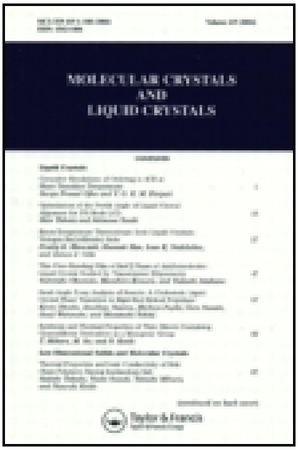

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ROTATIONAL VISCOSITY IN THE S_A PHASE OF A REENTRANT NEMATIC LIQUID CRYSTAL

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ABSTRACT
We report on what we believe to be the first measurement of rotational viscosity coefficient γ_1 of a smectic A phase. A value of ~4×10^3 poise is obtained by means of pulsed NMR in the middle of smectic A phase of a 6OCB/8OCB binary mixture exhibiting a reentrant nematic phase.

A recent study of Miesowicz viscosities[1] in a reentrant nematic mixture[2] shows that the flow behavior of a reentrant nematic (RN) phase is identical to that of nematic (N) phase but is qualitatively different from that of the intermediate smectic A (S_A) phase. The low temperature nematic is called[3] "reentrant" in order to distinguish it from the high temperature nematic phase. One of these viscosities diverges as the S_A phase is approached both from above and below. Consequently this particular viscosity was not measured in the S_A phase because the flow is blocked. Since the N-S_A transition of this reentrant nematic mixture is almost second-order, the divergence of this viscosity is due to divergence of the rotational viscosity coefficient γ_1 at the transition. A large number of studies[4-6] has been made on γ_1 above the nearly second-order N-S_A transition of CBOOA (p-cyanobenzylidene-p'-octyloxyaniline). Shear viscosities are reported recently[6] in the nematic and S_A phases of CBOOA. One of these again diverges as the S_A phase is approached and reaches a value of ~100 poise (p) at a temperature of 0.1° above the N-S_A transition. Measurements of this shear viscosity in the S_A phase are also impossible. Now the viscosities of nematic liquid crystals, measured either directly[1] or calculated by means of Poiseuille's law[7], are always of the same order of magnitude as in the isotropic liquid. However Poiseuille's law yields viscosities for cholesterics and smectics four to five orders of magnitude above those of similar nematic and isotropic liquids[7]. This was interpretted by Helfrich[8] that capillary flow of cholesterics and smectics may be controlled by mechanisms other than that underlying Poiseuille's law. He suggested a simple physical mechanism known as permeation to account for the observed high viscosity at low shear rates. It would be interesting to measure γ_1 in a S_A phase since to our best knowledge no such measurement has been reported.

Magnetic alignment of liquid crystals along an applied magnetic field is produced by the interaction of the applied field with the diamagnetic susceptibility anisotropy ($\Delta\chi$) of the molecules. In nematics, upon sudden change in the direction of applied field, the alignment of nematic director $\hat{n}$ will be reestablished quickly along the field under an opposing viscous force. A measure of the time constant for the reestablishment of the magnetic alignment will give γ_1. Since γ_1 is low (~1 p or less) in nematics the time constant is in seconds or less. On the other hand, γ_1 is usually much larger in ordinary smectics, the viscous force is large enough to maintain the nematic director in the sample indefinitely even when the applied field changes its direction. Pulsed NMR has been used to observe the recovery of $\hat{n}$ following a sudden change in the magnetic field direction so as to determine the ratio $\gamma_1/\Delta\chi$ in nematics[4]. The time evolution of the director reorientation process is governed by a linear differential equation in ϕ, where ϕ is the angle between the director $\hat{n}$ and the magnetic field:

$$\sum_i T_i = T_{mag} + T_{vis} = I \frac{d^2\phi}{dt^2} \qquad (1)$$

where $T_{mag} = -½ (\Delta\chi) H^2 \sin 2\phi$ is the magnetic torque, $T_{vis} = -\gamma_1 \frac{d\phi}{dt}$ is the viscous torque, and I is the moment of inertia of a molecule. Assuming that the reorientation process involves an equilibrium situation in which the angular acceleration $d^2\phi/dt^2 = 0$, one can write

$$2 \frac{d\phi}{\sin 2\phi} = - \frac{dt}{\tau} \qquad (2)$$

where $\tau = \gamma_1/\Delta\chi H^2$. The solution of eq. (2) is

$$\tan\phi = (\tan\phi_0)e^{-t/\tau} \qquad (3)$$

A measure of τ therefore gives the ratio $\gamma_1/\Delta\chi$. The free induction decay (FID) in a NMR experiment can be used to monitor the reorientation process since it is well known that the width of FID changes drastically as the nematic director is oriented away from the applied magnetic field. Thus the FID width can be used to determine the angle ϕ. It is however more convenient to measure the decay amplitude at some fixed time τ_o following the $\pi/2$ pulse. The amplitude of the decay will not be a simple function of ϕ but depends on the shape of the FID and the time τ_o. This functional dependence can easily be determined experimentally with the sample in the S_A phase. Thus it provides a calibration of the decay amplitude to the angle ϕ.

In ordinary smectics, an aligned sample in the S_A phase will not distort upon change in the direction of applied magnetic field. This enables angular dependence study of observables in this phase. Recently we report[9] on a proton NMR study of binary alloys of octyloxycyanobiphenyl (8OCB) and hexyloxycyanobiphenyl (6OCB). These mixtures[10] with more than 22 wt. % but less than 29 wt. % 6OCB show the following phases with decreasing temperature: isotropic, N, S_A, RN and solid. The 27.6 wt. % 6OCB mixture has a narrow S_A phase with N-S_A transition and S_A-RN transition at 40.5° and 34°C, respectively. As a result, we found that an aligned sample of the mixture in its S_A phase will not distort at low field (1.7 k gauss) when the direction of applied field is changed but will distort at a moderate field H = 7 k gauss. We exploit this to measure γ_1 in the S_A phase of this mixture at 30 MHz. Since the reorientation of the nematic director is slow enough in the S_A phase, the calibration curve for ϕ was made at each temperature by rotating the magnet to different ϕ for a short time and back to $\phi = 0$. A typical calibration curve is shown in the inset of figure 1 with τ_o ~20μs. To get the relaxation curve, the magnet was rotated suddenly to a ϕ value of ~70° and the FID amplitude at τ_o was monitored as a function of time. A plot of tan ϕ versus time at 36.1°C is shown in figure 1. As can be seen from the figure the reorientation process obeys eq. (3). The slope of the straight line gives $\Delta\chi H^2/\gamma_1$. At the end of each measurement, the sample was heated into the nematic phase and then cooled back into the S_A phase for an aligned sample.

To obtain γ_1, we must know $\Delta\chi$ for this mixture. Now $\Delta\chi$ follows the degree of order S which can be determined from the dipole-dipole splitting of the NMR line. But S is expected to be nearly constant[11] in the S_A phase, in particular if the temperature range is narrow. Thus one can take $\Delta\chi$ as a constant. Besides $\Delta\chi$ is almost constant in the S_A phase[12] of p-butyloxybenzylidene-p'-octylaniline (~1.3×10^{-7} cgs unit) and p-heptyloxybenzylidene-p'-pentylaniline (~1.0×10^{-7} cgs unit). In our evaluation of

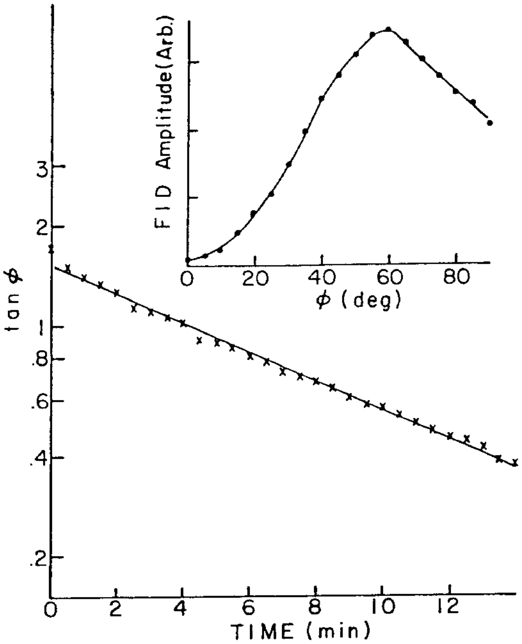

FIGURE 1 Plot of tan ϕ versus time. The inset shows the amplitude of the FID at a fixed time τ_o, following a $\pi/2$ pulse as a function of the angle ϕ.

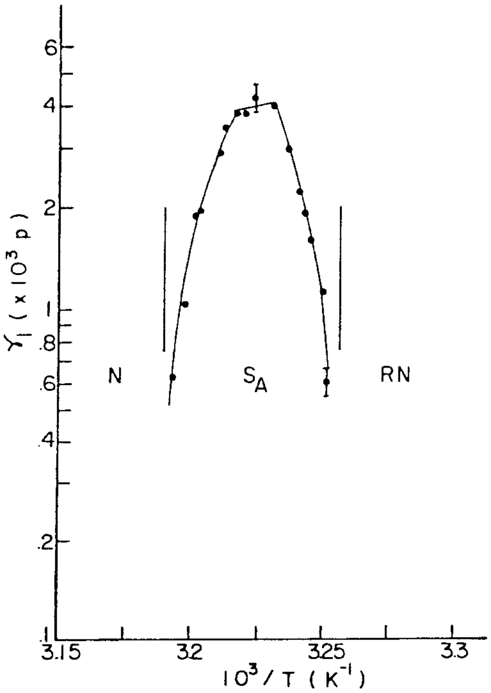

FIGURE 2 Plot of γ_1 versus the reciprocal temperature in the S$_A$ phase of 27.6 wt. % 6OCB in 8OCB.

γ_1 as presented in figure 2, we assume a value of 10^{-7} cgs unit for $\Delta\chi$. γ_1 has a value of ~4 x 10^3 p at the middle of the S_A phase but falls off quickly near the N and RN phases. No attempt has been made to measure γ_1 in either the N or RN phase. The high γ_1 value in the S_A phase seems consistent with relative viscosity measurements in smectics (η~10^2 p). It would be useful to measure γ_1 in a S_A phase with a wider temperature range to determine its activation energy.

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