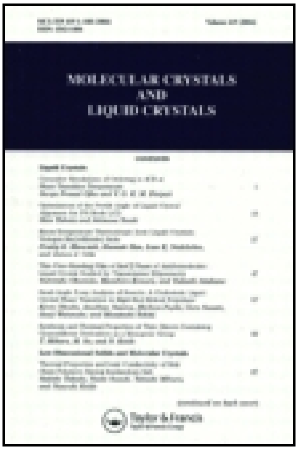

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ORIENTATIONAL FLUCTUATIONS IN A DISC-LIKE NEMATIC LYOTROPIC SYSTEM

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Abstract The hydrodynamic fluctuations in the lyotropic system which exhibits a discotic nematic phase with positive magnetic anisotropy were measured with photon correlation light scattering technique. The system is a mixture of potassium decanoate, potassium heptyloxybenzoate, KCl, decanol and deuterated water in the molar ratio of 1 : 0.25 : 0.866 : 0.349 : 24.6. The sample was oriented in a magnetic field with the director in the scattering plane. In this geometry one orientational fluctuation governed by the twist and bend elastic constants was investigated. It is of relaxational type. The relaxation time shows a weak angular dependence at constant magnitude of $\underset{\sim}{q}$ and an approximately exponential type of temperature dependence in the whole nematic range.

Amphyphylic molecules in an aqueous electrolyte exhibit a variety of ordered phases, depending on the molecular shape, temperature and solvent concentration. Many of these phases are analogous to the thermotropic liquid crystalline structures, in particular, it has been found, that either elongated or flattened micelles may form nematic phases phenomenologically quite similar to the thermotropic nematics[1,2]. The magnetic anisotropy of these lyotropic systems is either positive or negative, so that they order with the symmetry axis along or perpendicular to an external magnetic field.

In nematic systems, two collective orientational modes exist[3]. They are of relaxational type, with the relaxation time determined by the ratio of an orientational elastic constant and an effective viscosity. These modes can best be studied by dynamic light scattering, allowing the determination of the relaxation times[4]. In thermotropic nematics, orientational elastic constants can be independently determined through Frederick's transition, for example, and light scattering has been used to determine the viscosity coefficients[4,5]. The elastic constants can also be obtained from the scattered light intensity.

In lyotropic nematic liquid crystals it is more difficult to observe the collective orientational fluctuations as the scattering is much weaker and oriented samples are harder to prepare. Only a few such experiments have been performed[6]. In this paper we report light scattering measurements in a nematic lyotropic system composed of disc-like micelles as proved by NMR techniques.

The experiments were done on a mixture of 0.8 mole of potassium decanoate, 0.2 mole of potassium heptyloxybenzoate, 0.693 mole KCl, 0.279 mole decanol, and 19.7 mole D_2O which forms a discotic nematic phase in the temperature range from 17°C to 50°C. At higher temperatures, the system is isotropic. These micelles have a weak positive magnetic anisotropy so that the nematic phase can be oriented in a magnetic field[7]. Deuterated water was used because the same sample was used in NMR experiments. For light scattering, this is irrelevant.

The sample was placed in a round glass tube with 3mm internal diameter and immersed in a larger glass vessel, together with the poles of a permanent magnet. The vessel was filled with oil which served both as an index matching fluid and a temperature bath. The magnetic field between the poles was around 0.5T. The poles were formed so that they permitted light scattering measurements at scattering angles from 0 to 100° with different orientations of the the scattering vector. The temperature was kept constant to 0.1°C. We checked the alignment of the sample by observing it between crossed polarizers. Large monodomain regions were obtained by keeping the sample undisturbed in the magnetic field in the middle of the nematic range for several hours. About 50 mW of light with wavelenght 514.5nm was focused on the sample. The nematic director was in the scattering plane. In this geometry, strongest scattering is observed with incoming light polarized perpendicularly to the scattering plane, that is as an ordinary light wave, and scattered light polarized in the scattering plane, that is as an extraordinary wave. Scattering with incoming and scattered light polarized in the scattering plane was somewhat weaker, whereas ordinary-ordinary wave scattering was no stronger than in isotropic liquids.

To analyse the data we use the results of the hydrodynamic theory of nematics. It predicts two orientational modes with the inverse relaxation times[3]:

$$\Gamma_1 (q) = \frac{1}{\eta_1(q)} \left(K_1 q_\perp^2 + K_3 q_\parallel^2 \right)$$

$$\Gamma_2 (q) = \frac{1}{\eta_2(q)} \left(K_2 q_\perp^2 + K_3 q_\parallel^2 \right)$$

where K_1, K_2 and K_3 are the splay, twist and bend elastic constants and $\eta_1(q)$ and $\eta_2(q)$ are wavevector dependent combinations of the nematic viscosity coefficients. The magnetic field contribution is small enough to be neglected, judging from the long time necessary for the sample to orient. The first mode is a splay-bend mode, and the second is a twist-bend mode. They both reduce to the respective pure deformations when $\underline{q} \parallel \underline{n}$ or $\underline{q} \perp \underline{n}$.

In a light scattering experiment with the nematic director in the scattering plane, the first mode is observable in the extraordinary-extraordinary wave scattering and the second in the ordinary-extraordinary scattering. We have measured the relaxation time of the second mode at different scattering angles and with different orientations of the scattering vector with respect to the nematic director.

Figure 1. shows Γ_2/ q^2 at different scattering angles, that is, different magnitude of $\underline{q}$. As expected, there is no observable dependence. In Figure 2., the dependence of the ratio Γ_2/ q^2 is shown as a function of the angle between $\underline{n}$ and $\underline{q}$. The anisotropy of the relaxation time is not very

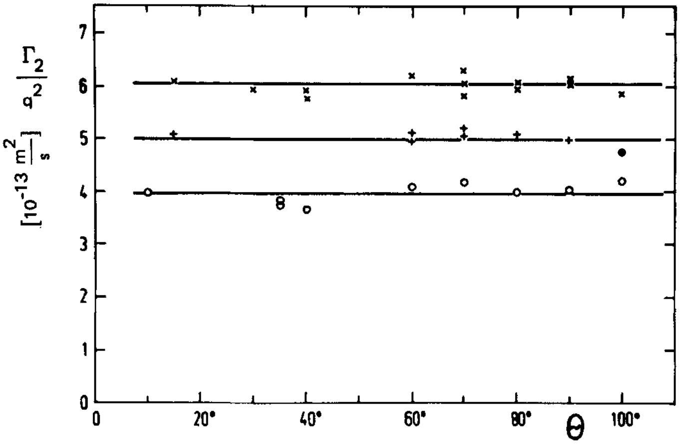

FIGURE 1. The dependence of Γ_2/ q^2 on the scattering angle: x - pure twist at 33°C, o - pure twist at 28°C, + - pure bend at 30°C.

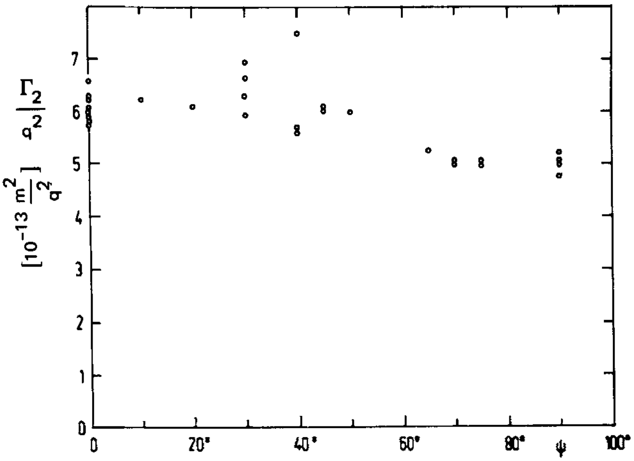

FIGURE 2. Angular dependence of Γ_2/q^2. ψ is the angle between q and n. The mode is pure bend at $\psi = 0$ and pure twist at $\psi = \pi/2$. Temperature is 33°C.

pronounced which may be understood by looking at the expression for the effective viscosity η_2

$$\eta_2 = \gamma_1 - \frac{(\gamma_1 - \eta_b + \eta_c)^2}{\eta_a q_\perp^2 + \eta_c q_\parallel^2} \frac{q_\parallel^2}{2} ,$$

where γ_1 is the director twist viscosity and η_a, η_b, and η_c are the fluid viscosities for various orientations of n and fluid velocity. Obviously, the effective viscosity is always smaller for q ∥ n, that is, for pure bend mode. On the other hand, in a discotic system, it seems quite reasonable that the bend elastic constant is smaller than the twist constant so that the overall dependence of Γ_2 on the direction of q is weak.

Figure 3. shows the temperature dependence of Γ_2/q^2 for q ∥ n and for q ⊥ n. As the high temperature phase is

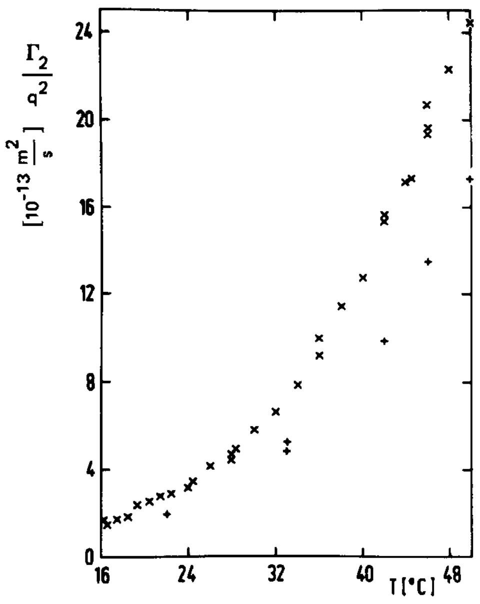

FIGURE 3. Temperature dependence of Γ_2/q^2 for pure bend (x) and for pure twist (+).

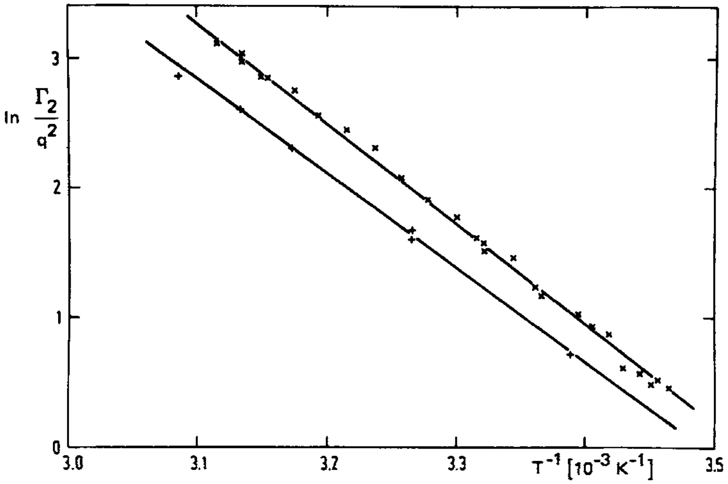

FIGURE 4. ln(Γ_2/q^2) for pure bend (x) and pure twist (+) as a function of 1/T, showing the activation energy type mechanism for the viscosities.

isotropic, it is unlikely that the increase of Γ with temperature is due to increasing elastic constant, so that in our opinion the temperature dependence of Γ is mainly caused by decrease in viscosity. Figure 4. is a semilogarithmic plot of the same dependence. It is for both bend and twist approximately a straight line. Such an exponential behaviour can probably be attributed to the activation energy type of the temperature dependence of the viscosity. The activation energy, deduced from Figure 4., is 0.065 ± 0.001 eV for pure bend and 0.062 ± 0.002 eV for pure twist. These values are surprisingly small, being similar to the activation energies of simple liquids.

To summarize, we have observed the director twist-bend fluctuation mode in a discotic lyotropic nematic system. Its behaviour is qualitatively quite similar to the director modes of the thermotropic nematic liquid crystals. The temperature behaviour of the relaxation time seems to be governed by an activation energy mechanism for the viscosities, with rather small activation energy.

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