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Anchoring properties of a lyotropic, nematic discotic CsPFO/water mixture

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A sample of a CsPFO/water mixture in the nematic discotic phase is used to investigate liquid crystal anchoring properties. A splay distortion is introduced in the uniform nematic alignment and orientation and relaxation processes are observed. From experimental values of the orientation and relaxation times we determine the rotational viscosity and the splay elastic constant for this mixture.

1. Introduction

Recently, the interactions of a lyotropic liquid crystal with boundary amorphous glass surfaces were investigated [1]. An unusual phenomenon was observed; the gliding of the director at the surface. In order to explain the experimental results, a new qualitative model was proposed. According to this model, at the boundary surface, there is a bilayer structure, with defects or channels, as in a lamellar structure. These defects or channels, are interpreted as large anisotropic objects that can glide and align parallel to an external magnetic field.

In this earlier study the lyotropic mixture of potassium laurate (LK), decanol (DeOH) and water was used and the experiments were performed in the uniaxial calamitic nematic phase (N_c) [2]. However it is known that this lyotropic mixture presents local biaxiality in the uniaxial phase, and a pseudo-lamellar order in all nematic phases [3, 4].

We now propose to extend the investigation of the anchoring properties of lyotropic liquid crystals using a binary mixture of caesium perfluorooctanoate (CsPFO) and water. This mixture is particularly interesting because it possesses only one uniaxial phase (discotic) with positive diamagnetic anisotropy (χ_a) and is chemically stable [5]. It was shown that the CsPFO amphiphile can form discoid or bilayer aggregates only [5, 6], and therefore, the microscopical symmetry is uniaxial.

2. Experimental

The lyotropic sample is a mixture of caesium perfluorooctanoate (33 wt%) and water. The sample becomes nematic discotic between approximately 20°C and 28°C, and is surrounded by a lamellar phase (lower temperatures) and an isotropic phase (higher temperatures) [5]. The sample holders are microslides, from Vitro Dynamics, 4 mm wide and 200 μm thick. The inner surfaces of these microslides were examined with an interferential microscope and no irregularities greater than 0.1 μm were observed.

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The laboratory frame is defined with the x axis parallel to the length of the microslide and the z axis normal to the biggest surfaces. Initially, the sample is introduced in the microslide and is uniformly oriented by a strong magnetic field parallel to the x axis. Since χ_a is positive the director orients parallel to H , resulting in a homeotropic texture. Then, the microslide is tilted by an angle θ , measured from the xy plane, and a magnetic field H is applied along the x direction. The process of orientation of the sample is studied observing the sample between crossed polarizers and measuring the intensity of the transmitted light (see figure 1). The same technique is applied to investigate the relaxation process, when H is turned off.

The experiments are performed with the sample in the N_D phase, the temperature is 23°C, within $\pm 1^\circ\text{C}$.

3. Experimental results and discussion

When the magnetic field is applied to the tilted sample, the director in the bulk tends to align parallel to H , introducing a splay deformation with respect to the boundary surfaces. There is an increase in the intensity of the transmitted light due to the orientation process along the magnetic field, as is shown in figure 2, for different values of H . Only one orientation process is observed, with a characteristic time τ_s , which does not depend on the tilt angle θ , but depends on H^{-2} (see figure 3).

When the magnetic field is applied, in the bulk, the director \mathbf{n} tends to align parallel to \mathbf{H} . This orientation process is much faster than the orientation process that takes place at the surface [1]. The characteristic director orientation time in the bulk is given by [7–9]

$$\tau_s = \frac{\gamma}{\chi_a H^2}, \quad (1)$$

where γ is the rotational viscosity. Typical values of τ_s for lyotropics are about 10 s [1].

The dependence on H^{-2} is experimentally observed and from the measured values of τ_s we determine $\gamma = 7 \text{ P}$. It is found from earlier experiments that the rotational viscosity of lyotropic mixtures is in the range 1–100 P, and is strongly dependent on temperature [10, 11].

The relaxation process was also investigated, and it is observed that at equilibrium the initial orientation returns, except for some local defects. The relaxation process does not depend on the magnetic field that has been applied or on the time it was applied, but is related to the angle θ . In figure 4, the relaxation curves for different values of θ are shown. Only one relaxation process is observed, with a characteristic time τ_r of about 10^3 s.

The splay distortion introduced by the magnetic field, relaxes in a purely viscous way with a characteristic time given by [1, 12]

$$\tau_r = \frac{\gamma L^2}{\pi^2 K_{11}}, \quad (2)$$

where L is the length associated with the distortion. Now, we must consider L , which is not equal to the thickness of the sample d . Since the sample is tilted by an angle θ , L must be equal to $d/\cos\theta$. This gives a dependence of τ_r on θ

$$\tau_r = \frac{\gamma d^2}{\pi^2 K_{11}} \frac{1}{\cos^2\theta}. \quad (3)$$

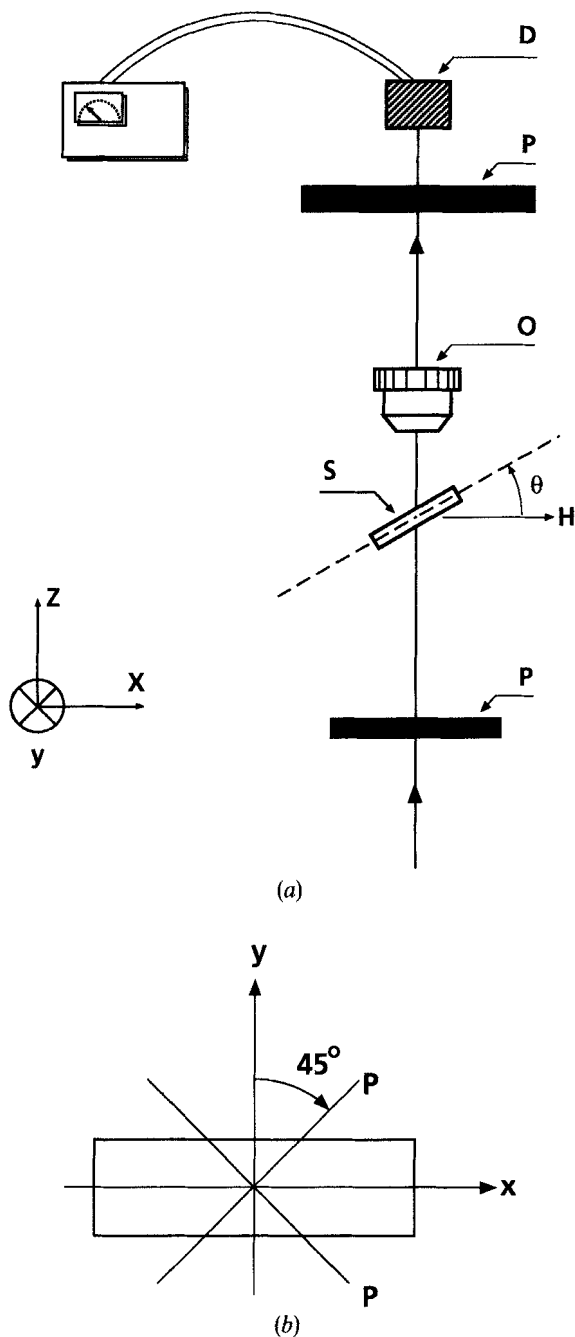


Figure 1. Experimental set-up. (a) The sample, initially oriented with the director \mathbf{n} parallel to the length of the microslide, is tilted by an angle θ , and the magnetic field \mathbf{H} is applied parallel to the x axis. (b) Orientation of the polarizers with respect to the laboratory frame axes. S = sample, P = polarizer, O = microscope objective, D = director.

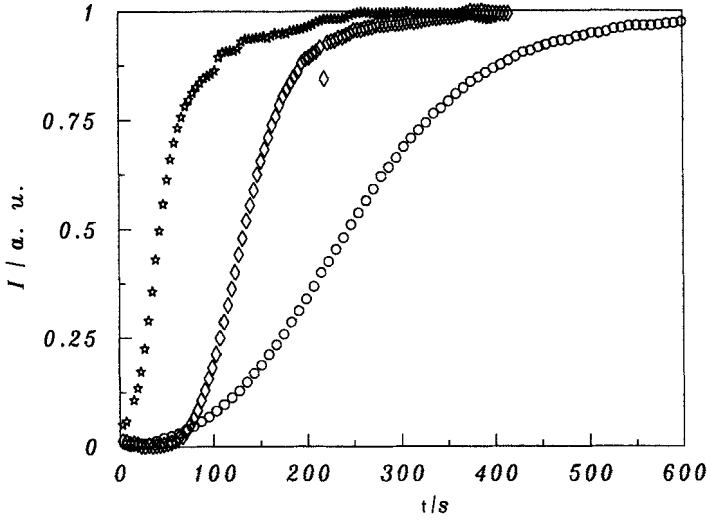


Figure 2. Orientation process. I is the intensity of the transmitted light, at $t=0$ the magnetic field is turned on. The tilt angle θ is 10° . \circ , $H=4$ kG; \diamond , $H=7$ kG; \star , $H=9.6$ kG.

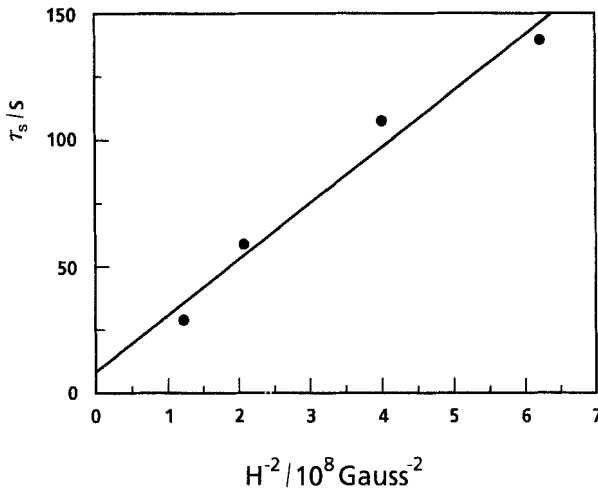


Figure 3. The characteristic orientation time τ_s as a function of H . The slope of the curve is proportional to γ/χ_a .

This is experimentally observed (see figure 5) and the value of the splay constant K_{11} is determined

$$K_{11} = (1.6 \pm 0.1) \times 10^{-7} \text{ dyne.}$$

In an earlier study [1] a different geometry was used; the distortion introduced by the magnetic field was a twist along the thickness. Two orientation processes were then observed; a fast one, due to the orientation of the director in the bulk and a slow one, due to the orientation of the director at the surface. The orientation at the surface takes place because the large anisotropic objects (defects or channels) in the bilayer structure can glide and align parallel to H . According to this picture the viscosity at the surface

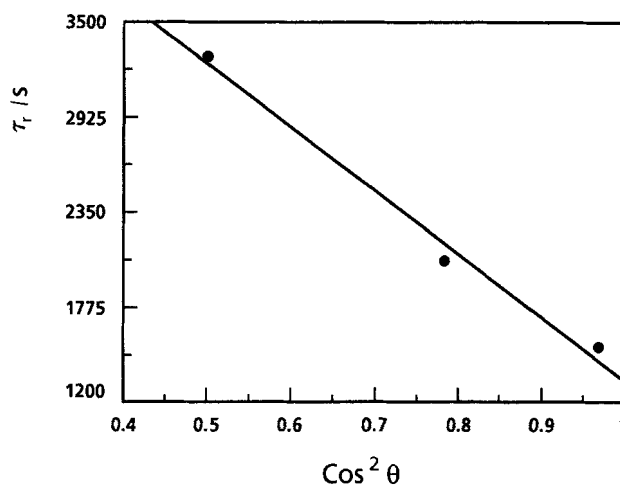


Figure 4. The relaxation time versus the tilt angle. It is observed that τ_r is related to the square of the 'effective thickness'; $L = d/\cos \theta$.

layer is increased by a factor of 10^4 . This gives rise to the long characteristic time involved in this process.

Measurements of electric conductivity and reorientation times made by Photinos and Saupe [9] for the CsPFO/water mixture showed that the reorientation time increases as the concentration of CsPFO is increased, at a given reduced temperature, and diverges at the transition to the lamellar phase.

In this experiment only one characteristic process is observed, with a characteristic time of about 10^2 s. This time compares, in order of magnitude, to the fast orientation process observed with the twist geometry in lyotropics [1]. The rotational viscosity, $\gamma = 7$ P, is obtained from equation (1) and the experimental values of τ_s . The value obtained is in the range of typical viscosities for lyotropic liquid crystals.

We remember, at this point, that equation (1) is derived from the balance of torques equation assuming strong anchoring at the boundary surfaces. For thermotropics, with typical values of γ and K we obtain $\tau_s = 10^{-2}$ s [7].

So, with the splay geometry, the lyotropic liquid crystal reproduces thermotropic behaviour. The difference in the values of τ_s and τ_r are only due to the differences in the viscosity and elastic constant. In this case well-known anchoring models can be applied [13, 14] and we can introduce an anisotropic surface energy F_s , as in thermotropics. Since the glass plate boundaries are locally isotropic the only defined direction is the normal \mathbf{w} ($w^2 = 1$) and F_s is expected to depend on $\mathbf{n} \cdot \mathbf{w}$.

However, new investigations need to be carried out to determine the form of the surface energy with more precision, as well as related parameters, like the extrapolation length.

4. Conclusions

With the geometry used in this experiment, only one orientation process is observed. This process is identified as the fast one observed before with a different geometry. The experimental values of the orientation and relaxation times, allow us to determine, for the first time, the rotational viscosity and the splay elastic constant for the CsPFO/water mixture.

The anchoring models known for thermotropics can be applied to this case, as no slow orientation process is observed, but an exact form for the surface energy must still be investigated, which takes into account the possibility of the director gliding parallel to the boundary surface.

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