Organic lyotropic lamellar liquid crystals

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X-ray diffraction experiments on smectic A and C forming thermotropic liquid crystals reveal that the smectic layer spacing increases with the addition of organic solvents to the host material. The rate of this increase indicates the formation of an organic lyotropic lamellar liquid crystal phase in which the solvent is intercalated between the smectic layers of the host liquid crystal.

1. Introduction

In this paper the author reports the discovery of non-aqueous lyotropic lamellar phases where organic solvents are intercalated between the smectic layers of a host thermotropic liquid crystal.

Lyotropic liquid crystals are strongly amphiphilic systems, usually mixtures of amphiphilic molecules and water which demonstrates a variety of ordered phases as the temperature and concentration is varied [1,2]. Thermotropic liquid crystals are weakly amphiphilic systems, usually pure materials or mixtures of like molecules which demonstrate a variety of ordered phases as the temperature is varied [3,4].

X-ray diffraction experiments on lyotropic lamellar liquid crystals indicate the formation of alternating sheets of amphiphilic molecules arranged in bilayers and water. The layering is uniform over micron length scales and the layers are well defined as evidenced by many orders of Bragg reflections. X-ray diffraction experiments on the smectic A (S_A) and smectic C (S_C) phases of thermotropic liquid crystals, show that the liquid crystal molecules are also arranged into sheets with the long axis of the molecules either normal (S_A) or tilted (S_C) to the plane of the sheets. Generally, a strong first order with vanishingly small second and third order Bragg reflections are observed. The lack of higher order Bragg reflections (Fourier components) led to a 'density wave' model in which layers are uniformly spaced, but the registration of neighbouring molecules is weak, resulting in ill-defined layer boundaries [5].

There is wealth of indirect evidence to suggest that the layers are well defined in the S_A and S_C phases. Optical observations include terraced droplets [6], focal-conic textures [6], and layer by layer freezing of freely suspended films [7]. More direct proof is obtained from X-ray scattering studies on layer fluctuations in freely suspended films [8,9] and on the chevron layer structure found in smectic liquid crystal display devices [10].

To further probe smectic layering in the S_A and S_C phases, organic solvents were added to thermotropic liquid crystals. The details of these experiments are discussed below.

2. Experimental

The following liquid crystals were selected for their room temperature smectic phases: 870E and 8CB are S_A, and W7-W82 is S_C^* [11–13]. These liquid crystals were mixed with various solvents; n-hexane, n-decane, benzene, and trichloroethylene (selected for its high electron density).

Samples were prepared from 0·0 to 2·0 mol ratio of solvent to liquid crystal. The host liquid crystal was introduced in a tared, 1 mm glass capillary tube and weighed. A predetermined amount of solvent was delivered by syringe, and the capillary tube quickly sealed by filling the end with a low vapour pressure epoxy. Finally, samples were heated into the isotropic (I) phase of the host liquid crystal for several hours to hasten diffusion of the solvent into the liquid crystal.

Smectic layer spacings were determined using a two circle X-ray spectrometer with a rotating anode (CuK_α) source (Rigaku RU-300), two circle goniometer, scintillation detector, bent pyrolitic graphite monochromator and slits. The resolution of the spectrometer is 0·07°, FWHH of a 2θ scan through the unscattered beam. Samples were placed in a single stage oven ($\pm$ 0·1°C) and data collected as Intensity versus 2θ at various temperatures.

The I–N phase transition temperature in the 870E/n-hexane system was determined by polarized light optical microscopy using a Nikon Optiphot-Pol microscope and an Instec hotstage.

3. Results and discussion

The amount of solvent incorporated into a smectic thermotropic liquid crystal depends on the host liquid crystal, the amount of solvent, the strength of the solvent, and temperature. In general, mixtures phase separate into a clear solvent rich layer above a cloudy liquid crystal rich layer for a solvent to liquid crystal mole ratio of $\geqslant 1 \cdot 0$. Mol ratios $> 0 \cdot 1$ of trichloroethylene in host liquid crystal were found to destroy the smectic phase.

At room temperature all host liquid crystal/solvent mixtures exhibited a single strong (0 0 1) Bragg peak with the exception of mixtures made with trichloroethylene. For the 870E/solvent and W7-W82/solvent mixtures this peak is of comparable intensity and FWHH to the pure liquid crystal with no enhancement of higher order reflections. The smectic layer spacing calculated from the measured Bragg peak monotonically increased with increasing volume of solvent.

Figure 1 shows the smectic layer spacing at room temperature for various amounts of n-decane, n-hexane, and benzene mixed with 870E. Note the initial linear increase in layer spacing with increasing solvent to liquid crystal volume ratio and the saturation of the layer spacing for the alkane solvents at about 1·4 times the S_A layer spacing of pure 870E. Samples above a mol ratio of 1·0 (volume ratio of 0·5) had visibly phase separated (data was collected in the liquid crystal rich layer).

The presence of a single Bragg peak indicates a single smectic phase. As the volume of solvent increases within the smectic phase one expects, initially, a linear increase in layer spacing. The slope of this linear increase can range from 0 to some maximum value dependent on how the solvent is incorporated in the host liquid crystal. If the volume of solvent contributes only to increasing the spacing between neighbouring liquid crystal molecules within the smectic layer then the slope is zero. The maximum slope occurs when the volume of solvent contributes only to increasing the smectic layer spacing, i.e. solvent is excluded from between liquid crystal molecules. The latter case is shown schematically in figure 2. The derivation of the relationship between layer swelling and solvent volume is as follows: consider a right circular cylinder of fixed cross section A, and height d, containing both a liquid crystal layer ($V = V_{LC}$, thickness $= d_0$) and a solvent layer ($V = V_s$, thickness $= d_s$). Differentiating the volume of this cylinder one obtains

$$\Delta V = A \Delta d. \qquad (1)$$

For zero solvent volume,

$$A = V_{LC}/d_0. \qquad (2)$$

Substitute (2) into (1) to obtain

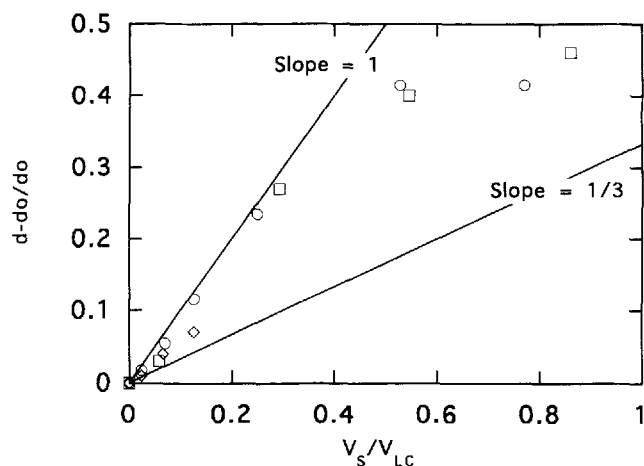$$\Delta d/d_0 = \Delta V/V_{LC} = V_s/V_{LC}. \qquad (3)$$

Figure 1. Fractional increase in smectic layer spacing ($(d-d_0)/d_0$) plotted against the ratio of solvent volume to liquid crystal volume. The points are experimental data; 870E mixed with, ($\square$) n-decane, ($\bigcirc$) n-hexane, and ($\lozenge$) benzene. The rate at which the layer spacing increases with addition of solvent is dependent on how the solvent is incorporated into the host liquid crystal. The maximum rate of increase (line with slope = 1) occurs when an added volume of solvent contributes solely to an increase in the layer spacing as in figure 2. If the solvent were incorporated isotropicly, the slope would be 1/3. If the solvent were incorporated entirely within the liquid crystal layers the slope would be 0.
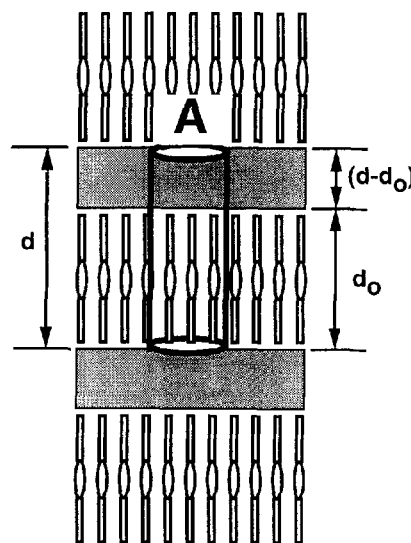

Figure 2. Schematic representation of the organic lamellar liquid crystal phase in which the solvent is intercalated between the smectic A layers of a thermotropic liquid crystal. Lamellar repeat distance, d, thermotropic liquid crystal layer thickness d_0, solvent layer thickness d-d_0. The cylinder is of cross-sectional area A and height d.

A similar analysis can be done for the case of uniform (3-d) expansion:

$$\Delta d/d_0 = 1/3 V_s/V_{LC} \qquad (4)$$

In order to plot the data for several solvents, the molar ratio for the various samples is converted to the form of equation (3),

$$\frac{V_s}{V_{LC}} = \frac{MW_s}{MW_{LC}} \frac{\rho_{LC}}{\rho_s} \frac{moles_s}{moles_{LC}}, \qquad (5)$$

where $MW_{870E} = 333 \, g \, mol^{-1}$ (manufacturer supplied), and $\rho_{870E} = 0.98 \, g \, cm^{-3}$ (determined experimentally by pycnometry using a 20 µl pipette).

The data for 870E/n-hexane, 870E/n-decane, and 870E/benzene are plotted in figure 1 along with the line representing the maximal increase in layer spacing with added solvent (slope = 1, equation (3)) and the line representing uniform incorporation of the solvent in the host liquid crystal (slope = 1/3, equation (4)). *The data points for 870E mixed with n-hexane and n-decane lie along the line of maximal slope (samples with $V_s/V_{LC} > 0.5$ had visibly phase separated). Therefore, these solvents must be incorporated as shown in figure 2, i.e. an organic lyotropic lamellar liquid crystal phase forms in which the solvent is intercalated between the smectic layers of a thermotropic liquid crystal.*

The 870E/benzene mixture (see figure 1), demonstrates a linear increase of the layer spacing with increasing solvent to liquid crystal volume ratio with a slope less than the maximal slope. This indicates that some of the benzene is incorporated within the liquid crystal layers. Benzene happens to be one type of probe molecule added to smectic phases in order to examine their structure by nuclear magnetic resonances [14]. These probe molecules are generally small and good solvents for smectic liquid crystals. Future work will investigate the effects of molecular size and solvent activity on the swelling of smectic phases.

The lyotropic lamellar layer spacing in the 870E/n-hexane mixtures is constant over a large temperature range, see figure 3. This suggests that the solvent layer thickness is constant and that the liquid crystal layer maintains the S_A layer structure as the temperature is varied.

In the 870E/solvent mixtures the smectic peak weakens in intensity and broadens as the temperature nears the S_A–N phase transition. At some sample dependent temperature the smectic peak is drastically reduced in intensity with the remaining peak similar in intensity and FWHH to that seen in the nematic (N) of the pure host liquid crystal. Depression of the I–N and N–S_A phase transition temperatures increases with increasing mol ratio of solvent to liquid crystal, see figure 4. The exact nature of the non-layered phase between the S_A and I phases has
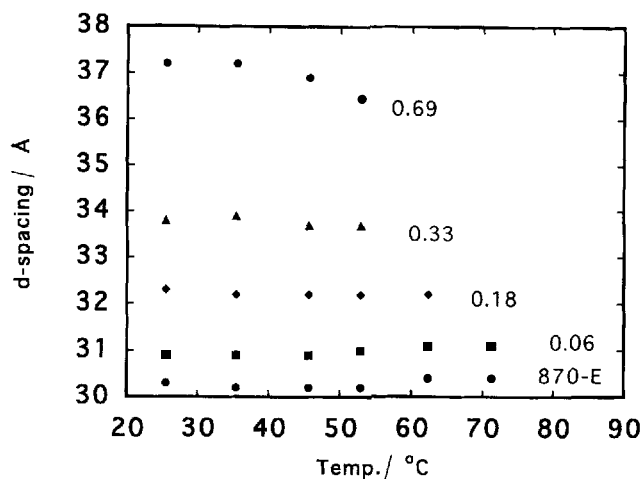

Figure 3. Lyotropic lamellar layer thickness against temperature for various mol ratios of n-hexane to 870E. The samples were cooled from the N phase to the lyotropic lamellar phase. 870E is a room temperature S_A material with S_A–N and N–I phase transitions at 71.2 and 82.4°C, respectively.

not been determined here, but is accepted as the N phase from NMR studies on similar systems [6].

Preliminary data on W7-W82 mixed with n-hexane or benzene indicate two regimes. At molar ratios of solvent to liquid crystal ≤ 0.25 the mixtures mirror the temperature dependent layer spacing behaviour of the solvent-free host material, i.e. the mixtures exhibit the characteristic shrinkage in the smectic layer spacing with decreasing temperature of the S_C phase [15]. At higher mol ratios this effect is masked by a temperature dependent inclusion (or exclusion) of solvent from the liquid crystal layers. Further investigation will be required to determine if there
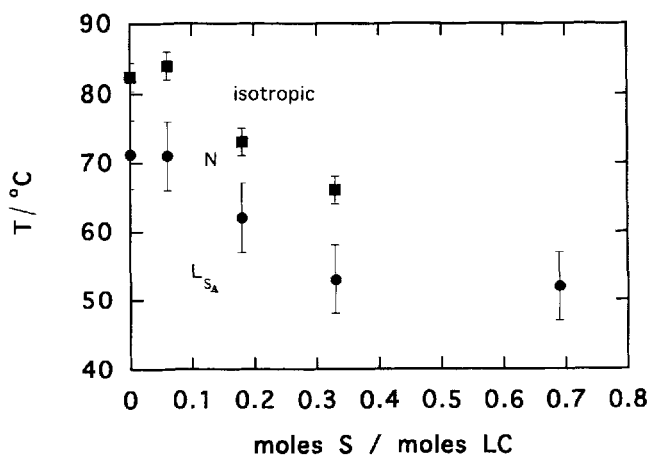

Figure 4. Phase diagram for the 870E/hexane system. The lyotropic lamellar S_A phase (L_{S_A}) to N phase transition temperatures were determined by X-ray scattering. The N–I phase transition temperatures were determined by optical microscopy.

is a S_C–S_A phase transition driven by solvent inclusion within the smectic layers.

Visual inspection of 8CB/n-hexane and 8CB/benzene mixtures shows that the solvent is not uniformly distributed throughout the host liquid crystal. Minimal, non-reproducible swelling was observed in the 8CB/n-hexane mixtures. No swelling was observed in the 8CB/benzene mixtures. 8CB has the S_{A_d} structure in which the molecules pack as dimers. It is likely that molecular packing within a smectic phase is important to the formation of the lyotropic lamellar phase.

4. Conclusions

The formation of an organic lyotropic liquid crystal phase in which solvents are intercalated between the layers of the S_A or S_C phases in a thermotropic liquid crystal has been demonstrated. The arrangement of alternating sheets of solvent and liquid crystal molecules requires that the smectic layers be well-defined sheets.

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[11] 870E is a proprietary mixture from BDH Limited, Broom Road, Poole, BH12 4NN, England. The phase sequence of 870E is S_C^* 17·2°C S_A 71·2 N* 82·4 I. $MW = 333\,\mathrm{g\,mol}^{-1}$.
[12] 8CB is 4-cyano-4'-octylbiphenyl and is available from BDH (catalogue name K24). 8CB has the following phase sequence: Cr 21·5°C S_A 33·5 N 40·5 I.
[13] W7–W82 is a 50:50 mixture of compounds W7 and W82 which are 4'-[(s)-2-methyl-3-oxa-1-pentyloxy]phenyl 4-(decyloxy)benzoate and 4'-[(s)-1-hexyloxy-4-methyl]-phenyl 4-(decyloxy)benzoate, respectively. The 50:50 mixture exhibits the following phase sequence Cr 22°C S_C^* 52 S_A 60 I.
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