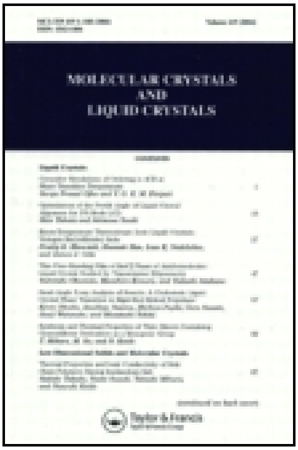

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Viscosity Measurements for the Nematic Liquid Crystal PAA

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Viscosity Measurements for the Nematic Liquid Crystal PAA

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An oscillating plate viscometer was used to measure the viscosities of PAA with the molecular axis oriented by an electromagnet. The experimental apparatus allowed measurement when the magnet was oriented in the three principal directions as well as angles in between. This permitted measurement of four independent viscosity coefficients, including μ_1. If the Parodi relation is assumed and a value of the twist viscosity is taken from other measurements, all the coefficients in the Leslie-Ericksen theory are available. The measurements are compared to those of Miesowicz[1] and the Orsay Liquid Crystal Group.[2]

INTRODUCTION

The Leslie-Ericksen theory provides a convenient description of the fluid dynamics of nematic liquid crystals.[3-5]

The predictions of the theory were tested by capillary flow experiments of Fisher and Fredrickson.[6] They used capillaries of different radii and found that the apparent viscosity depended only on Q/R, where Q is the flow rate and R is the capillary radius, rather than Q/R^3 as in the case for Newtonian and viscoelastic fluids. An *a priori* calculation was made by Tseng *et al.*[7] using the theory and parameter values obtained independently in other experiments. A non-linear boundary value problem was solved for the velocity and director field in "Poiseuille" flow. While the comparison between the experimental and theoretical results was quite satisfactory, some of the physical

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properties used in the calculation were either uncertain or unavailable.

The three principal viscosities measured by Miesowicz[1] in an oscillating plate viscometer do not agree with those measured by the Orsay Liquid Crystal Group[2] using a light-scattering technique. Depending on the orientation of molecules, the differences range from two to 40 percent. Confirmation of these values is desirable.

One of the principal viscosities is for the molecules oriented in the flow direction. Miesowicz's results[8,9] have frequently been interpreted to indicate he measured this value. However, his apparatus did not permit aligning the magnetic field in the direction of flow.[1] Recent evidence[10,11] indicates the Miesowicz depended on the oscillating plate and convection currents to maintain the molecular alignment in the absence of a magnetic field. Under a uniform shear the nematic liquid crystals are usually aligned in the shear plane and make an angle θ_0 with respect to the flow direction at high shear rates. Thus, if one assumes the oscillating plates leads to a constant orientation, that orientation must be given by θ_0 rather than in the flow direction.

The value of μ_1 was unknown since it had not been measured at all. Fortunately, its influence on the calculations is small, and the calculations were made for two typical values to show the minor effect of this parameter.

The experiment described below was designed to provide the three principal viscosity coefficients, including the one with the director oriented in the flow direction, as well as the value of μ_1. To do this is was necessary to have a magnet which could be oriented in various positions. Since the key measurement is with a magnetic field aligned in the flow direction, an oscillating plate viscometer was chosen and designed to oscillate between the poles of a magnet. The experiment is similar to that of Miesowicz except that we can orient the magnetic field in the direction of flow and we use a different calibration procedure, which accounts for the dynamics of the oscillating plate viscometer.

According to the Leslie-Ericksen theory, the viscosity in shear flow is given by the expression

$$\eta(\theta, \phi) = \mu_1 \cos^2\theta \sin^2\theta \sin^2\phi + \tfrac{1}{2}(\mu_5 - \mu_2) \sin^2\theta \sin^2\phi + \tfrac{1}{2}(\mu_6 + \mu_3) \cos^2\theta + \tfrac{1}{2}\mu_4 \quad (1)$$

where the angles are related to the flow direction in Figure 1. In all

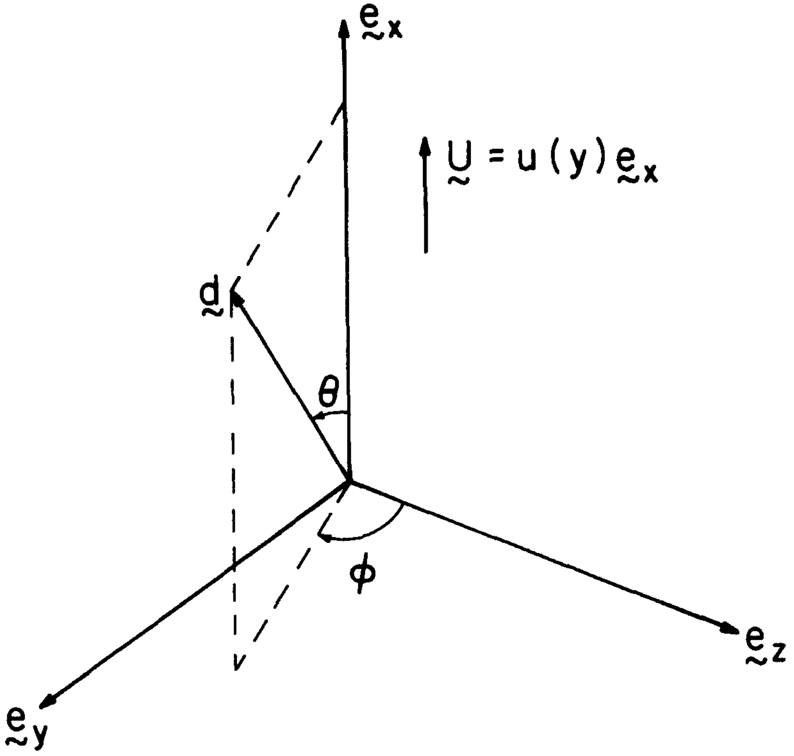

FIGURE 1 Coordinate system for the velocity field.

cases the plate is oscillating up and down in the x–z plane of Figure 1. The angular dependence of the viscosity arises because of the orientation of the director, given by

$$\underset{\sim}{d} = \cos\theta\, \underset{\sim}{e}_x + \sin\theta \sin\phi\, \underset{\sim}{e}_y + \sin\theta\cos\phi\, \underset{\sim}{e}_z \tag{2}$$

The three principal directions give the following viscosity coefficients.

Director oriented in the flow direction, $\theta = 0$

$$\eta_1 = \tfrac{1}{2}(\mu_4 + \mu_6 + \mu_3) \tag{3}$$

Director in the gradient direction, $\theta = 90°$, $\phi = 90°$

$$\eta_2 = \tfrac{1}{2}(\mu_4 + \mu_5 - \mu_2) \tag{4}$$

Director in a direction perpendicular to both flow and gradient direction, $\theta = 90°$, $\phi = 0°$

$$\eta_3 = \tfrac{1}{2}\mu_4 \tag{5}$$

For shear flow at high shear rates, the director takes the orientation $\theta = \theta_0$ and $\phi = 90°$. The viscosity then is

$$\eta_\infty = \mu_1 \cos^2\theta_0 \sin^2\theta_0 + \tfrac{1}{2}(\mu_5 - \mu_2)\sin^2\theta_0 + \tfrac{1}{2}(\mu_6 + \mu_3)\cos^2\theta_0 + \tfrac{1}{2}\mu_4 \tag{6}$$

If $\theta_0 = 0$, then η_∞ is the same as η_1, which is what Miesowicz assumed. However, no one has ever measured a $\theta_0 = 0$. If θ_0 is small, the error is likewise small, but the measurements described below are designed to give η_1 unambiguously.

In addition to the measured values of η_1, η_2 and η_3, the value of μ_1 can be obtained if one used angles θ and ϕ different from 0 and 90°. The oscillating plate viscometer, with the direction orientation possible in all directions, can then provide four viscosity coefficients. There are, however, six viscosity coefficients in the theory. Parodi[12] has derived a relation between the viscosity coefficients that represents Onsager's reciprocal relations

$$\mu_2 + \mu_3 = \mu_6 - \mu_5 \tag{7}$$

One more measurement provides the last viscosity coefficient. Chosen here is the twist viscosity, γ_1, which can be measured by a variety of techniques.

The flow orientation angle θ_0 is related to the twist viscosity by

$$\cos 2\theta_0 = -\lambda_1/\lambda_2 \tag{8}$$

$$\lambda_1 = -\gamma_1 \equiv \mu_2 - \mu_3,\ \lambda_2 \equiv \mu_5 - \mu_6 \tag{9}$$

The theoretical basis for these relationships is provided elsewhere (Leslie, 1966, 1968).

EXPERIMENTAL APPARATUS

The oscillating plate viscometer was designed to operate between the poles of an electromagnet. A thin glass plate oscillating in the liquid is suspended from one end of a balanced beam. The amplitudes of oscillations of the balance beam were recorded. After an initial impulse was applied to the balance beam, the amplitude decreased with time due to the viscous drag on the glass plate, and the rate of decrease can be related to the viscosity.

The oscillating plate viscometer (see Figure 2) consisted of a nonmagnetic, stainless steel knife-edge rested on a bearing used for analytical balances. The knife-edge was press-fitted into, and at right angles to, an aluminum rod that was ⅜ inch in diameter. The swing of the balance consisted of two glass rods (⅛ inch in diameter, approximately 8 inches long) hanging from the aluminum rod at the pivot point. A brass cylinder was connected to them near the bottom, and the distance from the pivot point to the center of gravity of the brass cylinder controlled the moment of inertia of the device. The brass cylinder was carefully attached so that its axis was parallel to the knife-edge and directly below it. The swings of the balance were begun with the balance arm raised at one end; a peg was released which allowed one end of the balance arm to lower under its own weight and the oscillation to begin.

The amplitude of oscillation was measured with a photo-diode which measured the amount of light not obstructed by a flag attached to the balance arm (see Figure 2). Calibration tests revealed that the induced voltage was linearly related to the height of the flag. The amplitude recorded on the strip chart was measured by hand at thirty positions to verify a logarithmic decay of the oscillations.

The oscillating plate was glued to a glass thread (0.2–0.3 mm O.D.), the other end of which was attached to the balance arm by means of a screw in the balance arm. By rotating the screw, it was possible to change the angle ϕ from 0° to 90°. Since under normal

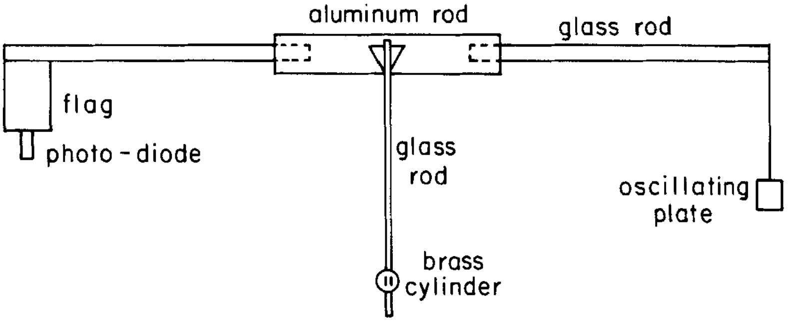

FIGURE 2 Schematic diagram of the oscillating plate viscometer.

operation the glass plate was not visible, a small pointer was attached to the screw and its direction was ascertained with a telescope. The glass plate was 2.5 × 2.5 cm No. 1 Corning thin cover glass (0.13 to 0.19 mm in thickness).

The glass plate was placed into a sample cell containing the liquid crystal. The cell was a brass tube (3.0 cm I.D. and 3.85 cm high) sealed at the end with a brass plate. The cell was electrolytically nickel-plated (0.5 mils). A removable circular lid was made with a narrow slot extending from the center to the edge. After the liquid crystal in the sample cell was melted, the cell was raised to cover the glass plate, and the lid was placed on the cell. The entire cell was insulated and provided with two Minco thermofoil heaters to maintain the temperature. A thermistor was placed between the heater and the outer insulation in order to monitor the temperature. To avoid disturbing the flow pattern, no devices were placed inside the cell. The temperature measurements were calibrated without the liquid crystal by placing a liquid in the cell and placing another thermistor in the cell before the glass plate was inserted. The two temperatures differed at most by 1°C and this was taken into account when determining the cell temperature. The temperature gradient in the axial direction of the sample cell was also measured to be about 0.1°C/cm. This measurement was for a stationary plate, and fluid circulation caused by the oscillating plate would make the temperature gradient even smaller.

The entire cell was placed on a sliding elevator, which was used to position it vertically until the glass plate was submerged 0.3 cm. The amplitude of oscillation was 0.25 cm in the calibration and 0.1 cm for liquid crystal, so that the glass plate was always submerged, and experiments were done with different depths to determine any effect of depth; there was none.

An electromagnet was designed and constructed with a gap of 7.5 cm and a pole diameter of 10 cm tapered down to 5 cm. It was designed to go around the sample cell and balance beam with the balance beam oscillating up and down between the poles. This arrangement was necessary to obtain η_1. The magnet was supported by a frame that could be rotated to six different positions, $\theta = 0°, 30°, 45°, 60°, 75°$, and 90°. The magnet was powered by a 28 volt, 130 amp DC power supply and could provide a measured 4000 gauss between the poles. Calibration runs at different magnetic fields indicated that 3800 gauss was sufficient to obtain complete alignment of the director in the direction of the magnet field.

The angle ϕ was thus changed by rotating the glass thread holding the glass plate while the angle θ was changed by rotating the magnet. For $\phi = 0°$, the glass plate was perpendicular to the balance beam and moved in an arc, while for $\phi = 90°$, the glass plate was parallel to the balance beam and in the plane of the swing. The viscometer was thus calibrated with the plate in both positions, and the small (2%) difference was taken into account when reporting the results.

The interpretation of the oscillating plate viscometer results is based on the theoretical analysis of Solomons and White[13] which has been confirmed experimentally.[14] The equation governing a body undergoing an oscillatory motion can be written as

$$(m + f_2)\ddot{X} + f_1\dot{X} + f_0X = 0 \tag{10}$$

where m is the mass, f_2 is related to the inertia of the fluid, $f_1\dot{X}$ is the damping force, and f_0X is the restoring force. Solomons and White had a system which was driven by a spring rather than a balance. We have analyzed the equations for the oscillation of a balance system and they are similar under appropriate assumptions, such as a small angle of oscillation. For underdamping, the solution is a simple harmonic oscillation with an exponential decay of the amplitude. The damping coefficient is defined as

$$\delta = \frac{1}{n} \ln \frac{X_0}{X_n} \tag{11}$$

where X_0 and X_n are the initial and $(n + 1)$-th amplitude, respectively. The damping coefficient is related to the other constants by

$$f_1 = K_f\delta, \; K_f = \frac{1}{\pi}\sqrt{(m + f_2)f_0} \tag{12}$$

This expression is valid for small D;

$$D = f_1/[4f_0(m + f_2)]^{1/2} << 1 \tag{13}$$

Here $D \sim 0.01 - 0.03$.

The term f_1 can be separated into two parts, one due to the drag on the plate (f_{1p}) and one due to other friction in the system (f_{1r}).

$$f_1 = K_f\delta = f_{1p} + f_{1r} \tag{14}$$

To determine the term for the drag on the plate, we use the solution for an infinite plate oscillating in an infinite media.† The governing equation is

$$\rho \frac{\partial u}{\partial t} = \eta \frac{\partial^2 u}{\partial y^2} \tag{15}$$

where u is the fluid velocity and y is the distance from the plate, ρ is the density, and η is the viscosity of the fluid. The solution is[15]

$$u = u_0 e^{-\beta y} \cos(\omega t - \beta y),\ \beta = \sqrt{\frac{\omega\rho}{2\eta}} \tag{16}$$

where ω is the frequency of oscillation of the plate. The drag force exerted on the plate of area A is

$$-\eta A \left.\frac{\partial u}{\partial y}\right|_{y=0} = \eta A \beta u(0, t) + \eta A \frac{\beta}{\omega} \frac{\partial u}{\partial t}(0, t) \tag{17}$$

However, $u(0, t)$ is the same as $\dot{X}$, since the plate moves with the balance velocity, and $\partial u/\partial t$ $(0, t)$ is the same as $\ddot{X}$, so that the drag force is

$$\text{force exerted by plate} = \eta A \beta \dot{X} + \eta A \frac{\beta}{\omega} \ddot{X} \tag{18}$$

The first term represents the drag and is included in f_{1p}, while the second term is inertial and is included in f_2. Thus,

$$f_{1p} = \eta A \beta = A \left(\frac{\omega}{2} \eta\rho\right)^{1/2} \tag{19}$$

and the damping coefficient is given by an equation of the form

$$K_1 \delta = \sqrt{\eta\rho} + K_2 \tag{20}$$

where K_1 and K_2 are apparatus parameters. In our balance, K_2 is

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†See the Appendix for the solution for a nematic liquid crystal.

extremely small, and K_1 is a function of ω which is not constant. A typical value of ω was 6 s^{-1}. The solution for an infinite plate oscillating near another stationary one was also examined, but for the conditions of the experiment the solutions to the infinite media and finite media problems were equivalent.

If δ is too large, the oscillations will damp out in a few strokes and it is not practical to measure δ. If δ is too small, viscous damping is not dominant, and the oscillations are governed by inertia and forces such as surface tension, friction at the pivot and the buoyant force on the balance beam. Therefore, an optimum value of K_1 is needed. K_1 can be adjusted by changing the size of the plate, and for a given plate, can be further adjusted by changing the moment of inertia of the balance system. This was done by raising or lowering the brass cylinder suspended beneath the pivot point.

The dependence of the damping coefficient on the square root of the viscosity times the density Eq. (20) was confirmed by tests with standard fluids having densities ranging from 0.8 to 1.6 g/cm^3. Miesowicz[1] on the other hand, calibrated his oscillating plate viscometer and found the damping coefficient varied linearly with viscosity. He mentions[1] calibration with paraffin oils (ρ = 0.8 g/cm^3) while the liquid crystal has densities much higher (1.16 g/cm^3). In the earlier, brief report,[8] he also mentions a calibration with sugar solutions, which have higher densities (1.0 to 1.58 g/cm^3). For some reason, his viscometer did not follow the analysis given above, whereas ours did.

The amplitude should decay in a logarithmic manner and plots of $\log A_n$ versus n should be a straight line whose slope is δ. We measured the slope of the line in three regions and compared them to ensure the apparatus was being properly used; occasionally a surface film formed. Generally, the three measurements agreed within 1%. For a few test fluids and the smaller glass plate, the standard deviation of δ was 3%. These fluids (aniline and nitrobenzene) had higher surface tensions (43 dyne/cm). An experiment with pure water and water with oleic acid confirmed that surface tensions in the range above 40 dyne/cm affected the measurements when the small plate was used, and this was always clear by comparing the damping coefficient over the entire measurement. Miesowicz[1] also mentioned difficulties for fluids with large surface tensions. We had to enlarge the size of our glass plate to minimize the effect, and in all cases we carefully checked the damping coefficient to ensure that the amplitude was decaying logarithmically. For the isotropic liquids, we could use an amplitude of 0.25 cm and maintain a logarithmic decay, whereas for the liquid crystal (surface tension of 38 dyne/cm) we needed to reduce the initial amplitude to 0.1 cm to ensure a logarithmic decay. This effect is especially important at low viscosities.

The viscometer was calibrated with the following test fluids: *n*-heptanol, aniline, *n*-pentanol, nitrobenzene, carbon tetrachloride, ethanol and acetone. The viscosities ranged from 1 to 7 centipoise and the densities ranged from 0.82 to 1.59 g/cm^3. In addition, Dow Corning 200 fluids were used with viscosities from 7 to 14 centipoise. The liquid crystal had densities ranging from 1.132 (at 150°C) to 1.163 (at 122°C). The viscosities varied from 2.2 to 12.9 centipoise. The calibration curve is shown in Figure 3. As mentioned above, the calibration curve is different when the plate is oriented in different directions. As the analysis suggests, the curve depends on $\sqrt{\eta\rho}$ but it is not linear, as is predicted by the analysis.

The para-azoxyanisole was obtained from the City Chemical Corporation of New York. The commercial product had a noticeably pungent odor, with a melting range of 2.5°C. We purified it by recrystallization from acetone and twice from 95% ethanol until the melting range was within 1°C. The melting point was 117.8 – 118.6°C

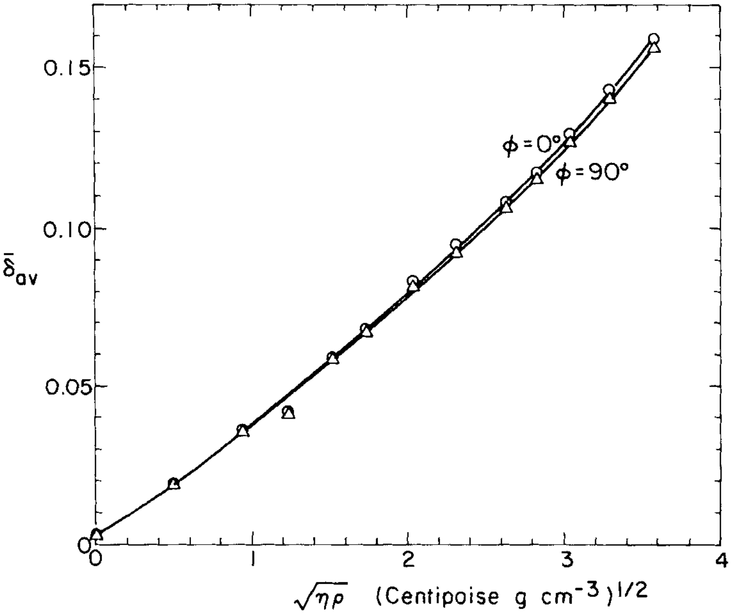

FIGURE 3 Calibration curve for the oscillating plate viscometer.

as measured in a Thomas-Hoover capillary melting point apparatus. The melting point was not measured again after the experiment, but when the experiments were repeated the same values resulted. The glass plate was cleaned with solvents, ending with acetone, before using it with the liquid crystal.

The sample cell was filled with crystals and heated to 125°C. After the crystals were melted, additional crystals were added until the liquid surface was at the desired level. Then the sample was allowed to cool, after which the cell was placed in the sample holder and heated again. This procedure was followed in order to avoid getting any crystals near the lid of the sample cell, which is in close proximity to the glass thread. The sample cell was then raised until the glass plate was submerged to the desired degree. The glass thread was never submerged more than would happen during the oscillations, again to avoid contamination of the thread with fluid, which could solidify and then rub on the sample lid. The cover of the cell was put on and the temperature controller set. At least one hour was allowed to reach a steady state temperature, which was checked with the thermistors. For each position of the oscillating plate (i.e., each ϕ), the magnet was turned from $\theta = 90°$ to 75°, 60°, 45°, 30°, 0° and back to 90° to double check the measurement at 90°. Then the glass plate was turned to a new ϕ and the sequence of measurements was repeated. At the end of the series of measurements, the lid was removed, the sample lowered and allowed to cool overnight. At the end of the experiments with PAA, the sample cell and oscillating plate were cleaned by filling the cell with acetone or benzene and letting the plate oscillate in the cell. This was repeated two or three times. Then standard liquids were introduced and the calibration was checked and found unchanged.

RESULTS

The measured viscosity of *p*-azoxyanisole at 122°C is given as a function of angle in Table I. These data were fit with Eq. (1) to obtain the best least squares fit. The parameters and the relative residuals are listed in Table II. The average percent deviation is 3%. These measurements confirm the prediction of the Leslie-Ericksen theory that the viscosity should follow Eq. (1). Typical variation with angle is shown in Figures 4 and 5. At other temperatures, measurements

TABLE I

The viscosities of PAA at 122°C, $\eta(\theta, \phi)$ in cp

θ/ϕ	90°	60°	45°	30°	0°
90°	——	10.9	9.1	7.0	4.7
75°	——	10.0	8.6	6.5	4.3
60°	——	8.3	7.6	5.5	3.8
45°	——	6.0	5.4	4.1	3.6
30°	4.3	4.3	4.1	3.5	3.1
0°	2.5	2.7	2.7	2.7	2.7
90°[a]	12.5	11.3	9.1	7.0	4.7

[a] Measured at different time to check the reproducibility.

TABLE II

Least-squares fitted values of $\eta(\theta, \phi)$ and the relative residuals

θ/ϕ	90°	60°	45°	30°	0°
90°	12.9 (3.2%)	10.9 (1.3%)	8.8 (3.4%)	6.7 (3.8%)	4.7 (0.2%)
75°	12.0 (——)	10.2 (1.7%)	8.3 (3.6%)	6.4 (1.2%)	4.6 (5.5%)
60°	8.7 (——)	8.4 (1.2%)	7.0 (8.7%)	5.6 (1.5%)	4.2 (8.9%)
45°	6.8 (——)	6.2 (3.4%)	5.4 (0.7%)	4.5 (9.0%)	3.7 (1.5%)
30°	4.4 (2.0%)	4.3 (0.3%)	3.9 (5.1%)	3.5 (0.6%)	3.1 (1.2%)
0°	2.6 (4.6%)	2.6 (3.0%)	2.6 (3.0%)	2.6 (3.0%)	2.6 (3.0%)

Best least-squares fit with $\mu_1 = -2.8$, $\mu_4 = 9.4$, $\mu_5 - \mu_2 = 16.4$, $\mu_6 + \mu_3 = -4.2$, $\eta_1 = 2.6$, $\eta_2 = 12.9$, $\eta_3 = 4.7$.

were made only at θ and ϕ of 0° and 90°. The results are shown in Table III for anisotropic fluids and Table IV for isotropic fluids.

COMPARISONS

Our measured value of viscosity in the isotropic region is compared to literature values in Table V. The value listed by Porter and Johnson[16–18] represents a survey of several investigations and is the accepted value. As seen in Table V, we agree nicely with this value, and Miesowicz's value is lower. The values for the anisotropic region are compared to literature data in Table VI. Here, significant disagreement exists, even among the literature values. Our work and

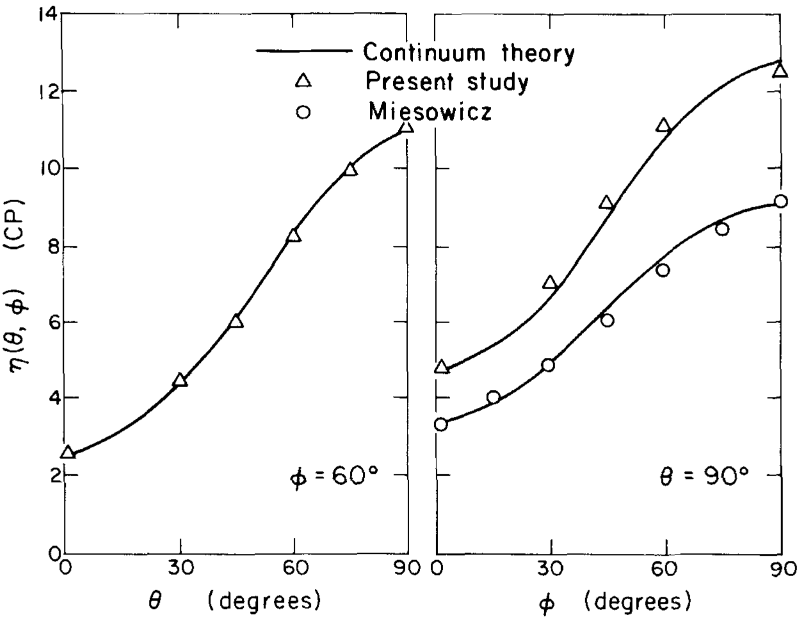

FIGURE 4 Comparison of theory with experiment at 122°C.

FIGURE 5 Comparison of theory with experiment at 122°C.

TABLE III

The three principal viscosities at different temperatures

T	η_1 (c.p.)	η_2 (c.p.)	η_3 (c.p.)
122°C	2.6	12.9	4.7
125°C	2.2	11.3	3.9
130°C	2.2	9.0	3.6
132°C	2.2	8.3	3.5
133°C	2.2	8.0	3.4
134°C	2.2	7.3	3.5

TABLE IV

The viscosities of PAA in the isotropic region

T (°C):	135	136	140	145	150
η (c.p.):	3.5	3.3	3.0	2.8	2.6

TABLE V

Comparison of isotropic viscosities

Investigator	T(°C)	η(cp)
This work	140.0	3.0
Porter and Johnson (1966) (many investigators)	140.0	3.0
Fisher and Fredrickson (1969)	140.6	2.9
Miesowicz (1936)	139.9	2.6
Berchet, Hochapfel & Viovy (1970)	140.3	2.6

TABLE VI

Comparison of anisotropic viscosities

Investigator	η_1	η_2	η_3
Viscosity Coefficients at 122°C, centipoise			
This work	2.6	12.9	4.7
Miesowicz (1936)	2.4	9.2	3.4
Berchet, Hochapfel & Viovy (1970)	1.6		
Langevin (1972)			3.6
Viscosity Coefficients at 125°C, centipoise			
This work	2.2	11.3	3.9
Miesowicz (1936)	2.3	8.6	
Orsay (1971)	1.5	8.6	4.1
Harvard (from Orsay data reported by Miesowicz, 1978)	2.1	12.6	6.0
Berchet, Hochapfel & Viovy (1970)	1.5		

Miesowicz's work both used an oscillating plate viscometer while Berchet *et al.*[19] used a capillary viscometer. The Orsay Liquid Crystal Group[2] used a light scattering experiment, and their experiments were reanalyzed by the Harvard group as reported by Miesowicz.[10] Finally, Langevin[20] used light scattering. Our values at 122°C are all higher than the literature values, while this is not true at 125°C. Figure 6 shows the viscosity plotted versus inverse temperature and several features stand out. Our measured values are higher than Miesowicz's values for η_2, but are the same for η_1 except at 122°C. Our values for the isotropic viscosity above 135°C are in good agreement with the summary of Porter and Johnson. Our value of η_3 is higher than Miesowicz's value (available only at 122°C). Given these comparisons, we believe our results are the most accurate, but we recognize

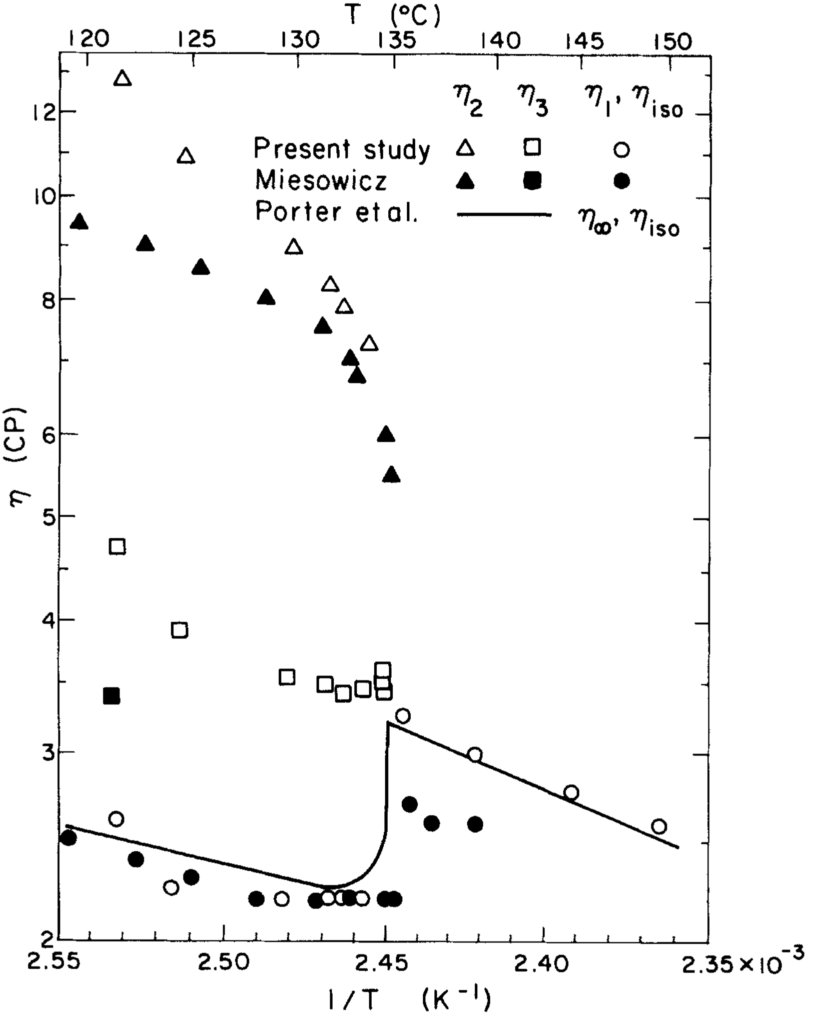

FIGURE 6 Viscosity of PAA as function of temperature.

that some extraneous factor may have caused the values at 122°C to be higher than actual.

The measurements were originally made so that we could obtain better values of the viscosity coefficients in order to improve the calculations of flow in a tube (without a magnetic field) for comparison to the data of Fisher and Fredrickson.[6] Since they measured a viscosity at higher shear rates of 2.4 centipoise, and we obtain η_1 of 2.6 centipoise at the same temperature, it is clear that calculations made with our values will give results which disagree with their experiments at least to this degree.

Our measurements, combined with Parodi's relation, are sufficient to determine only five of the six viscosity coefficients. To establish the last coefficient we use the twist viscosity, γ_1, since that one has been measured by several people and the results are reasonably consistent. These measurements are summarized in Figure 7. At 122°C, the average value of λ_1 is -7.1 centipoise (6.5 to 7.8). If this value is used in conjunction with our measurements, it predicts an ultimate angle under high shear in the absence of a magnetic field of $\theta_0 = 23°$ (20° to 25°). Meiboom and Hewitt[21] have measured a value of $\theta_0 = 20°$ at 122°C, whereas Marinin and Zwetkoff[22] measured 9.1°. The corresponding viscosity for $\theta_0 = 23°$ is $\eta_\infty = 3.8$ centipoise (3.6 to 4.1). Clearly, using this value in a calculation for flow through a tube will not agree with the data of Fisher and Fredrickson, who have $\eta_\infty = 2.4$ centipoise. At 125°C the average value of λ_1 is -6.1 centipoise, and this leads to $\theta_0 = 24°$; Meiboom and Hewitt[21] measured $\theta_0 = 21°$.

Thus we conclude that if we use our data with that of many in-

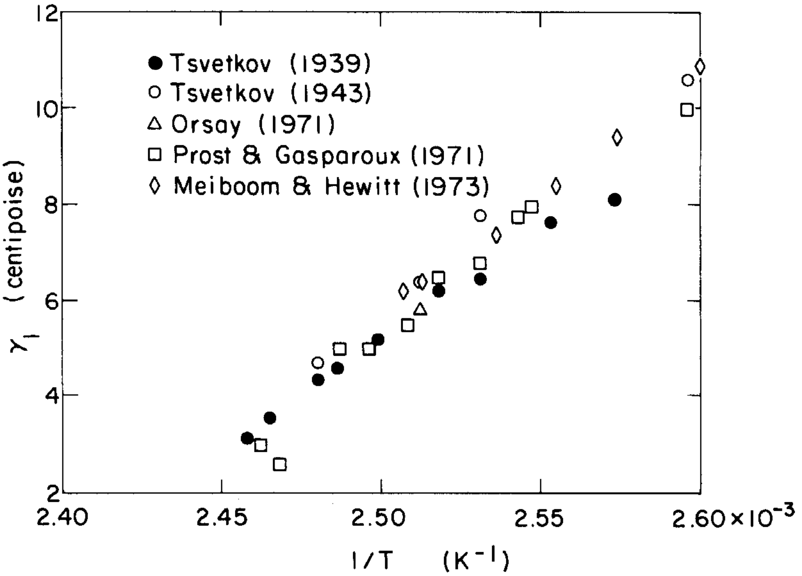

FIGURE 7 Twist viscosity for PAA.

vestigators for the twist viscosity, we obtain a value of θ_0 which agrees with that measured by Meiboom and Hewitt. The viscosity at high shear rates and 122°C disagrees with the measured values reported by Fisher and Fredrickson by about 1.4 centipoise. It is not known where the discrepancy lies.

CONCLUSIONS

The viscosity of *p*-azoxyanisole was measured by an oscillating plate viscometer between the poles of an electromagnet. The orientation of the director could be changed in all directions, and the results agree with the predictions of the Leslie-Ericksen theory. Our data can be compared to that of Fisher and Fredrickson at only one temperature (122°C), and there is a discrepancy. For temperatures above 122°C, the data agreed with available literature values except for η_2, which is the viscosity measured when the magnetic field is in the direction of the velocity gradient. Our value is higher than that measured by Miesowicz but gives values in agreement with twist viscosities and angle of orientation measured under high shear rates. These results provide the first measurement of μ_1 for PAA.

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APPENDIX†

The $v_x(y, t)$ creates other stresses than σ'_{yx} when the fluid is a liquid crystal. Thus the analysis of the oscillating plate viscometer must be revised. If v_x depends on y and t it generates stresses σ'_{yx}, σ'_{yz} and σ'_{yy}. The σ'_{yz} stresses create a velocity v_z while the σ'_{yy} stresses affect the pressure. Consider a solution with

$$v_x = v_x(y, t) \qquad v_y = 0 \qquad v_z = v_z(y, t)$$

and σ'_{ji} depends only on y and t. The equations are then

$$\rho \frac{\partial v_x}{\partial t} = \rho g - \frac{\partial p}{\partial x} + \frac{\partial \sigma'_{yx}}{\partial y}$$

$$0 = -\frac{\partial p}{\partial y} + \frac{\partial \sigma'_{yy}}{\partial y}$$

$$\rho \frac{\partial v_z}{\partial t} = -\frac{\partial p}{\partial z} + \frac{\partial \sigma'_{yz}}{\partial y}$$

The stresses are given by[5]

$$\sigma'_{ji} = \mu_1 d_k d_p D_{kp} d_j d_i + \mu_2 d_j N_i + \mu_3 d_i N_j + \mu_4 D_{ji} + \mu_5 d_j d_k D_{ki} + \mu_6 d_i d_k D_{kj}$$

Here these are

$$\sigma'_{yx} = \frac{\partial v_x}{\partial y} f_1 + \frac{\partial v_z}{\partial y} f_2$$

$$\sigma'_{yy} = [\mu_1 \sin^3\theta \sin^3\phi + (\mu_2 + \mu_3 + \mu_5 + \mu_6) \sin\theta \sin\phi] \left[\frac{\cos\theta}{2} \frac{\partial v_x}{\partial y} + \frac{\sin\theta\cos\phi}{2} \frac{\partial v_z}{\partial y}\right]$$

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†This analysis owes its genesis to a suggestion by an anonymous reviewer.

$$\sigma_{yz}' = \frac{\partial v_x}{\partial y} f_2 + \frac{\partial v_z}{\partial y} f_3$$

where

$$f_1 = \eta(\theta, \phi) \text{ in Eq. (1)}$$

$$f_2 = \cos\theta \sin\theta \cos\phi \left[\mu_1 \sin^2\theta \sin^2\phi + \frac{\mu_3}{2} \right]$$

$$f_3 = \sin^2 \left[\mu_1 \sin^2\theta \sin^2\phi \cos^2\phi + \left(\frac{\mu_3}{2} \cos^2\phi - \frac{\mu_2}{2} \sin^2\phi \right) + \frac{1}{2} (\mu_5 + \mu_6) \sin\phi \cos\phi \right] + \frac{\mu_4}{2}$$

The pressure is thus

$$p = p_0 + \rho g x + \sigma_{yy}'.$$

The equations to be solved are

$$\rho \frac{\partial v_x}{\partial t} = f_1 \frac{\partial^2 v_x}{\partial y^2} + f_2 \frac{\partial^2 v_z}{\partial y^2}$$

$$\rho \frac{\partial v_z}{\partial t} = f_2 \frac{\partial^2 v_x}{\partial y^2} + f_3 \frac{\partial^2 v_z}{\partial y^2}$$

Subject to boundary conditions

$$v_x(0, t) = U_0 \cos \omega t$$

$$v_z(0, t) = 0$$

The solution is

$$v_x = A_1 e^{-\beta_1 y} \cos(\omega t - \beta_1 y) + A_2 e^{-\beta_2 y} \cos(\omega t - \beta_2 y)$$

$$v_z = A_1' e^{-\beta_1 y} \cos(\omega t - \beta_1 y) + A_2' e^{-\beta_2 y} \cos(\omega t - \beta_2 y)$$

with

$$A_i' = \frac{2\beta_i^2 f_2}{\rho\omega - 2\beta_i^2 f_3}$$

$$A_2 = -A_1 \frac{\rho\omega - 2f_3\beta_2^2}{\rho\omega - 2f_3\beta_1^2} \frac{\beta_1^2}{\beta_2^2}$$

$$U_0 = A_1 \left[1 - \frac{\rho\omega - 2f_3\beta_2^2}{\rho\omega - 2f_3\beta_1^2} \frac{\beta_1^2}{\beta_2^2} \right]$$

$$\beta_{1,2}^2 = \rho\omega \frac{f_1 + f_3 \mp \sqrt{(f_1 + f_3)^2 - 4(f_1 f_3 - f_2^2)}}{4(f_1 f_3 - f_2^2)}$$

The drag on the plate is

$$\sigma'_{yx}\Big|_{y=0} = f_1 \frac{\partial v_x}{\partial y}\Big|_{y=0} + f_2 \frac{\partial v_z}{\partial y}\Big|_{y=0}$$

and for the following values of μ_i: $\mu_1 = -2.8$, $\mu_2 = -8.7$, $\mu_3 = -1.6$, $\mu_4 = 9.4$, $\mu_5 = 7.7$, $\mu_6 = -2.6$ [which satisfy Table II along with $\lambda_1 = -7.1$ and Eq. (7)], the drag is within 0.15% of the drag calculated by ignoring v_z.