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Study of Liquid Crystals in Flow: I. Conventional Viscometry and Density Measurements

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Study of Liquid Crystals in Flow

I. Conventional Viscometry and Density Measurements

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Using the technique of conventional viscometry (Haake-Hoefler Falling Ball and Ostwald-Poiseuille viscometers), we have measured the temperature dependence of the apparent viscosity of three liquid crystals: methoxybenzylidene butylaniline (MBBA), hexyloxybenzylidene amino benzonitrile (HBAB) and cyanobenzylidene octyloxyaniline (CBOOA). The measurements with the falling-ball show a small discontinuity in the apparent viscosity of (HBAB) at $\sim 91^\circ\text{C}$, where the flow properties of this compound have been found to change from one flow regime in which the "classical" molecular alignment with the flow can be observed ($T > 91^\circ\text{C}$) to another regime in which this alignment cannot be observed ($T < 91^\circ\text{C}$). However, in spite of this small discontinuity, the apparent falling-ball viscosity which we measured for (HBAB) is still very close to the Miesowicz viscosity, η_B , obtained by constraining the director \mathbf{n} to remain parallel to the velocity vector during the measurements. Measurements performed with the Ostwald-Poiseuille viscometer show: (i) that the apparent viscosity and the viscous heat of the nematic and smectic-A mesophases depend upon the radius of the capillary; (ii) that the apparent viscosity, in both the flow-alignment and the non-flow-alignment regimes, is very close to η_n and (iii) that there is no convincing evidence of a discontinuity in the apparent viscosity of (HBAB) at 91°C .

Our measurements of the temperature dependence of the density of the mesophases show that the isobaric coefficients of thermal expansion for (HBAB) and (CBOOA) are different in the flow alignment and in the non-flow-alignment regimes. This is consistent with the hypothesis that there is a greater degree of molecular association in the non-flow-alignment regime.

I INTRODUCTION

The flow of anisotropic liquids differs from the flow of isotropic liquids because the deformation and translational motion of the liquid element is coupled to the orientation of the highly anisotropic molecules within the fluid element. The coupling between orientation and flow has been described by Ericksen¹ and Leslie² via the conventional macroscopic approach of

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classical mechanics. This states that the local state of the anisotropic fluid element is described by a velocity vector \mathbf{v} , giving the local flux of matter, and a unit vector \mathbf{n} , called the "director", which gives the local state of molecular alignment. A nematic liquid crystal³ is an anisotropic liquid with uniaxial symmetry and long-range orientational order. Consequently, there is an elastic energy associated with deformations from a ground state.⁴ In the absence of boundary constraints and other external forces, the ground state for a nematic is one in which \mathbf{n} is a constant vector. The configurations of splay, twist and bend (see Figure 1a) cost energy, the amount of which depends upon the magnitude of the nematic elastic constants of splay (K_1), twist (K_2) and bend (K_3).⁴

In order to describe the viscous coupling between a liquid with nematic symmetry and a velocity gradient, six viscosity coefficients,^{1,2} usually called the Leslie viscosities, α_i , are required. Using Onsager's relation, Parodi⁵ has shown that $\gamma_2 = \alpha_6 - \alpha_5 = \alpha_3 + \alpha_2$; therefore five of these viscosities are linearly independent. Of these six viscosities, the combinations $\gamma_1 =$

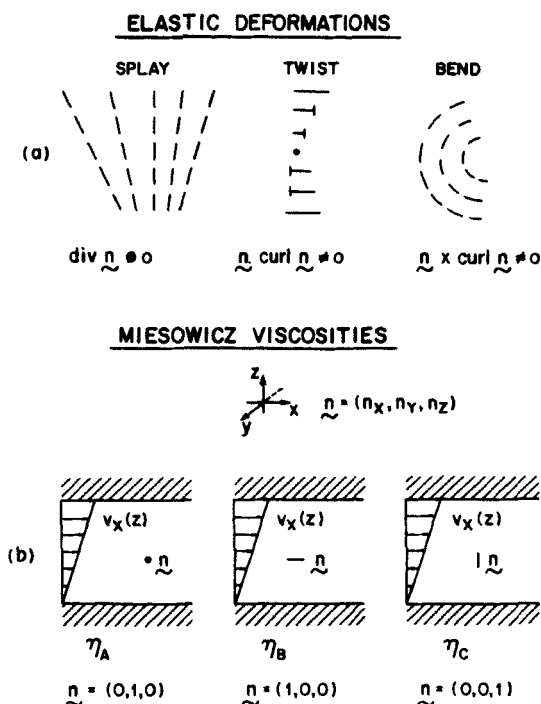


FIGURE 1 (a) Principle elastic deformations in nematic liquid crystals
 (b) Definition of the Miesowicz viscosities in a velocity field defined by $\mathbf{V} = (V_x, 0, 0)$.

$\alpha_3 - \alpha_2$ and $\gamma_2 = \alpha_3 + \alpha_2$ are the easiest to account for physically since the shearing rate ($\nabla \mathbf{v}$) associated with any velocity field, \mathbf{v} , is composed of both a rotational part (corresponding to the antisymmetric part of $\nabla \mathbf{v}$) and an irrotational part (corresponding to the symmetric part of $\nabla \mathbf{v}$). In the case of simple shear, the rotational part of $\nabla \mathbf{v}$ ($\equiv \text{curl } \mathbf{v}/2$) gives rise to a torque density, Γ , on the director of $\Gamma_r = \frac{1}{2}\gamma_1(dv/dZ)$. Due to the irrotational part of $\nabla \mathbf{v}$ [$= (v_{i,j} + v_{j,i})/2$] it is $\Gamma_{ri} = \frac{1}{2}\gamma_2(dv/dZ) [\cos^2 \theta - \sin^2 \theta]$ where θ is the angle between \mathbf{n} and \mathbf{v} . Consequently, the total torque density exerted on \mathbf{n} by $\nabla \mathbf{v}$ is given by

$$\Gamma_r = \frac{1}{2} \frac{dv}{dZ} [\gamma_1 + \gamma_2(\cos^2 \theta - \sin^2 \theta)] \quad 1(a)$$

which is zero when $\cos 2\theta = -\gamma_1/\gamma_2$. Using Parodi's relation, $\Gamma_r = 0$ leads to the condition $\tan^2 \theta = \alpha_3/\alpha_2$ which makes clear that the signs of both α_3 and α_2 must be the same if there is to be flow alignment (see below).

Since nematic viscosities are relatively large, $[(10^{-1} - 1) \text{ poise}]$ compared to the elastic constants (10^{-6} dynes), we require a dimensionless number which will give some indication of the relative significance of the elastic forces as compared to the viscous forces in the various flow regimes. This number has been called the Ericksen number^{6,7} \mathcal{E} , defined as

$$\mathcal{E} = \frac{\text{viscous stress}}{\text{elastic stress}} = \frac{\gamma S d^2}{K_i} \quad (1)$$

where γ , S , d and K_i are the characteristic viscosity, shear rate, distance and elastic constant respectively for the particular flow regime under consideration. For large \mathcal{E} ($\gtrsim 10^2 - 10^3$), elastic considerations are negligibly small and there are two possibilities:

1) The Leslie Viscosity $\alpha_3 \gtrsim 0$. In this case (assuming simple shear) we have "flow alignment." The director \mathbf{n} will adopt an orientation in the plane of the velocity and velocity gradient and will be inclined at an angle θ to the velocity where θ is given by^{1,2}

$$\tan^2 \theta = \frac{\alpha_3}{\alpha_2} = \frac{\gamma_1 + \gamma_2}{\gamma_2 - \gamma_1} \quad (2)$$

Equation (2) defines γ_1 . This angle is independent of shear rate and the condition $\alpha_3 < 0$ ensures that a solution to Eq. (2) exists since $\alpha_2 < 0$ always. Note that there are four solutions to Eq. (2), and, as shown by Ericksen,¹ two are stable and two unstable; the sign of the stable solutions [$\pm \theta$ and $\pm(\pi + \theta)$] being that of the velocity gradient. Within the restriction of simple shear flow, Ericksen¹ has shown that there is another possible solution for

which the director is perpendicular both to the velocity vector and to its gradient. This solution is unstable for large Ericksen numbers¹ but it becomes stable at Ericksen numbers below a critical value.⁸

2) The Leslie Viscosity $\alpha_3 > 0$. In this case, since $\alpha_2 < 0$, Eq. (2) has no real solution and the director is said to "tumble." From an experimental point of view the tumbling of the director manifests itself in different ways depending upon the pre-tumbling velocity field in the sample. For simple shear flows such as Couette and Poiseuille flows, tumbling of the director creates disclination lines (provided $\alpha_3 \neq |\alpha_2|$) with no apparent change in the velocity field about them. As the shear rate increases, the number of these disclination lines increases but the flow field remains unchanged until turbulence sets in at extremely high shear rates.

In the experiments with the falling-ball viscometer, tumbling of the director seems to affect not only the dynamic configuration of the director but also the flow field in the wake of the ball where flow turbulence appears to set in *abruptly* as soon as the temperature of the sample reaches the value at which α_3 changes sign. In the limiting case, $\alpha_3 \cong |\alpha_2|$, the coupling between \mathbf{n} and irrotational flows vanishes ($\gamma_2 = \alpha_2 + \alpha_3 \cong 0$) and we have observed a perfectly defect-free regime to prevail even at very large shear rates.

At present the mechanism by which the growth of disclination lines prevents the flow from becoming turbulent is not clear to us. We know that disclination lines boost the elastic energy of the nematic liquid crystal enormously. This increase in the elasticity of the medium keeps the Ericksen number small so that one cannot use the approximation $\mathcal{E} \rightarrow \infty$ which characterizes the behavior of anisotropic fluids of very low elasticity.¹ An additional property of these disclination lines is that when they nucleate their long axis is parallel to the velocity vector. This observation has also been made by Pieranski⁹ in the parallel plate geometry at high shear rates.

The observation that α_3 could change sign resulting in an undefined orientation angle θ (Eq. 2), was made first by Gähwiler in his study on hexyloxybenzylidene amino benzonitrile (HBAB).¹⁰ Gähwiler's results were contested by Meiboom and Hewitt¹¹ who observed that θ was always well-defined for (HBAB) in the temperature range in which the compound was nematic. However, further work on (HBAB) confirmed Gähwiler's original observation¹² and theoretical studies showed that α_3 not only changes sign but, for compounds with smectic-A mesophase, $\alpha_3 \rightarrow +\infty$ as the temperature is lowered to the nematic/smectic-A phase transition.¹³ On the basis of our experimental results we will show that the results of Gähwiler and Meiboom and Hewitt are not in contradiction, even though they led these authors to quite different conclusions.

A smectic liquid crystal is one in which the molecules lie in planes. The potential for this additional organization of the liquid crystal into planes

at some lower temperature is manifested in the nematic phase relatively far above the phase transition temperature, T_{NS} , (about 5°C in the case of CBOOA (cyanobenzylidene octyloxyaniline)), when this transition is nearly of second order. Specifically, it results in a pretransitional divergence (increase) in the elastic constants of twist and bend¹⁴ since these deformations (requiring curl $\mathbf{n} \neq 0$) are forbidden by the layered symmetry of the smectic phase in the absence of dislocations in the layering. Smectic pretransitional effects are also expected to contribute to an increase in the Leslie viscosities of α_1 , α_3 , α_6 but not α_2 , α_4 nor α_5 .¹³ Consequently, only the Miesowicz¹⁵ viscosity (see Figure 1b) $\eta_B = \frac{1}{2}(\alpha_3 + \alpha_4 + \alpha_6)$, $\gamma_1 = \alpha_3 - \alpha_2$ and $\gamma_2 = \alpha_3 + \alpha_2$ are expected to show pretransitional divergence as the smectic A phase is approached. In MBBA (methoxybenzylidene butylaniline) and HBAB¹¹ for example, it is known that $\eta_C > \eta_A > \eta_B$. In CBOOA as $T \rightarrow T_{NS}$, η_B is expected to approach infinity.

It is the overall purpose of our investigation to analyze the flow behavior of several liquid crystals under well-defined experimental conditions. It is the specific purpose of this communication to present our measurements of the *apparent viscosity* (defined as the value measured with conventional viscometers) and *density* of three representative liquid crystals: *N-p*-cyanobenzylidene-*p*-octyloxyaniline (CBOOA) in its three liquid phases: Isotropic, nematic, smectic-A; methoxybenzylidene butylaniline (MBBA) and hexyloxybenzylidene-amino-benzonitrile (HBAB) in their two liquid phases: Isotropic, nematic.

In the next section we will describe briefly our experimental apparatuses. Our experimental results are presented in Section III and discussed in Section IV. Finally, our main conclusions appear in Section V.

II EXPERIMENTAL DETAILS

The densities were measured with the conventional picnometer¹⁶ and with the Kahn Density Cell. The apparent viscosities were measured with the Haake-Hoefler falling-ball viscometer and the Ostwald-Poiseuille capillary viscometer. The characteristic properties of these viscometers are listed in Table I. Special care was taken to coat the glass surfaces of the instruments with the silane coupling agent (DOW Corning 2300) used by Kahn to produce homeotropic orientation of liquid crystal molecules on glass surfaces.¹⁷ The temperature was controlled by means of circulating baths to $\pm 0.02^\circ\text{C}$. The liquid crystals were used as obtained from the manufacturers: MBBA (Eastman Kodak #11246); CBOOA (Eastman Kodak #11963) and HBAB (Princeton Material Science, Inc.).

TABLE I

Viscometer characteristics

Type	Volume of flowing liquid (cm ³)	Pressure head (cm of H ₂ O)	Characteristic length ^b (microns)	Shear rates (sec ⁻¹)		
				CBOOA	HBAB	MBBA
Cl ^a	2	15	175	—	100-200	—
C2	3	15	240	2-200	—	—
C3	4	15	335	—	100-200	—
C4	4	15	452	—	200-400	—
C5	4	15	920	5-700	—	—
FB1	20	—	1400	0.1-1	1-4	1-3
FB2	20	—	650	—	—	0.8-2

^a Viscometers of Type C are the Ostwald-Poiseuille capillary tubes whereas those of type FB are the Haake-Hoefler falling ball.

^b The characteristic length of the Ostwald-Poiseuille viscometers is the inner radius of the capillary whereas the characteristic radius of the Haake-Hoefler viscometers is taken to be the average gap width between the falling ball and the outer stationary tube.

A Density measurements

These were performed in two ways. The first method¹⁶ consists in evacuating a U-tube sealed at one end. Part of the tube is then filled with the liquid crystal and the rest with mercury. The variation in specific volume is then determined by the change in height of the mercury meniscus at the open end of the U-tube. The sealed end containing the liquid crystal is immersed in an oil bath held at the required temperature to $\pm 0.02^\circ\text{C}$. This method is very sensitive to small changes in the specific volume of the liquid crystal but was not found to be very accurate for determining the absolute value of the density since it was not always possible to estimate correctly the mass of the liquid crystal contained in the U-tube.

In order to obtain a more accurate number for the density we used Archimedes technique in conjunction with a Cahn Electrobalance which could also be evacuated. This method consists of weighing a glass plummet first in air and then in a three gram sample of the liquid crystal. The glass container holding the liquid crystal was surrounded by a mercury filled region in which a thermometer was imbedded. Oil from a 4 gallon circulating bath flowed outside this region at the rate of 6 gallons per minute, thus maintaining the temperature of the mercury to within $\pm 0.02^\circ\text{C}$. While not as precise as the former method we found its accuracy to be about one order of magnitude better.

B Haake-Hoefler falling-ball measurements

In these experiments the time taken by a glass ball or marble of either 15.80 mm (FB1) or 15.65 mm (FB2) diameter to fall a distance of 100 mm through a

cylinder 15.922 mm diameter containing the liquid crystal is measured. The instrument we used was the Haake-Hoefler Falling-Ball Viscometer Model B/BH. Knowing the falling time of the ball, the density of the ball and liquid crystal and the ball constant, one then determines a viscosity in either units of centipoise or centistokes (cm^2/sec).

C Ostwald-Poiseuille capillary

Here, the time taken by a known quantity of liquid to fall through a capillary tube of known length is measured. The procedure consists of filling a glass capillary with the liquid crystal, and reversing the pressure head so that the liquid starts to flow down the tube. Then the times at which the meniscus passes each of two lines inscribed on the tube are recorded.

III RESULTS AND COMPARISONS

The experimental temperature dependence of the density $\rho(\text{g/cc})$ and of the apparent viscosity μ (centipoises) was analyzed by means of the standard relation for the isobaric thermal expansion coefficient, β , and the viscous heat, (ΔE).

$$\beta = \frac{1}{V} \frac{dV}{dt} \quad \text{or} \quad \rho = \rho_0 - \beta t \quad (3)$$

$$\Delta E = \kappa T \ln\left(\frac{\mu}{\mu_0}\right) \quad \text{or} \quad \mu = \mu_0 e^{(\Delta E/\kappa T)}, \quad (4)$$

where ρ_0 , μ_0 are reference values of density and viscosity respectively [$\rho_0 = \rho(t = 0)$ and $\mu_0 = \mu(\Delta E = 0)$], V is the specific volume of the mesophase, κ is the Boltzman constant and t , T are the temperature in centigrades and degree Kelvin respectively. The results are summarized in Table II and Figure 2.

A Density

The isobaric thermal expansion coefficient of (MBBA) was found to increase from $(7.0 \pm 0.4) \times 10^{-4} \text{ } (^{\circ}\text{C}^{-1})$ in the isotropic mesophase to $(8.3 \pm 0.2) \times 10^{-4} \text{ } (^{\circ}\text{C}^{-1})$ in the nematic mesophase (Figure 2a). The experimental error is expressed at the 95% confidence limit. These values compare favorably with the values of Press and Arrott¹⁸ ($\beta \simeq 8.2 \times 10^{-4} \text{ } (^{\circ}\text{C}^{-1})$ in the nematic mesophase and $\beta \simeq 7.6 \times 10^{-4} \text{ } (^{\circ}\text{C}^{-1})$ in the isotropic mesophase) and with the values of Chang¹⁹ ($\beta = 6.73 \times 10^{-4} \text{ } (^{\circ}\text{C}^{-1})$ in

TABLE II
Density and viscosity of mesophases

Material	Mesophase	Transition temperature (°C)	Thermal expansion coefficient $10^4 \times \beta$ (°C ⁻¹)	Reference density ρ_0 (g/cm ³)	Type of viscometer	Viscous heat $10^{-3} \times \Delta E/\kappa$ (°K)
MBBA	Isotropic	40	7.0 ± 0.4	1.0621	FB1; FB2	3.9 ± 0.1
HBAB	Nematic		8.3 ± 0.2	1.0697	FB1; FB2	3.4 ± 0.3
	Isotropic		8.3 ± 0.4	1.0990	FB1; C1; C3; C4	3.44 ± 0.02
	Nematic (I)	101	9.4 ± 0.1	1.1170	FB1; C1; C3; C4	—
	Nematic (II)	93	7.8 ± 0.1	1.1010	FB1; C3; C4	3.78 ± 0.08
CBOOA	Nematic (II)		7.8 ± 0.1	1.1010	C1	3.67 ± 0.06
	Isotropic	106.5	12 ± 5	1.1235	—	
	Nematic		9.2 ± 0.1	1.0890	C2	4.33 ± 0.04
	Nematic		9.2 ± 0.1	1.0890	C5; FB1	4.8 ± 0.2
	Smectic-A	83.1	—	—	C2; C5; FB1	99 ± 21

Note: The transition temperature for MBBA indicates that it is not pure. Compared to it, our HBAB and CBOOA compounds are of comparable purity to any other published data.

the nematic mesophase). The most interesting results were obtained with HBAB (Figures 2b and 2c). This compound shows a discontinuity in the isobaric expansion coefficient at approximately 93°C in the nematic mesophase where β varies from $(9.4 \pm 0.1) \times 10^{-4} \text{°C}^{-1}$ to $(7.8 \pm 0.1) \times 10^{-4} \text{°C}^{-1}$, the difference in β being significant to the 99% confidence limit. We will return to this point later in this paper. The density measurements with CBOOA (Figure 2d) show a discontinuity in the density at the nematic/smectic-A transition ($\Delta\rho = 1 \times 10^{-4} \text{ g/cc}$) which is in good agreement with previous results.¹⁶ We also observe a change in compressibility here when α_3 changes sign $\sim 105^\circ\text{C}$ (Figure 3d).²⁰

B Viscosity

A comparison of our results (Figure 3) with those of Gähwiller,¹⁰ Summerford *et al.*,²¹ Martinoty *et al.*,²² and Meiboom and Hewitt¹¹ is given in Table III. This comparison reveals two interesting facts:

i) The results obtained for (MBBA) by Summerford *et al.*,²¹ i.e., η_C , η_A (in the nematic mesophase) and μ (in the isotropic phase), and the respective

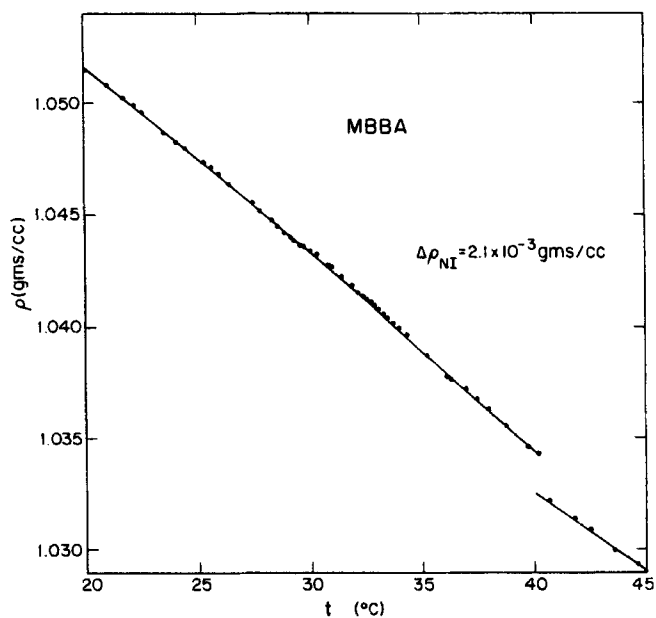


FIGURE 2 Temperature dependence of the densities of:
(a) MBBA (Cahn electro balance)

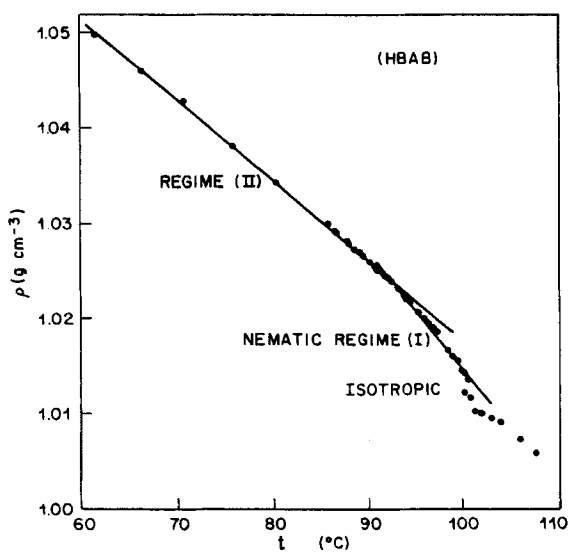


FIGURE 2 Temperature dependence of the densities of:
(b) HBAB (Cahn electro balance)

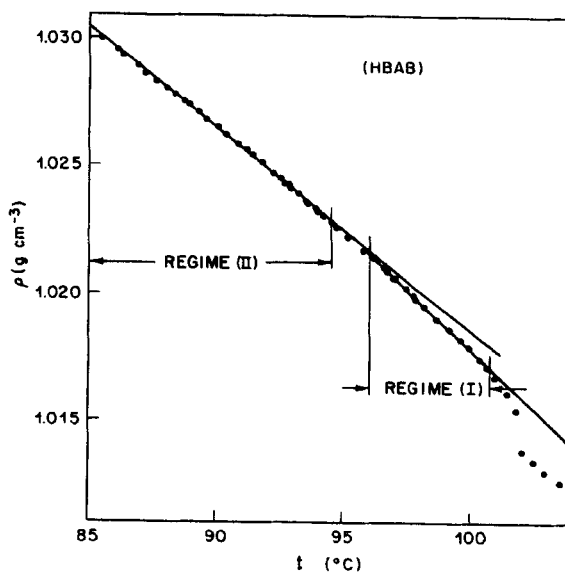


FIGURE 2 Temperature dependence of the densities of:
(c) HBAB (Picnometer)

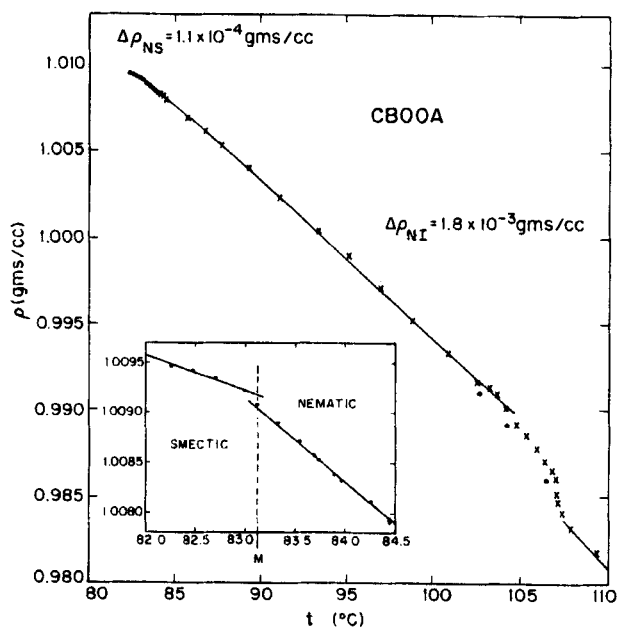


FIGURE 2 Temperature dependence of the densities of:
(d) CBOOA (Cahn electro balance)

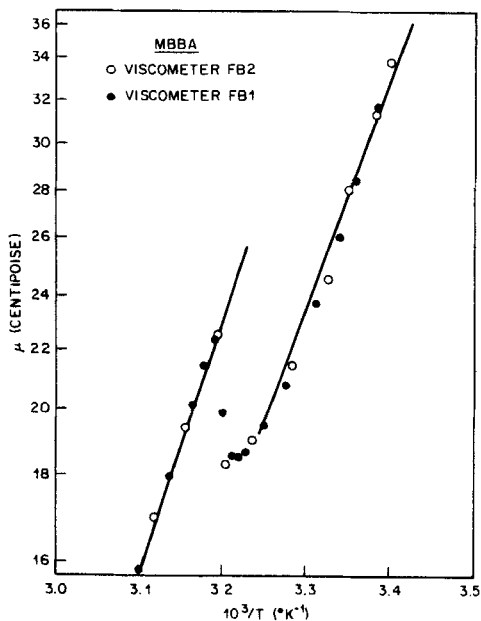


FIGURE 3 Temperature dependence of the apparent viscosities of (a) MBBA,

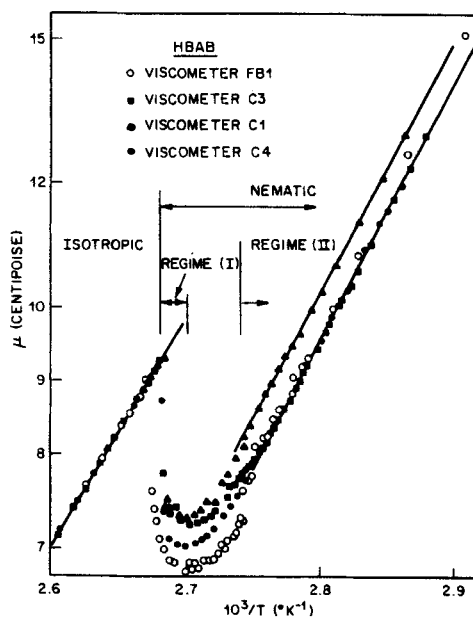


FIGURE 3 Temperature dependence of the apparent viscosities of (b) HBAB.

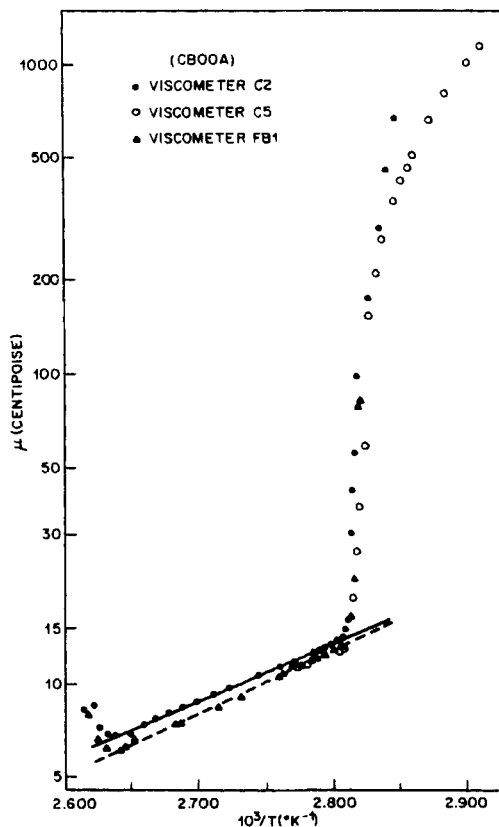


FIGURE 3 Temperature dependence of the apparent viscosities of (c) CBOOA.

viscous heats, $(\Delta E/\kappa)$, are consistently higher than those obtained by others. Summerford *et al.* suggested that their values were the most meaningful because they were obtained at very low shear rates ($\sim 0.08 \text{ sec}^{-1}$) whereas Gähwiler's data,¹⁰ for example, were obtained at a relatively high shear rate ($\sim 20 \text{ sec}^{-1}$). However, their argument fails to explain why their viscosity and their viscous heat for the isotropic mesophase are also much higher. We believe that Summerford *et al.*'s high values are inherent in their particular setup.

ii) Comparing our apparent viscosity μ and viscous heat $(\Delta E/\kappa)$ with the values of η_A , η_B and η_C , one observes that $\mu \simeq \eta_B$, i.e., the orientation of the director is mostly parallel to the velocity field and the boundary layer at the walls, which has the director oriented perpendicularly to the velocity field, contributes insignificantly to the value of the apparent viscosity μ because

TABLE III
Comparison of viscosity measurements

Material	Mesophase	Viscosity coefficient	Viscous heat $10^3 \times (\Delta E/\kappa)[^\circ\text{K}]$					Reference viscosity Viscosity (centipoises)					
			This paper	Gähwiler	Summerford <i>et al.</i>	Martiny <i>et al.</i>	Meiboom <i>et al.</i>	Temperature C	This paper	Gähwiler	Summerford <i>et al.</i>	Martiny <i>et al.</i>	Meiboom <i>et al.</i>
MBBA	Isotropic	μ	3.9	3.7	5.2	3.6	—	50	15	15	24	15	—
	Nematic	μ	3.4	—	—	3.6	—	30	23	—	—	22	—
	Nematic	η_c	—	5.0	6.5	5.1	—	30	—	78	100	31	—
	Nematic	η_b	—	3.9	—	—	—	30	—	19	—	—	—
	Nematic	η_A	—	4.0	4.9	3.9	—	30	—	31	55	22	—
	Nematic	γ_1	—	—	—	—	5.7	30	—	—	—	—	65
HBBB	Isotropic	μ	3.4	3.7	—	—	—	110	7.2	7.0	—	—	—
	Nematic	μ	3.8	—	—	—	—	80	—	10.8 (11.7)	—	—	—
	Nematic	η_c	—	5.0	—	—	—	80	—	41	—	—	—
	Nematic	η_b	—	3.9	—	—	—	80	—	8.8	—	—	—
	Nematic	η_A	—	4.5	—	—	—	80	—	13	—	—	—
	Nematic	γ_1	—	—	—	—	5.4	80	—	—	—	—	40

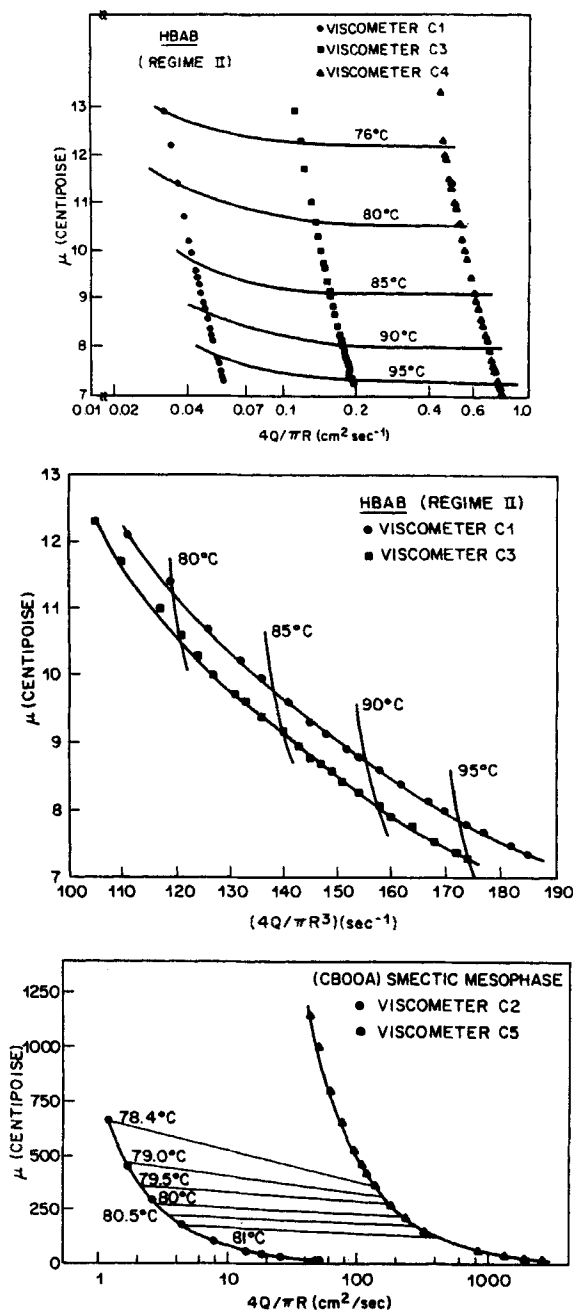


FIGURE 4 Apparent viscosity plotted versus Atkin's scaling parameters: $4Q/\pi R$ and versus the average shear rate $(4Q/\pi R^3)$.

of the relatively large diameters of the capillaries or gap widths (for the falling ball viscometer) and also relatively high shear rates (see Table I). However, when a small capillary (radius ~ 175 microns) was used to measure the viscosity of the nematic mesophase of HBAB, we observed a 10% increase in the apparent viscosity at comparable shear rates (see Figure 3b). This phenomenon has been predicted by Atkin,²³ who showed that the apparent viscosity μ in a Poiseuille flow is related to the pressure gradient (dP/dz) along the tube axis (z) by the relation:

$$\mu = \psi \left(\frac{4Q}{\pi R} \right), \quad (5)$$

where Q is the volumetric flow rate through the tube, R is the radius of the tube and ψ is a function which depends only upon the orientation of the director at the tube wall. Figures 4a and 4c show our viscosity measurements plotted versus $4Q/\pi R$ for different temperatures for the nematic mesophase of (HBAB) and the smectic phase of (CBOOA). They show that as R increases at fixed volumetric flow rate ($Q = \text{const}$), the apparent viscosity μ increases in a pattern similar to that observed by Fischer and Fredrickson²⁴ in their study on the apparent viscosity of *p*-azoxyanisole (PAA). Figure 4b shows that μ of HBAB decreases with the shear rate approximately with the same exponent, independent of the radius of the capillary. These figures also show that as Q/R increases, μ asymptotically approaches a constant value.

Inspection of Table II and Figures 3 and 4 reveals that not only the viscosity of the nematic mesophase but also the viscous heat depend upon the radius of the capillary tube. This suggests that the thickness (δ) of the homeotropic boundary layers depends not only upon the shear rate but also upon the temperature, probably via the temperature dependence of the bend elastic constant K_3 . This phenomenon is emphasized in Figure 4c, which shows that the Q/R dependence of the apparent viscosity μ of the smectic mesophase of (CBOOA) varies remarkably with temperature at constant shear rates (650 to 350 centipoises at 78.4°C versus 170 to 120 centipoises at 81°C).

IV DISCUSSION

A Density measurements

The most interesting result of the density measurements is the non-linearity as a function of temperature demonstrated by both HBAB and CBOOA. We have observed that this non-linearity becomes more pronounced as α_3 tended towards zero. Qualitatively this corroborates Gähwiller's hypothesis¹⁰ that the tendency for molecular association is decreasing as

temperature increases. Consequently, the energy provided by increasing the temperature by an amount ΔT (i) increases the average molecular separation and (ii) reduces the average number of associations. Since the average number of associations will decrease as temperature increases, a given ΔT will tend to produce a larger ΔV (and hence a greater decrease in density) in the higher temperature range where there are fewer molecular clusters to break up than in the lower temperature range.²⁵ Although we do not expect this to result in exactly two linear regimes, we see from the data that it is a good approximation of the data for both CBOOA and HBAB, thus suggesting that the tendency for clusters or associated groups to form does indeed seem to grow rather rapidly once $T < 91^\circ\text{C}$ for HBAB and $T < 105^\circ\text{C}$ for CBOOA.²⁰

B Falling-ball measurements

In these measurements the value of the apparent viscosity is very close to the Miesowicz viscosity, η_B (Figure 1b). This value does not depend upon the shear rate (Figure 3a). In the experiments with (HBAB) a small jump in μ was observed at the temperature where α_3 is changing sign. However, even if this small jump exists, the apparent viscosity is very close to η_B . As we have discussed above we believe that this abrupt change in the drag resistance encountered by the falling ball is caused by the abrupt onset of turbulence in the wake of the ball.

C Poiseuille flow measurements

Here we need to account for the fact that the effective viscosity for the larger tubes is smaller than that for the smallest tube in the regime where there is no flow alignment of HBAB ($T < 91^\circ\text{C}$).

It is easily understood why this should be the case when $T > 91^\circ\text{C}$ and there is flow alignment. In the $T < 91^\circ\text{C}$ case the model previously proposed^{23,24} requires the existence of two regions in the tube. One region is composed of the boundary layer where the director changes from a perpendicular orientation at the wall to a direction more or less parallel to the tube axis in the core region.²¹⁻²⁷ Fisher and Fredericksen²⁴ give a simple expression relating the effective viscosity μ to the viscosities in these two regimes:

$$\frac{R_c}{R} = \frac{R - \delta}{R} = \frac{\eta_{\text{core}}}{\mu} \cdot \left(\frac{\eta_{\text{wall}} - \mu}{\eta_{\text{wall}} - \eta_{\text{core}}} \right)^{1/4}, \quad (4)$$

where δ is the thickness of the boundary layer. In the flow alignment regime, e.g. $T = 96^\circ\text{C}$, if we take $\eta_{\text{core}} = \eta_B = 6cp$, $\eta_{\text{wall}} = \eta_C = 20cp$ and our

values for μ , we find that for the three tube sizes we used $R_c/R \sim 0.94 - 0.93$. This is a good order of magnitude estimate which agrees with microscopic observations of homeotropic tubes in flow. However, if we take $\eta_{\text{wall}} = (\eta_C + \eta_B)/2$, we then find $R_c/R \sim 0.65$ which can only be observed in flows of Ericksen numbers much smaller than we have employed here.²⁷

In the non-flow alignment regime, we cannot assume a single orientation for the director in the core region. One would expect that in this regime the average core viscosity is some spatial and/or temporal average of the three Miesowicz viscosities and consequently that it should be considerably bigger than the smallest viscosity η_B . This, however, does not agree with our experimental results which show that $\mu \simeq \eta_B$, i.e. the molecules are mostly oriented along the tube axis. One can speculate on several schemes to explain this phenomenon. For example, in Figure 5 we show essentially three

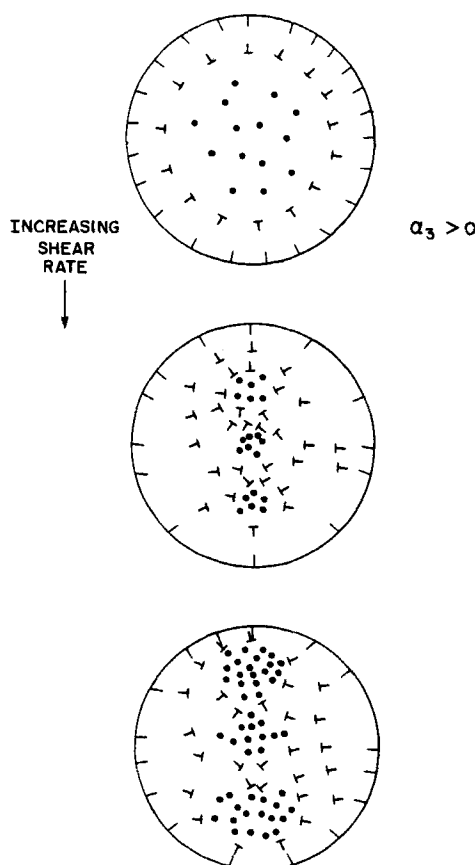


FIGURE 5 Schematic illustration of the growth of disclination lines in Poiseuille flow.

disclinations of the coreless type. At the centre of each disclination \mathbf{n} is parallel to \mathbf{v} . According to this scheme only an odd number of coreless disclination lines can exist in the tube. As the shear rate increases, this central zone of the disclination expands thus driving $\mu \rightarrow \eta_B$. Although, at present, this is only a speculation, it could account for our result in which $\mu \simeq \eta_B$ and for the results of Meiboom and Hewitt,¹¹ who did not observe the microscopic flow pattern in their cell but measured only the global director orientation in their samples via capacitance techniques.

V CONCLUSIONS

Once one has measured the rate of flow of Newtonian liquids through a pipe, one has completely defined the liquid. In the case of liquid crystals where there are five viscosities and an elasticity to take into account, such experiments pose more questions than they answer.

We have found that given homeotropic boundary conditions it is always possible to measure an apparent reproducible viscosity, even in the case where there is no flow alignment. This apparent viscosity is very close to η_B , the viscosity defined when the director \mathbf{n} and the velocity \mathbf{v} are parallel. Despite the large shear rates we have employed it seems that we are still in the regime of small Ericksen numbers since the director configuration is mostly composed of disclinations, which have very large elastic energies.

We have observed that the change in sign of α_3 is accompanied by a change in the compressibility. This substantiates the conjecture of Gähwiler that the formation of molecular associations will on the average produce clusters having a preferred orientation in the velocity field. Their orientation need not be compatible with that of the completely dispersed system.

In the falling ball experiment, we have observed an abrupt change in the effective viscosity when α_3 changes sign. Since we have not observed a similar jump in the Poiseuille flow experiments, we attribute it to an abrupt change in the flow pattern (onset of turbulence) in the wake of the ball.

The Poiseuille flow experiments indicate that the effective viscosity of a nematic depends upon the capillary diameter. We have observed that the effective viscosity in this flow is very close to η_B , the viscosity obtained when \mathbf{n} and \mathbf{v} are parallel. This is also the case in the non-flow-alignment regime, suggesting that measurements of director orientation over a large region of the sample (Meiboom and Hewitt¹¹) cannot give evidence on the occurrence of tumbling. Only experiments on small samples where the director configuration can be suitably observed, will provide a deeper understanding of our results, allowing us to correlate them to the predication of the continuum theory. This will be discussed in the following papers of this series.

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