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Large anisotropy of orientational fluctuations in a lyotropic nematic liquid crystal

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Two hydrodynamic modes of the orientational fluctuations were investigated in a homeotropically aligned sample of a lyotropic uniaxial nematic mixture of potassium decanoate, potassium heptyloxybenzoate, potassium chloride, decanol and deuteriated water, which forms discotic micelles. The relaxation times, measured with a photon correlation light scattering technique, show a large anisotropy over the whole nematic range: the pure splay relaxation time is much larger than the pure twist and pure bend relaxation times. This is caused by the anisotropy of the effective viscosity, probably resulting from a backflow effect. The relaxation time exhibits an approximately exponential temperature dependence, caused by the temperature dependence of the viscosity coefficients, with activation energies 0·54 eV and 0·40 eV for the deformations close to pure bend and pure splay.

1. Introduction

Mixtures of amphiphilic compounds, electrolyte and water form a variety of liquid crystal phases, depending on the molecular shape, temperature and water concentration. Both elongated and flattened micelles may form nematic phases, phenomenologically similar to the thermotropic ones [1–5]. In some cases they exhibit positive magnetic anisotropy and can be oriented by a magnetic field.

In uniaxial nematic liquid crystals, the second order elasticity associated with the deformations of the director field results in two collective orientational modes [6]. They are of the relaxational type, with the relaxation time determined by the ratio of an orientational elastic constant and a viscosity coefficient. In lyotropic systems, exhibiting a biaxial nematic phase [7], the loss of rotational symmetry results in the existence of the biaxial orientational mode, associated with small rigid rotations about the nematic axis [8, 9]. In both uniaxial and biaxial lyotropic nematic phases the micellar deformations create two, uniaxial and biaxial, non-hydrodynamic normal modes. These are observed at low frequencies: $\Gamma < 50\,\mathrm{Hz}$ [9]. Since optical observations of the phase transitions in our lyotropic system do not indicate the existence of a biaxial phase, the existence of a biaxial orientational mode is excluded.

As the nematic phase is birefringent with the optic axis pointing along the director, orientational fluctuations are strongly coupled to the optical properties and so are well studied by light scattering techniques [10]. The correlation function for the scattered light intensity allows the determination of the relaxation time [11]. The absolute scattered intensity, although difficult to measure, can give independent information on the orientational elastic constants [11–13]. The scattering from orientational

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fluctuations in thermotropic nematics is very strong and causes the characteristic turbidity of these phases. In lyotropic systems, which have at least an order of magnitude smaller birefringence, the scattering is much weaker. Lyotropic systems are also more difficult to orient. In consequence only a few light scattering studies of the orientational fluctuations in lyotropic nematics have been performed [8, 9, 14–17]. The present work is a continuation of an experiment, presented in a previous article, in which the sample, placed in a round tube, was oriented by a magnetic field [16]. We observed only ordinary–extraordinary scattering, which is the strongest and gives the relaxation time for just one of the orientational modes. Also, the cylindrical geometry of the sample introduced some distortions in the orientation. We wished therefore to remove these drawbacks and to complete the analysis.

2. Experiment

In the present experiment, the samples were prepared from 23·7 per cent (by weight) potassium decanoate, 7·3 per cent potassium heptyloxybenzoate, 7·3 per cent potassium chloride, 6·2 per cent decanol and 55·5 per cent deuterium oxide [18]. Heavy water was employed in the original reference on this mixture for use in N.M.R. experiments. We also tried to use ordinary water but obtained inconsistent results. Before mixing with the other components, the heavy water was filtered through 0·22 μm Millipore filters to remove large dust particles, which can seriously affect the light scattering data. The mixture was first thoroughly stired with a magnetic mixer, then sonicated and centrifuged to expel air bubbles. This mixture exhibits a discotic nematic phase in the temperature range from 17°C to 50°C; at higher temperatures, the system is isotropic. We do not know the exact nature of the phase below 17°C. However, the system seems to segregate at low temperatures into a crystalline component and a liquid, but does not return to the nematic phase upon heating. This indicates that there is no lamellar phase below the nematic.

The sample was placed in cells made from two parallel glass plates either 1 mm or 0·1 mm apart and sealed with epoxy resin. The alignment of the samples was obtained by placing them in a magnetic field of about 2 T for several hours. The sample has a positive magnetic anisotropy and so a homeotropic alignment resulted when the magnetic field was perpendicular to the glass plates. The alignment was checked by examination of the sample between crossed polarizers and was usually very good. On removal from the magnetic field the good alignment was preserved for several days in thick samples and even longer in thin ones.

For light scattering measurements the cell with the aligned sample was immersed in a larger glass vessel filled with oil, which served both as a temperature bath and as an index matching fluid. The temperature was kept constant to 0·1°C. Up to 50 mW of light with wavelength 514·5 nm from an argon laser was focused on the sample; the intensity of the laser beam was adjusted to give about 0·3 counts per correlator time step. Figure 1 shows the scattering geometry; the nematic director was in the scattering plane. In this geometry, one orientational mode is observed in ordinary–extraordinary scattering, that is with the incoming polarization perpendicular to the scattering plane and scattered polarization in the scattering plane, and the other mode in extraordinary–extraordinary scattering, that is with both polarizations in the scattering plane.

To calculate the true scattering angle in the sample and the scattering wave vector, both indices of refraction are also needed. We have measured them by observing the angle of total internal refraction in the cell for both polarizations. The values that we

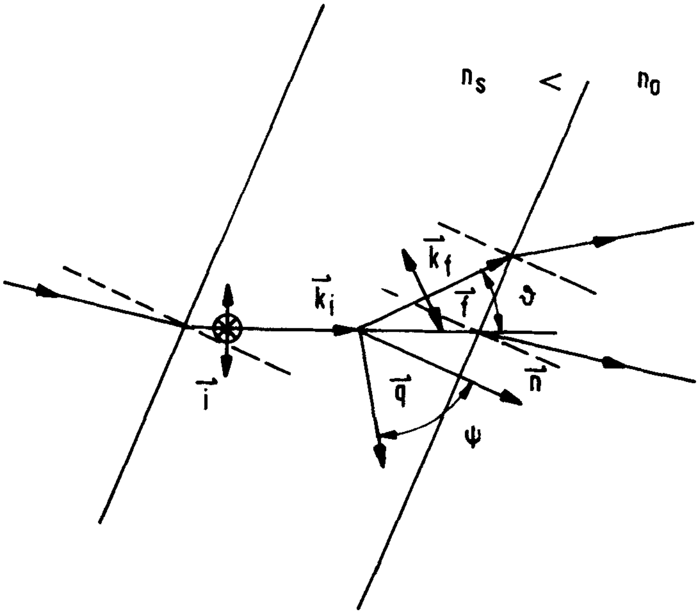

Figure 1. Experimental scattering geometry: $\mathbf{k}_i$ and $\mathbf{k}_f$ are wave vectors of incident and scattered light with polarizations **i** and **f** respectively. $\mathbf{q} = \mathbf{k}_i - \mathbf{k}_f$ is the scattering vector, determining the angle ψ with **n**, the nematic director.

obtained at room temperature were 1·34 for the ordinary ray and 1·33 for the extraordinary ray. Our method is not precise enough to allow measurement of their temperature dependence. The values obtained, however, are sufficiently accurate for the purpose of calculating the magnitude of the scattering vector and its direction with respect to the nematic director.

3. Results and discussion

The hydrodynamic theory of uniaxial nematics predicts two orientational modes with the inverse relaxation times given by [6]

$$\Gamma_1(\mathbf{q}) = (K_3 q_\parallel^2 + K_1 q_\perp^2)/\eta_1(\mathbf{q}), \tag{1}$$

$$\Gamma_2(\mathbf{q}) = (K_3 q_\parallel^2 + K_2 q_\perp^2)/\eta_2(\mathbf{q}), \tag{2}$$

where K_1, K_2 and K_3 are the splay, twist and bend elastic constants, respectively. $\eta_1(\mathbf{q})$ and $\eta_2(\mathbf{q})$ are effective viscosities, which are wave vector dependent combinations of the nematic viscosity coefficients

$$\eta_1(\mathbf{q}) = \gamma_1 - \frac{(\alpha_3 q_\perp^2 - \alpha_2 q_\parallel^2)^2}{\eta_b q_\perp^4 + (\eta_a + \eta_b + \eta_{ab}) q_\perp^2 q_\parallel^2 + \eta_a q_\parallel^4}, \tag{3}$$

$$\eta_2(\mathbf{q}) = \gamma_1 - \frac{\alpha_2^2 q_\parallel^2}{\eta_c q_\perp^2 + \eta_a q_\parallel^2}, \tag{4}$$

where γ_1 is the director twist viscosity. η_a, η_b and η_c are the fluid viscosities for various orientations of the director and fluid velocity which can be expressed in terms of the Leslie coefficients

$$\left.\begin{aligned} \gamma_1 &= \alpha_3 - \alpha_2, & \eta_a &= (-\alpha_2 + \alpha_4 + \alpha_5)/2, \\ & & \eta_b &= (\alpha_3 + \alpha_4 + \alpha_6)/2, \\ \eta_{ab} &= \alpha_1, & \eta_c &= \alpha_4/2. \end{aligned}\right\} \quad (5)$$

In a coordinate system in which the director lies along the z axis and the scattering vector lies in the xz plane, the first orientational mode contributes to light scattering with both the incoming and the scattered polarization in the xz plane. The corresponding intensity correlation function is given by [14]

$$\langle I(0)I(\tau)\rangle = A^2(kT)^2\varepsilon_a^4(K_3q_\parallel^2 + K_1q_\perp^2)^{-2}(1 + \exp(-2\Gamma_1\tau)), \quad (6)$$

where $\varepsilon_a = \varepsilon_\parallel - \varepsilon_\perp$, and A is a constant depending on collection optics but independent of the sample. The second orientational mode scatters light with the incoming polarisation along y and the scattered polarisation in the xz plane, with the intensity correlation function

$$\langle I(0)I(\tau)\rangle = A^2(kT)^2\varepsilon_a^4(K_3q_\parallel^2 + K_2q_\perp^2)^{-2}(1 + \exp(-2\Gamma_2\tau)). \quad (7)$$

The decay times of the correlation functions give the relaxation times of the modes, while the amplitudes of the correlation functions allow the determination of the elastic constants alone. In the presence of the biaxial phase in a lyotropic nematic system the light scattered from the biaxial orientational mode, with its relaxation time, contributes to ordinary–extraordinary scattering. The single exponential decay of the measured correlation functions confirms the uniaxiality of the nematic phase. The latter fact is also supported by the measured q^2 dependence of the inverse relaxation times. The scalar modes [9], with their inverse relaxation times considerably different from the measured orientational modes, were not observed.

Figure 2 shows the dependence of the first mode relaxation time versus the angle between **q** and **n** (ψ). From equation (1) it follows that the mode is pure bend when the direction of **q** is along the nematic director, and it is the pure splay mode when **q** is perpendicular to **n**. The outstanding feature of figure 2 is the large difference between the relaxation time for the pure bend and pure splay modes. The large anisotropy of the relaxation time in our sample persists over the whole temperature range of the nematic phase. Since we do not have any evidence for a smectic phase at low temperatures, a pretransitional increase of one elastic constant does not seem to be a likely explanation. Before continuing the discussion of this anomalous behaviour, let us look at the angular dependence of the second mode, which can be observed in the ordinary–extraordinary scattering and is shown in figure 3. These data are in complete agreement with our previous measurements [16], which were done in around glass tube with 3 mm internal diameter and with the continuous application of an aligning magnetic field. The second mode is again pure bend with **q** along **n** and pure twist with **q** perpendicular to **n**.

Figure 4 shows the dependence of the logarithm of the relaxation time on inverse temperature for the first mode at two different values of ψ, one close to the pure bend direction and the other close to pure splay. The data lie approximately on a straight line. This temperature dependence probably results from that of the viscosity coefficients, as we have already discussed elsewhere [16]. Additional support for this hypothesis can be obtained by looking at the temperature dependence of the total scattering intensity, which is shown in figure 5. According to equation (6) the total

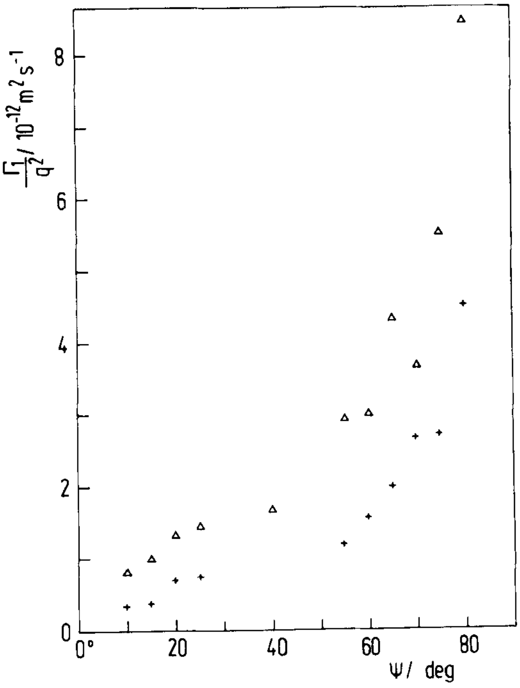

Figure 2. Angular dependence of Γ_1/q^2 at 22°C (+) and 40°C (△). ψ is the angle between **q** and **n**. The mode is pure bend at $\psi = 0$ and pure splay at $\psi = \pi/2$.

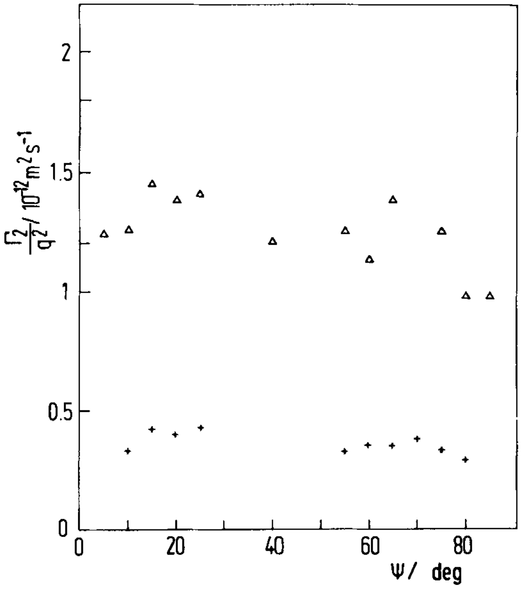

Figure 3. Angular dependence of Γ_2/q^2 at 22°C (+) and 40°C (△). The mode is pure bend at $\psi = 0$ and pure twist at $\psi = \pi/2$.

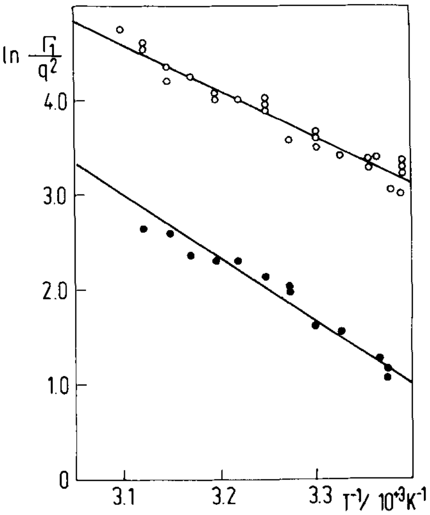

Figure 4. ln (Γ_1/q^2) for the deformation close to pure bend, $\psi = 15°$ (○) and close to pure splay, $\psi = 70°$ (●) as a function of T^{-1}.

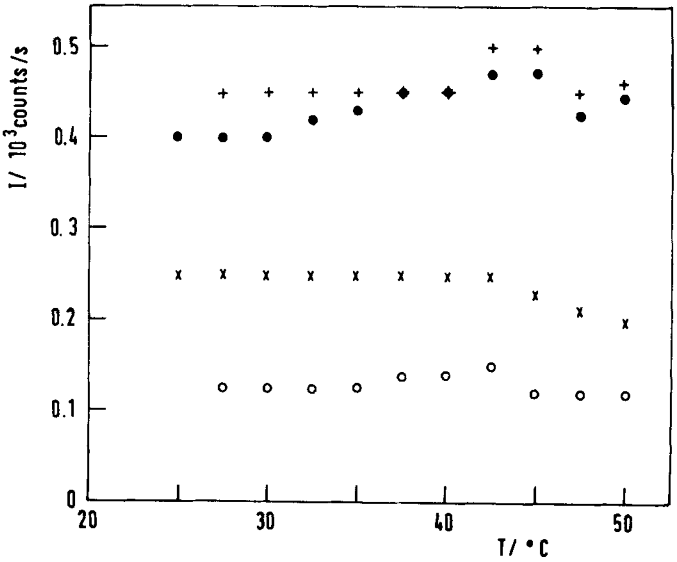

Figure 5. Temperature dependence of the scattered light intensity in ordinary–extraordinary for $\psi = 15°$ (×) and 70° (+) and extraordinary–extraordinary for $\psi = 15°$ (○) and 70° (●) light scattering.

scattering intensity depends only on the elastic constants. We were not able to make absolute measurements and so we cannot determine the elastic constants from the data. However, the scattering intensity is nearly independent of temperature and therefore we can say that the elastic constants are also only weakly dependent on temperature. In consequence most of the temperature dependence of the orientational relaxation time comes from the viscosity coefficients. From figure 4 we can deduce a value of 0·54 ± 0·03 eV for the activation energy at $\psi = 15°$, and 0·40 ± 0·03 eV at $\psi = 70°$.

These values are somewhat smaller than for the activation energy of the viscosity coefficient of the second mode, which is 0·65 eV, and which agrees with our previous measurements.

Let us return to the discussion of the large anisotropy of the relaxation time for the first mode. A large ratio of the splay and twist relaxation times has been reported for a disc-like lyotropic nematic phase of a potassium laurate-D_2O-decanol mixture [15], while the bend relaxation time was predicted to be of the same order of magnitude as for the twist. Our scattering geometry enabled us to observe the same anisotropy effect, $\Gamma_{\text{splay}}/q^2 \gg \Gamma_{\text{twist}}/q^2$, and to confirm the prediction concerning the bend relaxation time, namely $\Gamma_{\text{bend}}/q^2 \approx \Gamma_{\text{twist}}/q^2$. The model of backflow effect, proposed by Lacerda Santos *et al.* [15], can certainly be applied to our disc-like nematic lyotropic system. In this model the elastic constants are assumed to be approximately equal and so the anisotropy effect arises from the effective viscosities for different deformations. The considerably smaller splay viscosity compared to the twist and bend viscosities in a discotic system is a result of a backflow effect; that is, individual micellar rotations induce local shear flows, which can interfere constructively to produce a macroscopic backflow. For the splay deformation in a disc-like system the backflow suppresses the splay viscosity from the shear flows perpendicular to the discs. This reduction is an order of magnitude larger than for the bend deformation, where the bend viscosity is only reduced for the shear flows parallel to the discs. For a twist deformation the interference is destructive and no backflow occurs.

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