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An X-ray scattering study of the lamellar/nematic/isotropic sequence of phases in decylammonium chloride/H_2O/NH_4Cl

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An X-ray scattering study of the lamellar/nematic/isotropic sequence of phases in decylammonium chloride/H_2O/NH_4Cl

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An X-ray scattering study is presented of the lamellar/nematic/isotropic sequence in the lyotropic system DACl/H_2O/NH_4Cl. The whole reciprocal space of monocrystalline samples oriented in magnetic fields are reconstructed from their two dimensional sections on photographic films. Intense diffuse scatterings are observed in the lamellar phase, around and away from the Bragg spots. Their evolution close to the lamellar/nematic transition reveals the presence of intense structural fluctuations. They take place over temperature ranges which are significantly greater than those associated with the smectic/nematic transitions in thermotropic liquid crystals. A similar situation is observed in the isotropic phase in the vicinity of the nematic/isotropic transition.

1. Introduction

We present an X-ray scattering study of the lamellar/nematic/isotropic sequence in the ternary lyotropic liquid crystal DACl/H_2O/NH_4Cl. The whole sequence was systematically explored, particularly in the vicinity of the phase transitions and attention was focused on the diffuse scatterings in order to obtain more information about the structural fluctuations in this system. This work continues that started several years ago [1], in which it was established that lamellar phases in lyotropic liquid crystals are not necessarily composed of infinite lamellae but, in certain cases, can be fragmented on a microscopic scale of about 60 Å. Since its original presentation this idea has been confirmed and the size and shape of the aggregates delineated [2, 3].

It is clear now that the structural elements in the three phases of the sequence are oblate aggregates, composed of amphiphilic molecules of small aspect ratio in the range 2 to 4. The micelles in the lamellar phase are translationally ordered along one dimension and also orientationally ordered, whilst in the nematic phase they are only orientationally ordered. Thus, it is tempting to make a direct analogy with smectic and nematic phases of classical thermotropic liquid crystals, substituting the individual molecules by micelles as elements of structure. However, it is not clear how far this analogy can be taken, particularly in respect of the models and conclusions concerning the phase transitions. Indeed the properties, shape, size, lability, and interactions of these micelles are very different from those of the molecules, their counterparts, in thermotropic liquid crystals. Such large differences might be expected to lead to mechanistic differences in the behaviour of the two types of system, manifest in the type of long range structural order.

One approach to this question was to detect and analyse the diffuse scatterings in three dimensional reciprocal space, reconstructed from two dimensional sections on photographic films, of monocrystalline samples aligned by a magnetic field. At this stage of the study, our results suggest differences between the behaviour of thermotropic and lyotropic liquid crystals.

2. Experimental

2.1. *Materials*

Decylammonium chloride was prepared by the method of Radley and Saupe [4]. Samples were made by weighing out the components into glass tubes containing a constriction and closed by a teflon stopper sealed with an O-ring. Mixing was achieved by repeated centrifugation back and forth; this was further repeated several times over a period for several days. Samples were stored at 30°C and recentrifuged before use. In this study the sample used had a composition of 40·91 per cent DACl, 55·00 per cent ^2H_2O and 4·09 per cent NH_4Cl by weight with the transitions

$$L_\alpha \xrightarrow{37\cdot5^\circ C} N_D \xrightarrow{55\cdot8^\circ C} (N_D + I) \xrightarrow{61\cdot6^\circ C} I,$$

these were determined by observation of the textures under a polarising microscope [1].

2.2. *X-ray scattering*

The experiments were performed using the high flux source of synchrotron radiation at the Laboratoire d'Utilisation des Rayonnements Electro-magnetiques (LURE) with the small angle scattering spectrometer D_{16} (responsible person S. Megtert). Samples were contained in 1·5 mm diameter Lindemann capillaries. They were held in a copper block through which thermostated water was circulated. Temperatures were measured using a calibrated thermocouple. Samples were aligned in the N_D phase by slow manual rotation about the tube axis (x axis), whilst an *in situ* magnetic field of 3 kG was applied along the z axis (see figure 1 (*a*)). This procedure resulted in the sample being aligned with the director $\hat{\mathbf{n}}$ lying along the x axis. This alignment was maintained on cooling into the L_α phase. The beam was collimated to 0·2 mm and had a wavelength of 1·61 Å. The sample to flat film distance was 251·55 mm, much of it in helium to reduce parasitic scatter. Exposure times were typically 30 to 60 min in order to detect weak features of the scattering. The beam stop limited the observations to $s \geqslant 0\cdot005\,\text{Å}^{-1}$, where s is $2\sin\theta/\lambda$. These observations were complemented by using a Kratky camera by Anton Parr, Austria, mounted on a conventional X-ray generator and using a computer controlled counter in order to observe the scattering of powder samples at very small angles, up to $s = 0\cdot0013\,\text{Å}^{-1}$. Compared to our first study of the same system [1] this study is characterized by much better control of sample orientation, instrumental resolution and access to small angles.

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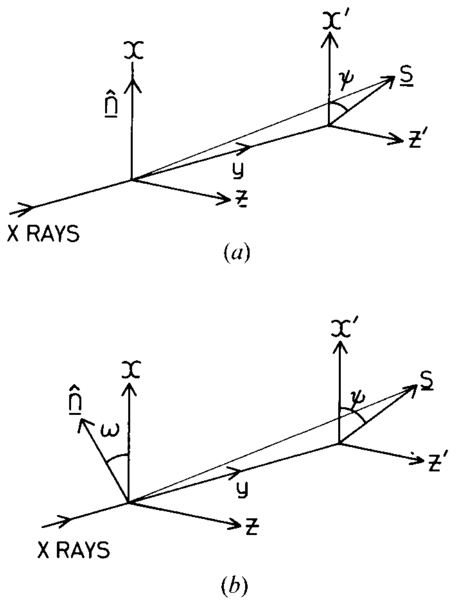

Figure 1. The axes used and referred to in the text, x is the sample tube axis, z the magnetic field direction and x' and z' are axes parallel to x and z but in the plane of the film. ψ is the angle between the scattering vector **s** and x'; (*a*) the director **n̂** (i.e. the capillary axis) parallel to x and (*b*) **n̂** tilted by an angle ω to x in the xy plane.

2.3. *Investigation of recriprocal space*

Photographs of the X-ray scattering can only provide a two dimensional section of the three dimensional reciprocal space. In order to obtain a complete three dimensional picture of it, several different two dimensional sections were recorded by orienting the sample about the z axis so that **n̂** lay in the xy plane and made an angle ω with the x axis (see figure 1 (*b*)). This was useful in examining the lamellar phase.

3. Results and discussion

On the principle that more ordered systems are more readily understood than disordered, scattering from the L_α phase is considered first before examining how this order breaks down as the system moves to the nematic and then to the isotropic phases.

3.1. *The lamellar phase*

Figure 2 shows a typical scattering pattern for the lamellar phase with **n̂** parallel to the x axis, of figure 1 (*a*). Crudely it consists of intense Bragg reflections, both first and higher orders in the ratio 1 : 2 : 3, etc., along the x' axis and long lateral bands parallel to the x' axis but located at an s of about 0·017 Å^{-1} on z'. This scattering pattern has been interpreted previously as follows [1]: the Bragg peaks come from scattering the lamellar planes which here have a spacing of 42·2 Å at 24·5°C and exhibit a high degree of translational order in the x direction as evidenced by the sharpness of the peaks. The more diffuse lateral bands show that the structure of the lamellae departs from their classical description as infinite and continuous lamellae with flat interfaces. We have shown in a previous paper [1] that the lateral bands are associated with

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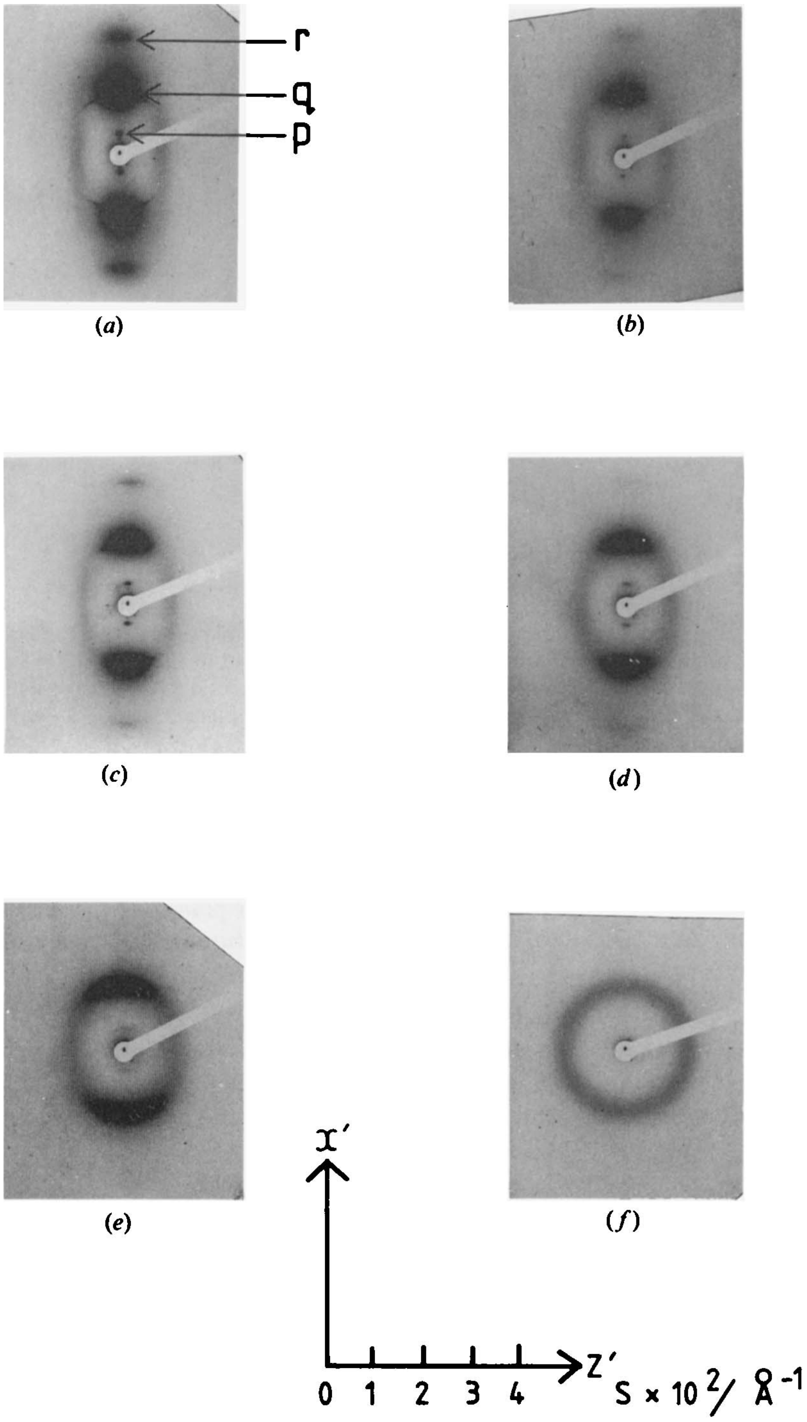

Figure 2. X-ray scattering from a 40·91 per cent DACl, 55·00 per cent ^2H_2O and 4·09 per cent NH_4Cl by weight sample at the temperatures (*a*) 24·5°C; (*b*) 36·0°C; (*c*) 39·0°C; (*d*) 42·0°C; (*e*) 53·0°C; (*f*) 62·5°C. The axes are defined in figure 1 (*a*) and the scales on x' and z' axes are identical. Reflections q and r are the first and second order Bragg reflections, respectively. Reflection p is an artifact resulting from a $\lambda/3$ component which remains unfiltered by the monochromating crystal on D_{16}.

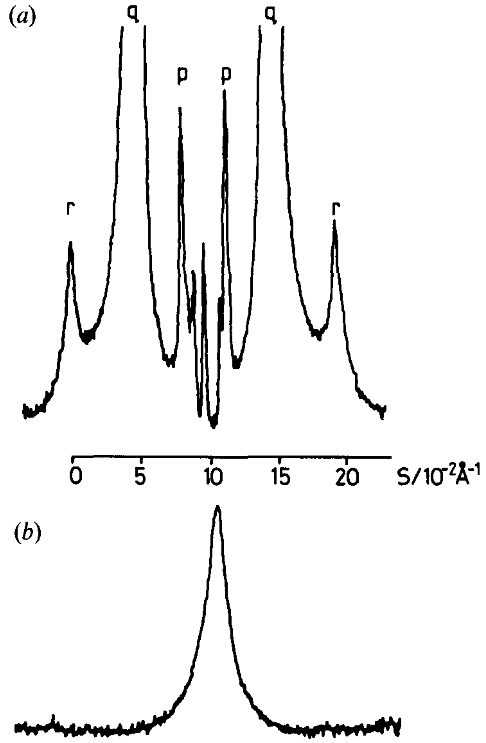

Figure 3. The microdensitometer traces of the X-ray picture taken at 24·5°C (figure 2(*a*)) recorded (*a*) along the x' axis and (*b*) parallel to the z' axis, the latter through the second order Bragg peak. The intensity is in arbituary units. (*a*) shows both first and second order Bragg peaks, (q and r respectively). Comparison should be made of the width of the second order peak in the x' and z' directions.

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discontinuities within the lamellae having separations of approximately 60 Å, which probably correspond to discoidal aggregates. Rotating $\hat{\mathbf{n}}$ away from x allows the scattering to be explored as a function of ω, and to reconstruct reciprocal space which has cylindrical symmetry around $\hat{\mathbf{n}}$. The lateral bands appear as the wall of a cylinder, and the Bragg spots as disks with relatively small thickness and larger lateral extension. This is illustrated for configuration 1 (*a*) ($\hat{\mathbf{n}} \parallel x$) in figure 3 which compares x' and z' scans of the second order Bragg peak, showing the increased width in the z' direction. It is important to notice here that the lateral extension of the first and second order Bragg spots are comparable and that nothing similar is observed around the zeroth order spot. These diffuse scatterings are more extended and more intense than those observed in a thermotropic smectic [5].

The extension of the first and second order Bragg spots indicates the presence of a displacement of the translational ordering transverse to the z' direction. The absence of scattering around the zeroth order shows that we are not dealing with modulations of the density of scattering centres, either within the lamellae or between domains of finite size, but rather with modulations of displacements of the lamellae [6]. The latter can be caused by fluctuations of undulations of the lamellae or by a distribution of dislocation defects. The contribution of the fluctuations is probably quite important [7]. In the case of dislocations the diffuse scatterings along z' cannot be due to the regions of the sample directly perturbed by individual dislocations, because for a region of parabolic extension where the orientation of the lamellae are perturbed by the presence of an edge dislocation [8], as well as for a helical core of a screw dislocation [9], the lateral extension of the scattering around the Bragg peaks should increase from the first to the higher orders. As this is not so the scattering must be dominated by interferences between the parabolic walls of neighbouring edge dislocations or the walls created by associations of screw dislocations [7, 9] which, in both cases, limit the lateral extension of the lamellar domains. The two possibilities, fluctuations and dislocations are certainly highly likely in this lamellar system, because of its fragmented state, but cannot be distinguished by these results.

The intensity profile of the Bragg peaks along the x' axis (see figure 3 (*a*)) shows both first and second order to be intense and sharp but with broad asymmetric bases with more intensity to large angle or smaller lamellar spacing. This should also be considered in the light of the fluctuation approach proposed in [7]. However, our observations do not allow for an accurate quantitative analysis. It might also be thought that the asymmetry of the profile is related to the compression of the water layer from its equilibrium separation being more common than expansion. This might be related to the fragmentation of the lamellae and might reflect the particular shape of the inter-aggregate potential energy curve. Water layer narrowing is limited by the approach of charged interfaces. With displaced water being accommodated within the microscopic bilayer defects, the maximum thickness of the water layer is determined by the approach of the aggregates within a lamellar plane. Thus, since water layer thinning or thickening will involve quantitatively different interactions, it should not be surprising that the X-ray scattering exhibits asymmetry.

The lateral band running parallel to x' shows a profile in the z' direction which is broad and, liquid-like, which changes little with temperature. This has been interpreted as showing that the lamellae are two dimensional fluids of finite oblate aggregates of amphiphiles [1, 2]. Parallel to x' the profile of the lateral band is broad (see figure 4). The monotonic slow decrease of this profile, which extends for s values larger than that of the first order Bragg spot, strongly suggests that it is determined by the form factor of a lamellar aggregate and that there is an absence of correlation between the positions of the aggregates between different lamellae. The lamellar aggregate form factor may be calculated from the Fourier transform of its electron density profile. The major dimensions of an aggregate parallel and perpendicular to $\hat{\mathbf{n}}$ may be estimated from the scattered X-ray peak positions in those directions. The electron density of the lipid and aqueous regions are known whilst the width and density of the head group region were treated as two adjustable parameters in a computer fit, using only the form factor of a single aggregate and without inclusion of interaggregate interferences (see figure 4). The success of this fit supports the idea that there is no correlation between the aggregates in different layers.

The features of the lamellar phase described here do not vary significantly with temperature in the range studied, there being little difference between the scattering pattern at 24·5°C and that at 35·8°C.

3.2. *The nematic phase*

The transition to the nematic, N_D, phase at 37·5°C is hardly detected with X-ray scattering. The scattering pattern at 39·0°C (see figure 2) is qualitatively identical to that at 36·0°C or indeed to any in the lamellar phase. The Bragg spots are only slightly

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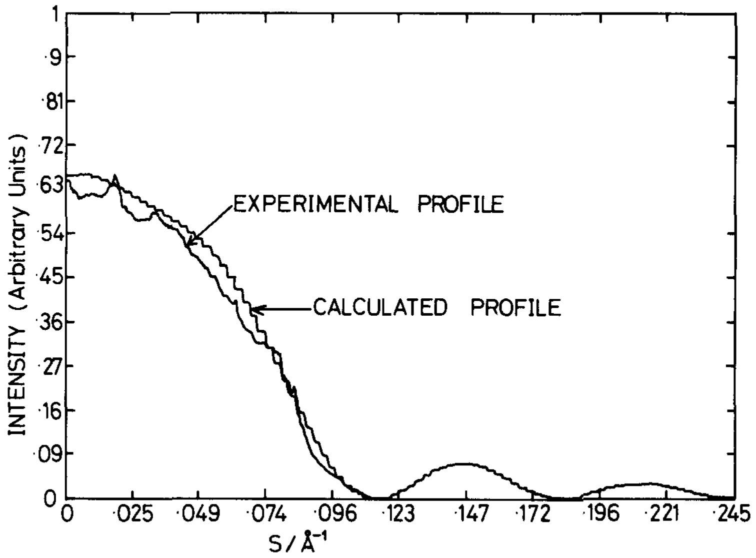

Figure 4. The microdensitometer profile from the sample at 33°C through the lateral band parallel to the x' direction. The fit shown was obtained by assuming the aggregate to have an ellipsoidal cross-section with semi axes of 10 Å and 19 Å. These values were chosen because a bilayer thickness of about 20 Å was the mean value of the bilayer calculated using data from the classical bilayers of [1] whilst 19 Å was estimated from the maximum in the lateral band measured along z'. The electron densities were $\varrho_{\mathrm{aq}} = 0{\cdot}335\,\text{Å}^{-3}$ and $\varrho_{\mathrm{chain}} = 0{\cdot}273\,\text{Å}^{-3}$. The best fit gave a head group width of 2·7 Å and an associated electron density of $0{\cdot}360\,\text{Å}^{-3}$.

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broader, indicating the disappearance of the long range order, and the long straight lateral bands are still present, indicating the persistance of a local lamellar organization of the aggregates in the nematic phase. This behaviour is in contrast to that observed in thermotropic liquid crystals where the smectic–nematic transition has a discontinuous change in the X-ray scattering. As the temperature increases in the nematic phase both positional and orientational disorder increase as evidenced by the broadening of the Bragg peaks in the x' direction and the curvature of both the Bragg peaks and the lateral bands into arcs.

The scattering pattern from the nematic phase at high temperature ($>42°$C) is typical of lyonematics in general. It consists of an anisotropic ring with meridional reinforcement along x'. The lateral bands have been lost and the scattered intensity varies smoothly with ψ. Lamellar order no longer exists and the aggregates may approach all directions although the interaggregate separation in the x direction is better defined than in the z direction. The angular distribution of scattered intensity, $I(\psi)$, about the Bragg peak through the point of maximum intensity has been used to extract the second rank orientational order parameter $\bar{P}_2$ for the aggregates [11, 12]. Figure 5 shows $\bar{P}_2$ as a function of temperature. The values of $\bar{P}_2$ are high but values determined this way in other lyonematics are also found to be consistently higher than in thermotropic liquid crystals [2, 13].

3.3. *The isotropic phase*

The scattering pattern is an isotropic ring (see figure 2). If we assume that the phase is made of spherical micelles it can be deduced, from the position of the

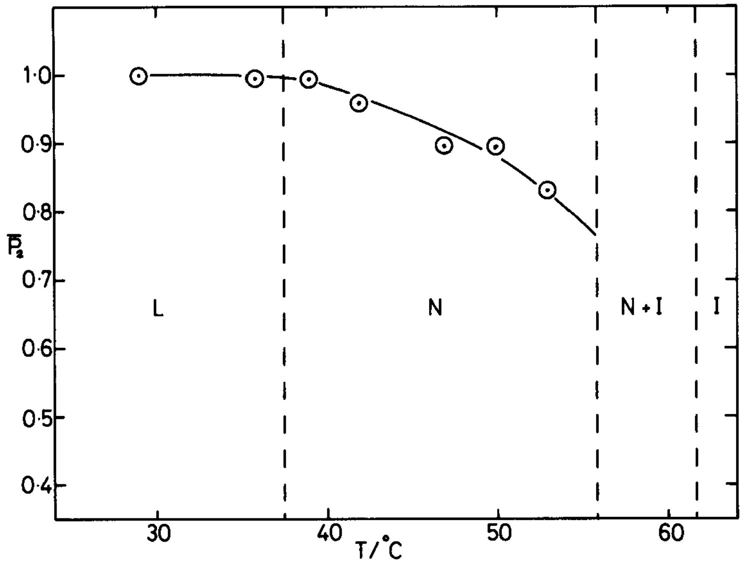

Figure 5. The variation of the second rank orientational order parameter $\bar{P}_2$ with temperature.

maximum of intensity of the ring, that their radius would be about 21 Å. This is unphysical as the all-trans molecular length is 14 Å. This implies that the micelles are not spherical; indeed they might be expected to be very close in shape to the discoidal aggregates of the nematic phase as already observed in another lyotropic system [14], with some local nematic order. Moreover the width of the ring is directly comparable to the width of the scattering in the z' direction in both nematic and lamellar phases and is narrower than might be expected from a micellar phase [15].

4. Conclusions

The evolution of the structure along the lamellar/nematic/isotropic sequence of phases may be described as follows. At low temperatures the system forms a lamellar phase, the lamellae of this lamellar phase are fragmented on a microscopic scale of about 60 Å. The positions of the fragments are disordered within each lamella without any correlation from lamella to lamella. The order of this lamellar phase is perturbed by displacement disorder. One component is longitudinal along the normal to the lamellae, a second is transverse along the lamellar plane. These might be related to the same phenomenon of smectic fluctuation modes, but also, particularly for the second component, to the presence of walls associated with defects of dislocation which limit the propagation of the translational ordering along directions parallel to the lamella. This is supported by a recent freeze fracture and electron microscopy study [3], in which walls associated with dislocation have been identified in this system.

At intermediate temperatures a continuous transition to a nematic phase takes place. The transition is continuous in the sense that there is no intervening biphasic region and that thermodynamic parameters such as the second rank orientational order parameter vary continuously across it. This phase is an assembly of aggregates without long range translational order, but with orientational order; they have a very similar shape to those of the lamellar phase. This phase is characterized by two aspects which make it appear much more ordered than nematic phases of thermotropic

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materials. First, it is characterized by the persistence of significant short range lamellar order (cybotactic groups) far from the transition. Secondly, it exhibits the high degree of orientational order measured in all lyotropic materials even at the approach of the transition to the isotropic phase. At higher temperature, the orientational order is lost and the isotropic phase appears, which is characterized by significant short range nematic order, even a long way from the transition.

This sequence of phases can be structurally similar to a smectic/nematic/isotropic sequence in a thermotropic liquid crystal if we consider that the element of structure are aggregates of molecules in the first case, whereas they are individual molecules in the second [15]. This similarity between the two materials concerns the nature of the order of their phases, or the symmetries of their structures; if the degrees of order are considered the two materials behave differently. Order fluctuations take place over much larger temperature ranges in the lyotropic material than in the thermotropic. This suggests that lyotropic material may provide a new experimental situation for testing the models proposed for understanding the mechanisms of phase transitions in liquid crystals, particularly those involving dislocation mechanisms at the smectic A–nematic transition [16, 17].

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