more fluid and nematic-like. Optical microscopy, differential scanning calorimetry and deuterium N.M.R. of both labelled (I-2) and water as well as of the water ^{17}O were used to construct the (I-2)-water phase diagram and to characterize the various mesophases. It is found that both *M* and M_F are uniaxial with negative birefringence and negative anisotropic magnetic susceptibility. The M_F phase readily aligns in a magnetic field and is characterized by fast ($\sim 10^7\ s^{-1}$) reorientation of the mesogen molecules about the director. The *M* phase is apparently columnar, highly ordered and is not readily aligned by a magnetic field. The rate of molecular reorientation in this mesophase is much slower ($\sim 10^3\ s^{-1}$) compared with M_F.

1. Introduction

Several thousands of thermotropic mesomorphic compounds have been identified [1] and many other compounds are known to exhibit mesomorphic solutions with non-mesogenic solvents (lyotropic mesophases) [2]. However only a few examples are known of thermotropic mesophases which remain stable after addition of large amounts of non-mesogenic solvents. These include the ionic compounds sodium stearate (with hexadecane) [3], bis (stilbazole) silver (I) (with several mesogenic and non-mesogenic anions) [4], and the non-ionic mesogens, *n*-decyl-*β*-D-glucopyranoside (which forms a stable mesophase with water) [5, 6], and 4-hydroxy-4′-methoxyazobenzene-4-(2,2-ethoxyethoxycarbethoxycinnamate), which consists of one hydrophilic side chain (with diethyleneglycoldiethylether and with water) [7], as well as a number of polymers [8].

Here we report on a new mesogenic, discotic-like, series of non-ionic compounds of which at least two members exhibit both thermotropic and lyotropic (with water)

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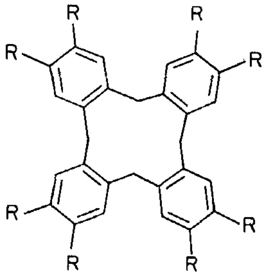
mesophases. The series consists of the tetrabenzocyclododecatetraene (I) core, symmetrically substituted with eight $CH_3O(CH_2CH_2O)n$-side chains. So far we have studied the three first members of the series, i.e. methoxyethyleneoxide (I-1), methoxydiethyleneoxide (I-2) and methoxytriethyleneoxide (I-3).

I-1 $R = -OCH_2CH_2OCH_3$
I-2 $R = -(OCH_2CH_2)_2OCH_3$
I-3 $R = -(OCH_2CH_2)_3OCH_3$
I-OH $R = -OH$
I-OCH$_3$ $R = -OCH_3$



In general the stability range of a lyotropic mesophase is increased by increasing the number of hydrophilic groups attached to an hydrophobic core. This has been used by Boden *et al.* [9] who substituted six methoxydiethyleneoxide chains on the triphenylene core resulting in a lyotropic mesogen which exhibits a series of lyomesophases with water. This compound is not, however, mesogenic in the neat form. When I is substituted with eight methoxyethyleneoxide groups the hydrophilic nature of the side chains is not sufficient to stabilize a lyotropic mesophase, but the neat compound, I-1, is mesogenic. Substitution with eight methoxydiethyleneoxide chains results in a water soluble mesogen, I-2, with the same thermotropic mesophase as I-1, which, however, remains stable even in the presence of 40 wt per cent water (at room temperature). At higher water content it transforms to yet another, nematic-like, mesophase which at room temperature can accommodate up to 65 wt per cent water. This compound I-2, which is the main subject of the present paper, is in many respects similar to triphenylene hexa-methoxydiethyleneoxide [8, 9], but unlike the latter, I-2 also shows a mesophase in the neat form. The third homologue, I-3, is highly water soluble, yet it is mesogenic exhibiting the same mesophase as I-1 and I-2, and as in I-2, it will sustain large amounts of water (up to 40 wt per cent at room temperature). In fact in its lyotropic state it becomes stabilized by small amounts of water as evidenced by the increase in the temperature range of its stability, reaching a maximum of 70°C when 12 wt per cent water is added.

We have shown previously that the tetrabenzocyclododecatetraene core (I) when substituted with eight sufficiently long aliphatic ether or ester chains exhibits thermotropic columnar mesophases similar to those found in discotic liquid crystals [10]. This core differs however from the other discotics in that it is highly flexible, undergoing fast interconversion between two symmetry related sofa forms [11].

2. Experimental

2.1. *Synthesis*

The compounds I-1, I-2 and I-3 were synthesized from octahydroxytetrabenzocyclododecatetraene (I-OH) [10, 11] by alkylation with the respectively, mono-, di- and tri-oxaalkylbromide under pressure. In a typical experiment 0·5 g I-OH, 2·5 g potassium carbonate and 5 g of 1-bromo-2-(2-methoxyethoxy)-ethane, (3,6-dioxaheptylbromide) in 50 ml acetone were enclosed in a stainless steel pressure vessel and stirred for 50 h at 200°C. The cooled mixture was filtered and the solution evaporated until a semi-solid product was obtained. Crystallization from a minimum quantity of

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diethylether followed by a short column chromatography on neutral alumina/methylacetate and recrystallization from ether yielded I-2 as a white crystalline product (0·83 g equivalent to 62·4 per cent yield, clearing point 108 to 109°C). The purity of the compound as checked by HPLC (RP 18 column 250 × 4·6 mm, ODS-Hypersil 5 μ, linear gradient of acetonitrile/water, 0-50 per cent CH_3CN in 30 min) was found to be better than 98 per cent. The purity was subsequently increased to better than 99 per cent by middle pressure chromatography (Labochrome PGC-column on Organogen reversed phase, silica 20–45 μ 60 Å, linear gradient of methanol/water, 50–80 per cent CH_3OH, flow rate 40 ml/min. Detector: 254 nm). Elementary analysis gave: C = 61·94, H = 8·07 per cent (calculated for $C_{68}H_{104}O_{24}$, C = 62·55, H = 8·02 per cent). ^1H N.M.R. at 500 MHz in $CDCl_3$/TMS at -30°C gave 6·80 (s, 4 H arom.), 6·23 (s, 4 H arom.), 4·32 (m, 4 H 2 × $-OCH_2-$), 4·23 (m, 4 H 2 × $-OCH_2-$). The other aliphatic hydrogens appear between 3 and 4 ppm and are also consistent with a molecular C_2 symmetry [11]. Upon heating to above -30°C the lines broaden due to interconversion between the sofa forms.

The synthesis of I-3 required the preparation of 3,6,9-trioxadecylbromide since it is not commercially available. This was done by bromination of triethyleneglycol-monomethylether (Fluka) via the corresponding p-toluenesulphonate and LiBr. The distilled trioxaalkylbromide (b.P. 58–60°C/0·005 torr) was used to alkylate I-OH as described. The solvent acetone and the excess of the trioxadecylbromide were removed by continuous (24 h) high vacuum pumping, resulting in a birefringent waxy liquid-crystalline compound I-3. No crystallization of this compound could be affected even after middle pressure chromatography, as described for I-2.

Deuteriated isotopomers were prepared only for the I-2 homologue and included, deuteriation in the unsubstituted aromatic sites $(I\text{-}2)^i$, and in the dodecatetraene ring methylene $(I\text{-}2)^{ii}$. The former was obtained by alkylation of the corresponding aromatic deuteriated I-OH which in turn was derived by ether cleavage of deuteriated I-OCH_3 using BBr_3 in chloroform [10, 11]. Deuteriated $(I\text{-}OCH_3)^i$ (i.e. deuteriated in the unsubstituted aromatic sites) was obtained by refluxing the normal compound for 24 h in CF_3COOD [10].

Deuteriated $(I\text{-}2)^{ii}$ was prepared in a similar way using $(I\text{-}OCH_3)^{ii}$, i.e. deuteriated in the crown ring methylene groups. This compound was prepared by acid catalysed condensation of $\alpha,\alpha\text{-}d_2$-3,4-dimethoxybenzylalcohol [10, 11]. The deuteriated alcohol was obtained by reduction of 3,4-dimethoxybenzoic acid (Aldrich) using $LiAlD_4$ in THF. Mass spectra and ^1H N.M.R. of the intermediate and final products verified that the specific deuteriation of the desired sites was better than 95 per cent.

2.2. *Differential scanning calorimetry*

Transition temperatures and transition enthalpy changes of the neat compounds were measured using a Mettler, T.A. 3000 differential scanning calorimeter. The D.S.C. results are reported for increasing temperature (heating rate 1 to 5°C/min).

2.3. *Optical microscopy*

Thin samples were observed between two untreated cover slips of ordinary glass. The textures as well as the miscibilities were studied using a polarizing microscope (Leitz, Panphot or Zeiss, Universal) equipped with a (Mettler, FP52) hot stage. Binary phase diagrams were constructed by observation of contact preparations [12] between two cover slips or in flat capillary tubes (Vitro Dynamics Inc.) 0·1 mm thick.

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The solubilities of the solids were calculated using the Le Chatelier-Schröder relation [13].

2.4. *N.M.R. measurements*

N.M.R. measurements were performed on ^{2}H and ^{17}O nuclei using a CXP 300 spectrometer operating at 46·07 MHz for deuterium and 40·68 MHz for oxygen-17. Sample rotation experiments were performed on deuterium at 13·8 MHz using a WH90 spectrometer. The measurements on the water nuclei (^{2}H and ^{17}O) were performed with single pulses, while for the deuterium of deuteriated I-2 the quadrupole echo method was used (pulse width 3 μs, intervals between pulses 25 μs). The samples were prepared gravimetrically in sealed 5 mm N.M.R. tubes and equilibrated at room temperature for several days or even several months depending on the water concentration.

3. Results and discussion

3.1. *The thermotropic mesophases of the neat compounds*

3.1.1. *Optical microscopy and differential scanning calorimetry*

Transition temperatures and molar enthalpy changes for compounds I-1 to I-3 are summarized in the table. The compounds are stable in air in the temperature range of the measurements. Compounds I-1 and I-2 exhibit fine birefringent needles in the crystalline state, while I-3 is waxy. The mesophases of the neat compounds appear as viscous birefringent pastes (as observed by pressing with a fine steel needle over the coverslip) and transform to fluid isotropic liquids on heating to above the clearing temperatures. Cooling back to the mesophase region yields birefringent needles with acute angles (see plate 1). The neutral lines are parallel to the elongation direction and the optical sign is negative. Defects with rectilinear axis, perpendicular to the elongation direction of the needles, can be observed. Such defects are common in columnar discotic and pyramidic phases. By observing the defect axes with the analyzer removed and shifting the focus plane of the microscope lens up and down within the sample, it can be deduced [14] that the optic axes are tangential to spirals contained in planes perpendicular to the defect axis. No Grandjean terraces have been observed in free surface preparations.

By pressing the cover slips the number of defects increases despite the high viscosity of the mesophases. The supercooled mesophases of I-1 and I-2 can be maintained at room temperature for several hours but will rapidly crystallize on submersion in liquid nitrogen. The textures of *M* are indicative of highly organized mesophases in accord with the large clearing enthalpies. The optical properties

Transition temperatures (in °C) and enthalpy changes (in kJ/mole) for the octasubstituted tetrabenzocyclododecatetraenes I-*n* studied in the present work†.

n	C_1		C_2		C_3		*M*		*I*
1	●	81·9(54·9)					●	211(~30)	●
2	●	12·6(12·7)	●	29·9(20·4)			●	109·2(25·6)	●
3	●	7	●	15	●	22(72·4)‡	●	63·0(12·1)	●

† Here C_i stands for crystalline phases; *M* for mesophase and *I* for isotropic liquid. The molar enthalpy changes are given in parentheses.

‡ The enthalpy change corresponds to the sum of the three unresolved peaks with the dominant contribution coming from the C_2–C_3 transition.

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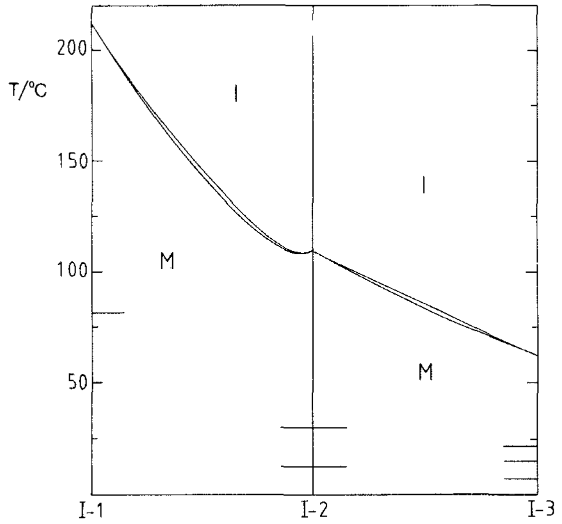

Figure 1. The binary phase diagram of compounds I-1, I-2 and I-3. Only the mesophase (*M*)-liquid (*I*) equilibrium curves are shown. The horizontal bars represent solid-solid and solid-mesophase transitions.

described and their similarity to those of the columnar discotics indicate that the mesophases are columnar.

3.1.2. *Miscibility studies*

The phase diagram of the binary mixtures of I-1 with I-2, and I-2 with I-3 (see figure 1) indicates that all three compounds exhibit the same mesophase. The equilibrium curves of both mixtures show that the binary solutions are almost ideal. To check whether this mesophase is the same as that exhibited by the hydrophobic derivatives of the tetrabenzocyclododecatetraene core we have examined contact preparations of I-2 with several octa-*n*-alkyloxy derivatives of I having similar side chain length [10]. No total miscibility could be observed between corresponding pairs of compounds in either the liquid or the mesomorphic states.

3.1.3. *N.M.R. results*

To obtain additional information about the molecular dynamics in the various phases of neat I-*n*, deuterium N.M.R. measurements of the mesogen specifically labelled in the aromatic ring, $(\text{I-2})^i$ and the dodecatetraene ring $(\text{I-2})^{ii}$, were performed in the solid and mesophase regions. Examples of the spectra of $(\text{I-2})^{ii}$ in each of the C_1, C_2 and *M* phases are shown in figure 2. All spectra are almost identical, exhibiting a nearly uniaxial quadrupole interaction ($\eta = 0$) with $\nu_Q = 130\,\text{kHz}$ in C_1 and C_2, which is typical for rigid methylene deuterons [15], and 129 to 125 kHz in the mesophase. Similar spectra with $\nu_Q = 135\,\text{kHz}$ ($\eta \approx 0{\cdot}06$) are obtained for the aromatic deuterons in $(\text{I-2})^i$. These results indicate that in the crystalline phases of the neat compound no molecular reorientation occurs on the N.M.R. timescale. Likewise, only very slow molecular reorientations, if at all, take place in the mesophase; the small reduction in the quadrupole interaction parameter may reflect low amplitude fluctuations of the columnar axes. This situation is different from what is commonly

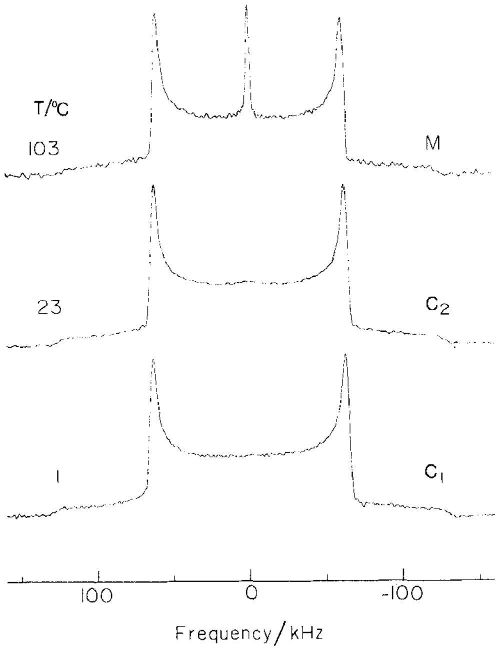

Figure 2. Deuterium N.M.R. spectra of (I-2)^{ii}, deuteriated in the methylene groups of the cyclododecatetraene ring in the solid C_1 and C_2 phases, and in the *M* mesophase.

found in columnar discotics where fast molecular reorientation about the columns' axes, is usually observed [16].

3.2. *Aqueous lyotropic mesophases*

In a contact preparation of I-1 and water we have not observed any lyotropic mesophase between room temperature and 70°C. After complete evaporation of the water no deposits of I-1 were found on the glass surfaces, indicating that this compound is practically insoluble in water in this temperature range. Binary mixtures of I-3 and water show that these two compounds are totally miscible in the liquid state. The equilibrium curve for the mesomorphic and liquid state exhibit a maximum of 70°C at approximately 12 wt per cent water, indicating that addition of water stabilizes the mesophase of I-3. At room temperature the mesophase remains stable up to ~40 wt per cent water.

Most of the measurements were performed on mixtures of I-2 and water. These are described in detail in the following sections.

3.2.1. *General description of the I-2 -water phase diagram*

Contact preparation of crystalline I-2 with water exhibits a succession of phases ranging from solid crystals, the mesophase *M*, a fluid mesophase (M_F), and an isotropic liquid (I_l) (plates 2 and 3). The I-2 -water binary phase diagram is depicted in figures 3 (*a*) and 3 (*b*). The data in figure 3 (*a*) were obtained by optical microscopy and correspond to isotopically normal water; those in 3 (*b*) were mainly obtained by N.M.R. and correspond to heavy water (D_2O). Consequently some features in the two parts do not completely conform, e.g. the characteristic line at −5°C in figure 3 (*a*)

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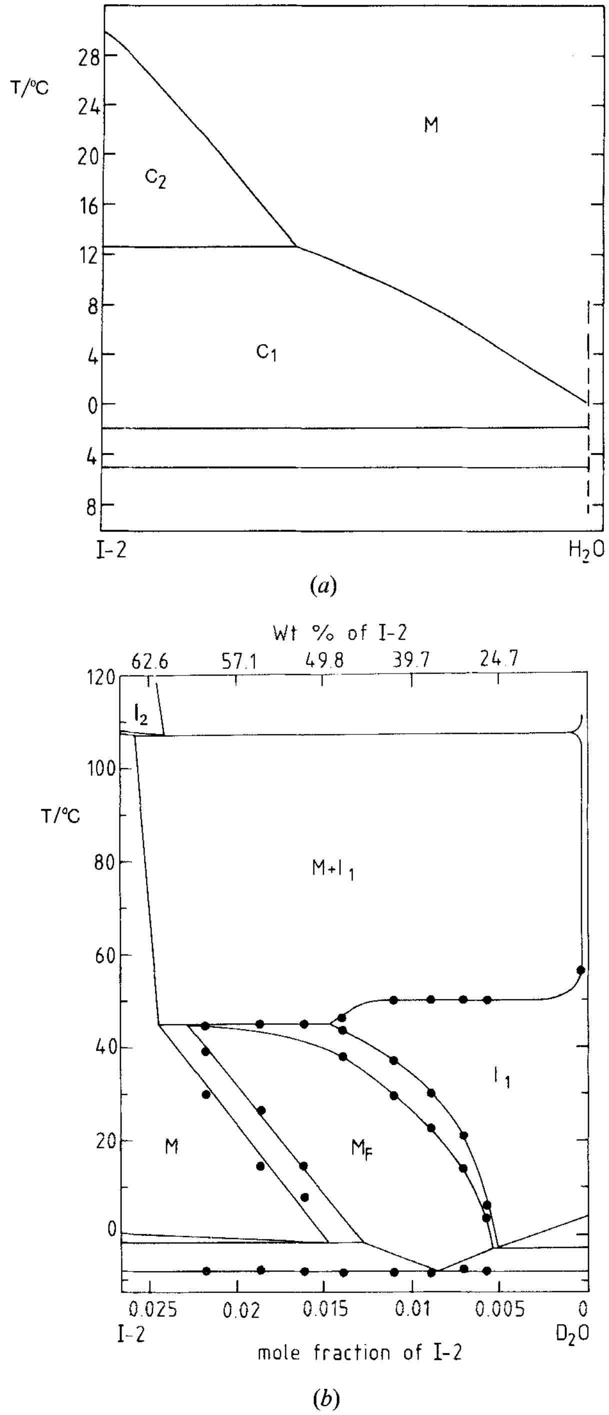

Figure 3. The phase diagram of mixtures of I-2 with water. (*a*) The low water content region —results obtained from optical microscopy with isotopically normal water. (*b*) The high water content region—results obtained by N.M.R. with D_2O (as well as qualitative observations on bulk samples and optical microscopy on mixtures with normal water). The vertical dashed line in (*a*) corresponds to the left-hand edge of (*b*).

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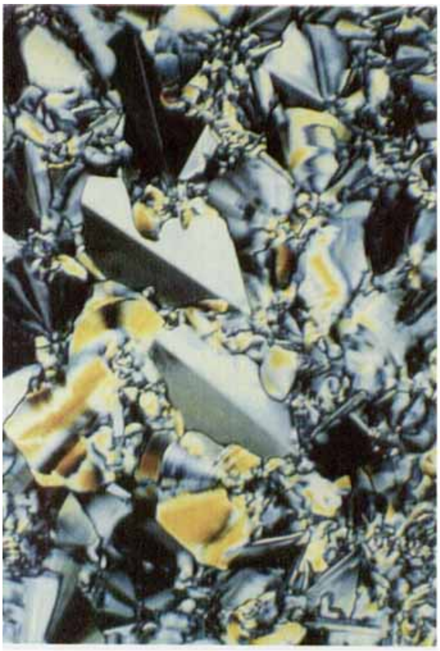

Plate 1.

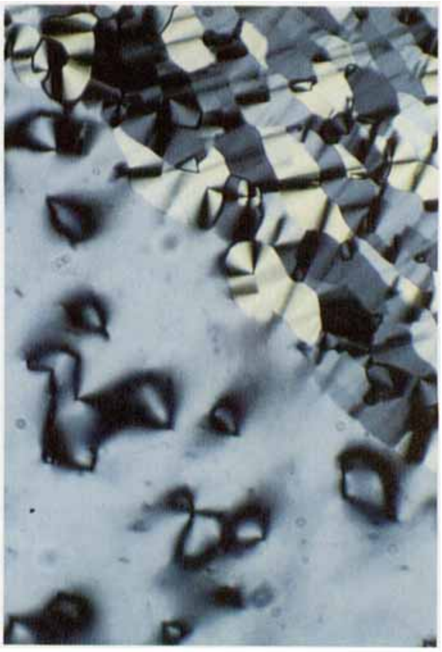

Plate 2.

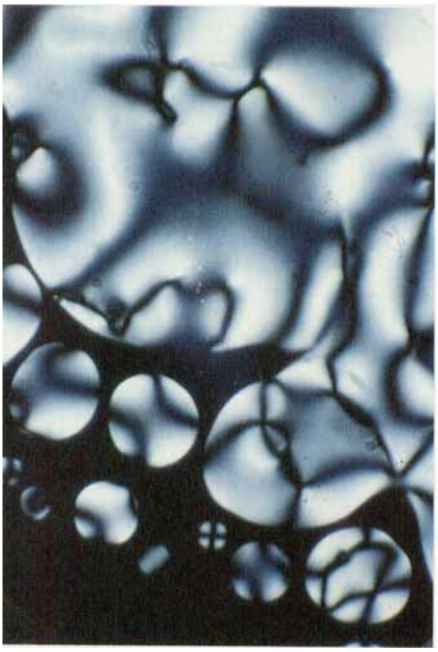

Plate 3.

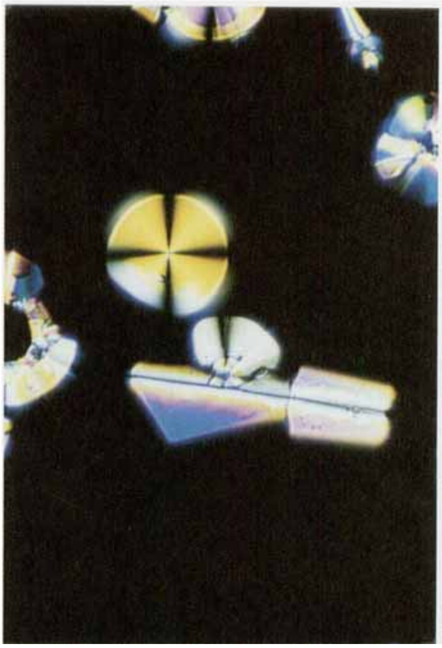

Plate 4.

falls at −8°C in figure 3 (*b*). The line at −2°C was observed by optical microscopy and extended without modification to figure 3 (*b*). Note in the latter diagram the melting point of water at 3·8°C which corresponds to D_2O. The vertical dashed line in figure 3 (*a*) corresponds approximately to the left edge of figure 3 (*b*). It may be seen that the mesophase M persists even in the presence of considerable amounts of water. The maximum water content in M increases with decreasing temperature, and is about 45 wt per cent at room temperature. Further addition of water results in the fluid mesophase, M_F, which at room temperature can contain up to 65 wt per cent water. In mixtures of higher water fraction an isotropic aqueous solution, I_1, of I-2 is obtained which, depending on the temperature can contain up to about 48 wt per cent of the amphiphile. The M_F phase is stable only up to 45°C. Above this temperature, phase separation into M and I_1 takes place (see plate 4). Above 50°C the (I-2) solubility in I_1 decreases strongly.

In large bulk samples, sealed in glass tubes transformation into two immiscible liquids, I_1 and I_2, may be observed at still higher temperatures. From observations on such samples the following relations concerning the specific masses, ϱ, of the different phases were deduced: at 52°C, $\varrho_M < \varrho_{I_1}$; at 85°C, $\varrho_M > \varrho_{I_1}$; at 112°C, $\varrho_{I_2} > \varrho_{I_1}$.

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3.2.2. *Optical microscopy of contact preparations*

Under crossed polarizers the fluid mesophase M_F exhibits a schlieren texture, in which threads and brownian motion are clearly observed (see plates 2 and 3). The optical sign of this phase is negative. On cooling a heated sample the growth of the ordered mesophase, M, from the fluid mesophase is readily observed. The contours are digitized (finger-like) and as for M_F the optical sign of M is also negative. Defects with rectilinear axes, and optical properties similar to those described for the neat thermotropic mesophase can be observed [14, 17]. In flat capillaries large domains of this mesophase are seen. The habit is clearly formed by developable surfaces and the intersections of these surfaces make well defined angles. On rapid growth this mesophase appears as birefringent rectilinear or curved needles.

On cooling below room temperature crystallization occurs only after appreciable supercooling and is accompanied by a volume increase due to formation of ice. On slow heating (1°C/min) the appearances of the fluid mesophase, the liquid phase and the ordered mesophase is observed. The boundary between the crystals of I-2 and the ordered mesophase move continuously towards neat I-2 until its melting. The disappearance of the fluid mesophase between the ordered and liquid phases occurs at 42·6°C.

3.2.3. *N.M.R. results of the water nuclei*

Complementary measurements, which allowed us to obtain a more precise phase diagram, were performed using deuterium and oxygen-17 N.M.R. of isotopically enriched water. These measurements were performed on a series of I-2 -heavy water mixtures, sealed in N.M.R. tubes which were allowed to equilibrate at room

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Plate 1. The M phase of neat I-2 at 100°C.

Plate 2. The M and M_F mesophases in a contact preparation of I-2 and water, at room temperature.

Plate 3. Same as plate 2 for the M_F and I_1 phases.

Plate 4. The M and I_1 biphasic region at 53°C in a mixture containing I-2 and water.

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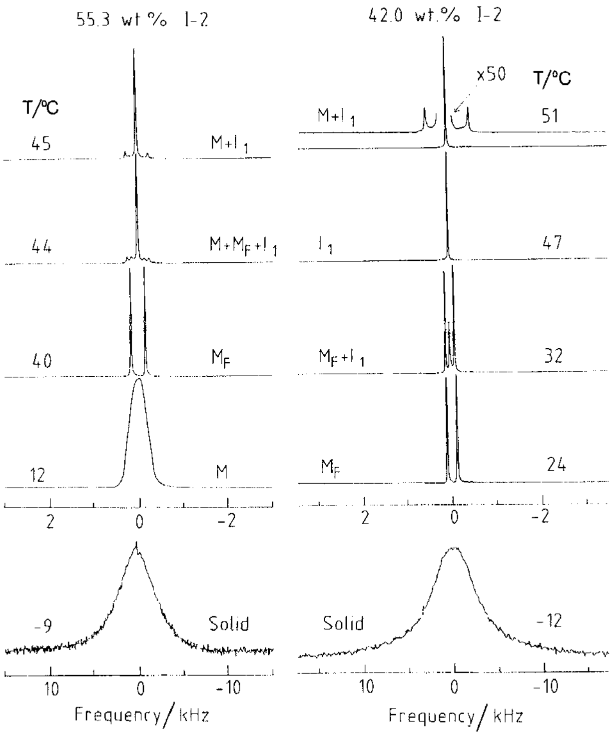

Figure 4. Deuterium N.M.R. spectra of I-2 $-D_2O$ mixtures containing 42·0 (right) and 55·3 (left) wt per cent amphiphile. Note the different frequency scale for the bottom traces, which correspond to the solid phase, and the other spectra which are due to the various mesophases. The temperature and phases are indicated for each spectrum (cf. the phase diagram in figure 3(*b*)).

temperature for several days. For the measurements the samples were first cooled to about $-15°C$ and then heated gradually. Eight mixtures with I-2 concentrations ranging from 27 to 59 wt per cent were used for the deuterium N.M.R. and three more with heavy oxygen enriched water for the ^{17}O measurements.

In figure 4 are shown the deuterium spectra for two I-2 $-D_2O$ mixtures with amphiphile concentrations of 42·0 and 55·3 wt per cent. In the 42 wt per cent sample (right hand side of figure 4), the bottom trace corresponds to a low-temperature solid solution. From the width of this signal it can be deduced that rapid translational diffusion of water takes place in this phase. Transition to the fluid mesophase, M_F, results in a discontinuous change into a sharp doublet indicating that this phase is well aligned by the magnetic field. Sample rotation experiments [18] are consistent with this mesophase being uniaxial and of negative anisotropic magnetic susceptibility; When the sample is rotated by 90° about an axis perpendicular to the field direction a new doublet appears whose splittings is twice that of the original pair. The sample however immediately realigns to give the original pattern. Consequently $\Delta\chi$ of M_F is negative, as commonly observed for discotics with aromatic cores [19]. On further heating a biphasic region, $M_F + I_1$, is obtained followed by a monophasic isotropic liquid, I_1. This phase persists until about 50°C, when it undergoes phase separation into $M + I_1$. The spectrum in this region consists of a superposition of a singlet due to bulk water in I_1 and a powder-like spectrum due to water molecules in M. In the

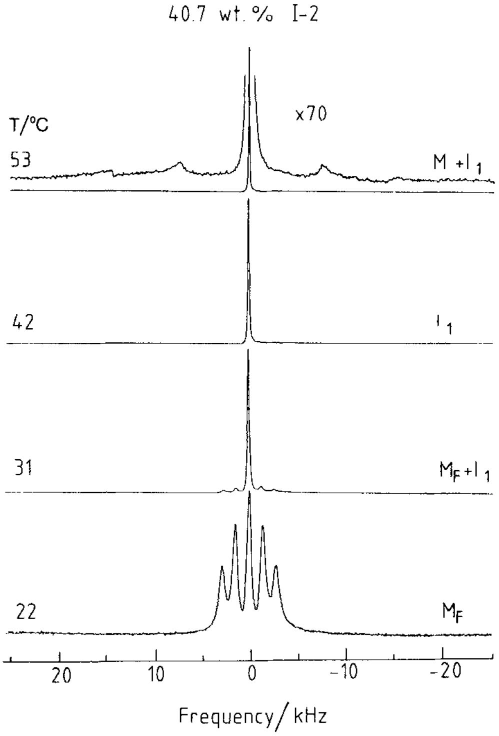

Figure 5. Oxygen-17 N.M.R. spectra of a I-2 -$H^{17}O$ mixture containing 41 wt per cent amphiphile. The ^{17}O content is ~2 at per cent.

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latter spectrum the perpendicular features are clearly seen in figure 4 at an amplification of × 50, the parallel features are only observed at a much higher gain.

In the 55·3 wt per cent sample (left hand side of figure 4) the solid solution (bottom trace) first transforms to the organized phase M yielding an unresolved structureless pattern since it is not aligned by the magnetic field. In the range 27°C to 44°C the sample is in the M_F phase and exhibits a sharp doublet. It then undergoes a phase separation into $M + I_1$, through a narrow triphasic region consisting of M_F, M and I_1. When this sample is cooled back via M_F into M the spectra in both phases consist of sharp doublets, indicating that the alignment induced in M_F persists also in the M phase. Rotation of the sample with the aligned M phase by 90° about an axis perpendicular to the magnetic field yields a powder pattern typical of a planar distribution of uniaxial domains. Thus as for M_F, the M phase is also uniaxial with negative $\Delta\chi$.

The results for ^{17}O are similar to those for ^2H. A series of spectra for a 40·7 wt per cent solution are shown in figure 5, showing from bottom upwards, spectra due to the fluid M_F mesophase, a $M_F + I_1$ biphasic mixture, isotropic I_1 and $M + I_1$.

3.2.4. *N.M.R. results for labelled I-2*

Further information on the state of the amphiphilic molecules in the lyomesophases of I-2 was obtained by ^2H N.M.R. measurements of the specifically deuteriated isotopomers $(I\text{-}2)^i$ and $(I\text{-}2)^{ii}$. Spectra of both compounds recorded at various I-2 concentrations upon heating from the solid are shown in figures 6 and 7. In both

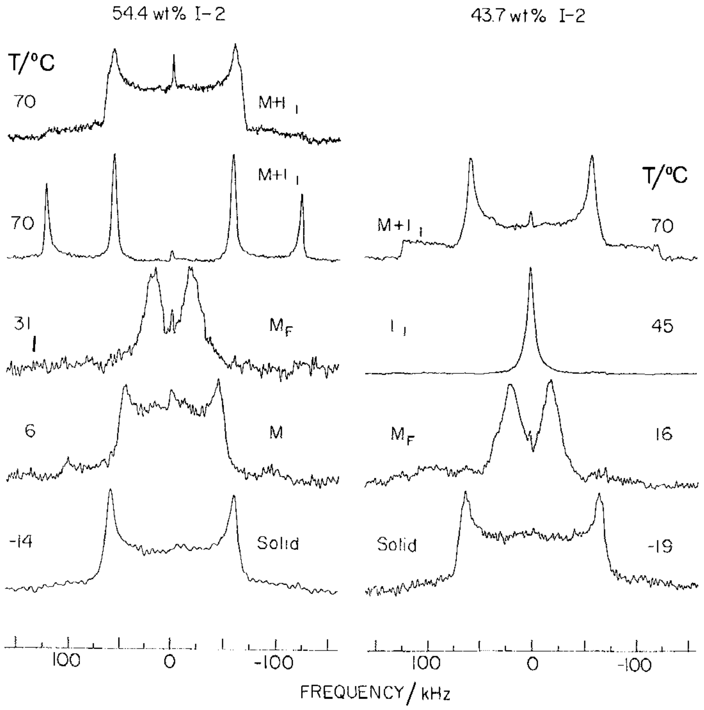

Figure 6. Deuterium N.M.R. spectra in I-2 –H_2O mixtures containing 43·7 (right) and 54·4 (left) wt per cent deuteriated $(I\text{-}2)^i$ (deuteriated in the aromatic ring), at the indicated temperatures and phases.

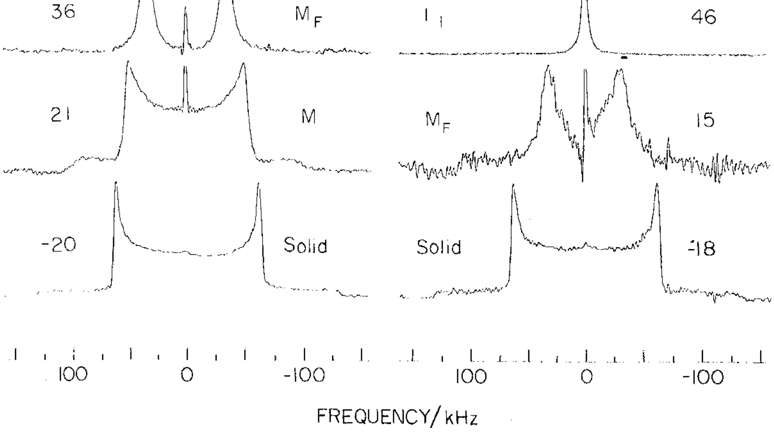

Figure 7. As in figure 6 for 40·3 and 57·4 wt per cent solutions of $(I\text{-}2)^{ii}$ (deuteriated in the methylene groups of the dodecatetraene ring).

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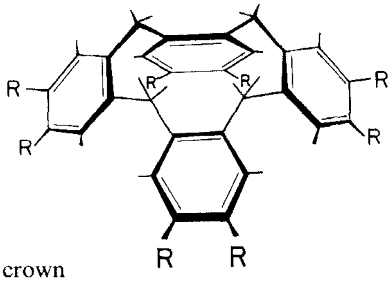
figures two vertical paths through the phase diagram are depicted. In the left hand columns spectra of samples (54·4 and 57·4 wt per cent) are shown which upon heating undergo the transformation, solid → M → M_F → M + I_1, while the spectra on the right hand side correspond to samples (43·7 and 40·3 wt per cent) which undergo the transformation, solid → M_F → I_1 → M + I_1. We discuss first the results for the aromatic deuterons in the (I-2)^i isotopomer (see figure 6). The bottom spectra in both columns correspond to the solid phase and are characteristic of a rigid powder with a deuterium quadrupole interaction $\nu_Q \approx$ 135 kHz ($\eta \approx$ 0·06). Heating the 54·4 wt per cent sample (left hand column) into the M phase yields a similar lineshape as in the solid but with a slight decrease in the quadrupole interaction parameter (to about 125–130 kHz) and a considerable reduction in the signal intensity. This is most likely due to the setting-in of some molecular reorientation which results in the shortening of T_2 with a corresponding reduction in the sensitivity. Further heating into the fluid M_F phase yields a doublet with quite broad (~22 kHz) components, indicating that the I-2 molecules undergo rapid reorientation but at a rate not sufficiently fast for complete averaging of the quadrupole interaction. The doublet splitting is about 36 kHz and within the M_F region is almost independent of temperature and concentration. Assuming that the aromatic C–D bonds are perpendicular to the principal axes of the I-2 molecules and recalling that the director aligns perpendicular to the field direction, yields an orientational order parameter, S_{zz}, of about 0·53 for the mesogen molecules. The results do not indicate, however, whether in this mesophase (M_F) the mesogenic molecules are isolated or whether they are stacked in columnar micelles as in the M mesophase.

When this sample is heated to above 45°C, phase separation takes place into M + I_1 with most of the I-2 molecules in the M phase and only very few in the isotropic I_1 liquid. The resulting spectrum of the (I-2)^i molecules in this phase is shown in the fourth (from bottom) trace of the left hand column in figure 6. It consists of what appears as two sharp doublets with a splitting ratio of very nearly 2 : 1 (246 and 115 kHz). The most likely interpretation of this unusual spectrum is that the M phase formed after the phase separation of M_F remains aligned with the director perpendicular to the field direction as in M_F. This results in an equal distribution of the aromatic C–D bonds in planes which include the direction of the magnetic field, yielding a characteristic powder pattern with a two dimensional distribution of the director of the type previously observed in aligned mesophases with $\Delta\chi < 0$ [20]. Such spectra show sharp features corresponding to the parallel and one of the perpendicular orientations of the C–D bonds with respect to the magnetic field, which may be identified with the peaks observed in the experimental spectrum of the aligned M mesophase. The observed lineshape is however not exactly identical to that expected from a rigid planar distribution of C–D bonds, in particular the signal intensity between the sharp features is considerably lower than expected. The discrepancy can be explained by assuming the existence of slow reorientational motion of the I-2 molecules about their symmetry axes. In the slow motion regime such a reorientation process will result in an anisotropic T_2, with the parallel and perpendicular orientations being least affected by the motion and therefore maintaining a longer T_2. Quadrupole echo spectra of such systems will exhibit intensity distortions, depending on the reorientation rate and the time interval, τ, between the $\pi/2$ pulses. Preliminary analysis of these lineshapes indicate that the reorientation of the I-2 molecules in the M component of the M + I_1 biphasic region can be characterized by a planar diffusion constant, D_R [20], of the order of 10^3 rad^2/s.

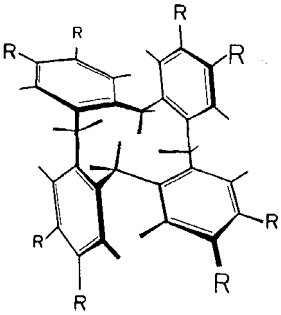
Further support for this interpretation comes from an experiment performed on a non-aligned sample of the M + I_1 biphasic mixture. This sample was prepared by heating the same 54·4 wt per cent solution from the M_F mesophase to the biphasic region outside of the magnetic field before insertion into the preheated probe of the N.M.R. spectrometer. The deuterium spectrum of $(I\text{-}2)^i$ at 70°C is shown in the top left hand trace of figure 6. Its shape is indeed characteristic of a non-aligned sample although no distortions due to dynamic effects are observed. Simulation using the same model as we have described for the oriented sample show that the lineshape of a disordered sample is indeed much less sensitive to slow reorientational motion than that of an oriented sample.

The spectra in the right hand column, which correspond to the 43·7 wt per cent solution, are consistent with the interpretation given for the high concentration sample and with the phase diagram in figure 3 (*b*). The spectrum in the M_F mesophase is similar to that obtained for the same mesophase in the more concentrated solution. Heating to the isotropic I_l phase yields a relatively sharp singlet which transforms into a powder pattern at the phase separation temperature of 50°C. Since I_l is not oriented the M mesophase in the $M + I_l$ biphasic mixture obtained from I_l, even within the magnetic field is not oriented. This explains the different patterns observed in the $M + I_l$ mixtures obtained from the high and low concentration samples.

We turn next to the deuterium spectra of the crown methylene in the $(I\text{-}2)^{ii}$ samples (see figure 7). Their general behaviour is similar to that of the aromatic deuterons but quantitatively we do not yet understand them fully. We note that for the $(I\text{-}2)^{ii}$ isotopomer a superposition of two sets of spectra is expected due to the two inequivalent crown ring deuterons. In the solid where no motion takes place they are indistinguishable and therefore give the same powder pattern. Surprisingly in the M_F mesophase only a single doublet is observed rather than two. This may be due to accidental equivalence of the two splittings, however we have not sufficient information about the molecular conformation of I-2 in the mesophase region to speculate on the origin of this equivalence. Likewise the spectrum of $(I\text{-}2)^{ii}$ in the oriented M mesophase formed from M_F by phase separation into $M + I_l$ (top left hand trace in figure 7) exhibits an uncommon lineshape which we find difficult to explain. As discussed in connection with the corresponding spectra of $(I\text{-}2)^i$ in this sample (see figure 6) there is a planar distribution of directors perpendicular to the field direction and slow reorientation of the mesogenic molecules about their main axes. The observed spectrum is consistent with such a distribution, for C–D bonds making a small ($< 35°$) angle with the main molecular axis, a structure which will yield a N.M.R. pattern with perpendicular features having sharp edges, as observed in the experiments. The overall lineshape, in particular in the centre of the spectrum is, however, sensitive to the exact molecular conformation and their detailed motion. Two main conformations can be visualized for the I-*n* molecules [11], viz. the sofa form which apparently exists in solutions and the crown form which is pyramidic-like.



crown



sofa

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Both structures are very non-rigid and can readily undergo fast high-amplitude vibrations in addition to the much slower ring inversion. It is tempting to assume that in the columnar mesophases the I-2 molecules are in the crown form, but we have no evidence for that. Our attempts to obtain an exact simulation of the observed spectra, in particular in the central region, using various geometries were only partially successful. It appears that the main difficulty is to estimate the averaging effect of the large-amplitude vibration. We have also tried to determine the conformation of I-2 in nematic solvents [21], but so far failed because of its low solubility.

4. Summary and conclusions

We have shown that the first homologues of the series I-n with $n = 1, 2, 3$ are mesogenic, exhibiting the same thermotropic mesophase, M. In I-2 and I-3 this mesophase is also lyotropic and can sustain up to 40 wt per cent water. This shows that the structure of the M mesophase in the neat and aqueous forms is the same and that there is therefore no fundamental difference between the thermotropic and lyotropic liquid-crystalline states. In this particular case the mesophase is columnar and in the lyotropic form the water molecules probably occupy the intercolumnar region together with the polar ethyleneoxide side chains.

The homologue I-2 has especially pronounced lyotropic properties as reflected by the fact that further addition of water to the aqueous M mesophase ($>$ 40 wt per cent at room temperature) yields another mesophase, M_F, which is quite fluid and can sustain even more than 70 wt per cent water. Both M and M_F are uniaxial with negative $\Delta\chi$ and Δn. Under crossed polarizers, M shows characteristic features of a columnar phase while M_F exhibits schlieren textures, typical of nematics. Our results do not indicate however the nature of the basic units of M_F which are oriented in the mesophase, i.e. whether the I-2 molecules are stacked into micellar structures or whether they are randomly distributed in the bulk water. For the I-2 molecules in M_F the second rank order parameter is about 0·5 while for the water molecules it is considerably lower (of the order of 10^{-3}). The stability of the M_F mesophase is limited to 45°C above which temperature it undergoes phase separation into M and I_1. If this phase separation occurs within a magnetic field, the M phase keeps the orientation of M_F resulting in a planar distribution of domains with the directions perpendicular to field direction.

It is very likely that the mesophases M_F and M may be identified with the fluid N_C and the hexagonal C_H mesophases discovered by Boden *et al.* in aqueous mixtures of triphenylenehexadiethyleneoxide [9]. Like our M_F the N_C mesophase is nematic-like, while M is uniaxial-columnar as is C_H. It is therefore possible that M is also hexagonal, but so far no X-ray measurements on this mesophase have been performed.

We have examined the possibility of inducing a twist in the fluid mesophase by replacing the pure water component with aqueous solutions of chiral compounds, however with no success: In contact preparations with a saturated brucine sulphate [22] solution at 23°C the fluid mesophase appears but no evidence of twist (colours due to rotating power dispersion, finger prints etc.) [23] has been observed. Contact preparations with aqueous D(−) mandelic or D(−) tartaric acid solutions, did not exhibit the fluid mesophase between 21 and 30°C. Compounds I-1 and I-2 are soluble in chiral S 2-methyl-1-butanol, but no fluid mesophase appears in the mixtures in the temperature range 25°C to 90°C.

This research was supported by grants from the German-Israeli Foundation (GIF) for Scientific Research and Development, and by the Israel Academy of

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Sciences. One of us (J.B.) thanks the France-Israel Scientific Exchange Program for a visiting fellowship at the Weizmann Institute of Science.

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