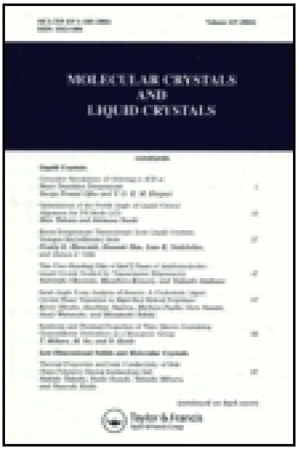

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Interfacial Effects on the Viscosity of a Nematic Mesophase

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Interfacial Effects on the Viscosity of a Nematic Mesophase‡

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Abstract—The effects of interfacial orientation on the viscosity of nematic *p*-azoxyanisole have been studied. Viscosity was measured in four glass capillary tube viscometers with diameters ranging from 78μ to 516μ. The surfaces of the capillaries were subjected to two standardized pretreatments —acid cleaning or acid cleaning followed by rubbing with a fiber—in order to produce different interfacial orientations.

Both treatments resulted in non-Newtonian viscosity behavior and a dependence of viscosity on tube diameter not in agreement with that predicted for a homogeneous fluid. However, it was found that the treatment of the interface had a profound effect on viscosity. Non-Newtonian viscosity and diameter effects were much more striking in the case of interfaces subjected to acid cleaning only.

The significance and implications of these findings is discussed.

Introduction

The work reported herein represents part of a program of research whose aim is to elucidate the nature of transport phenomena in mesophases. The term " transport phenomena " includes the transport of mass (diffusion), energy (heat conduction), and momentum (viscous stress). The present paper deals with the process of momentum transport in a nematic mesophase.

The properties that distinguish mesophases from ordinary liquids of relatively low molecular weight are due presumably to a residual degree of order—in arrangement and orientation—of the molecules of the mesophase. It is well known that orientation is

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affected by a number of influences such as (i) proximity to an interface, (ii) shear fields, and (iii) magnetic or electric fields (at least in nematic mesophases). Since it is reasonable to suppose that transport behavior is affected by local structure, it follows that mesophases should exhibit (i) anisotropic transport behavior, and (ii) transport properties that are dependent on the presence and strength of orienting influences. A corollary of these statements, not important for the present work but of considerable importance for studies of mass and energy transport, is that mesophases should violate Curie's law[4]; viz., the couplings between momentum and mass transport and between momentum and energy transport forbidden by Curie's law should be present in mesophases.

Experimental evidence supporting the foregoing conclusions exists. Thus, nematic mesophases are non-Newtonian fluids of the shear-thinning (pseudoplastic) type. The usual explanation of this phenomenon is that shear brings about alignment of the molecules, with their long axes in the direction of flow, and that the resulting alignment lowers the viscosity. The experiments of Miesowicz[8] and several subsequent workers proved that the viscosity of nematic *p*-azoxyanisole is indeed affected by a magnetic field. The evidence provided by rheological studies has been presented and fully discussed in a recent review article,[14] and no further remarks on this topic seem called for here.

Mass and energy transport have not been studied as extensively as has momentum transport, but the meager information available again supports the conclusions drawn above. Svedberg's experiments[15] demonstrate anisotropy of diffusivity. The experiments of Picot and Fredrickson[12] show that the thermal conductivity of nematic *p*-azoxyanisole is affected by an electric field and by proximity to an interface. This experimental evidence, while incomplete, seems sufficient to establish the validity of our two conclusions.

Since orientation is affected by proximity to an interface, it follows then that viscosity should be altered near an interface. This is not a new hypothesis; indeed, Porter and Johnson[14] remark that " Such effects [i.e., of an oriented region near an interface] have been widely noted and may be responsible for the apparently non-Newtonian flow results with *p*-azoxyanisole ". However, the data available are qualitative and were not taken with the specific aim of testing the hypothesis that proximity to an interface affects viscosity. The present paper reports the results of experiments designed to test that hypothesis and to clarify the nature of the effects of proximity to an interface on the viscosity of nematic mesophases.

Two facts are of material importance to the design of experiments for testing the foregoing hypothesis. The first concerns the length scale of interfacial effects. Gray[6] describes experiments by Riwlin on static orientation of a nematic mesophase on a glass surface. Optical transparency measurements indicated that the oriented layer had a thickness of about 0.02 mm (20μ). This is then the order of magnitude of distance from a glass interface in which interfacial orientation is expected to influence viscosity.

The second fact of importance is that the direction of orientation at a surface depends on the previous chemical or physical treatment of the surface. Zocher[17] showed that the long axes of molecules can be oriented parallel to an interface by previous rubbing of the surface (always rubbing in the same direction); the molecules are oriented in the direction of rubbing. Chatelain[2] made a thorough study of orientation produced by rubbing and by chemical treatment. He showed that molecules oriented with their long axes perpendicular to an interface previously cleaned with sulfuric acid-dichromate cleaning solution and not subsequently rubbed. Thus, the condition of the interface is a factor that must be carefully controlled in experiments on viscosity.

Experimental

APPARATUS

Viscosity measurements were made in glass, capillary-tube viscometers of the kind shown in Fig. 1. The driving force for flow was provided by drawing a vacuum at the point shown. The change in hydrostatic head as the fluid moved into the known volume during an experiment was negligibly small compared to the pressure difference due to the vacuum. By drawing different vacuums, different shear stresses could be applied.

Four viscometers of the type shown in Fig. 1 were constructed.

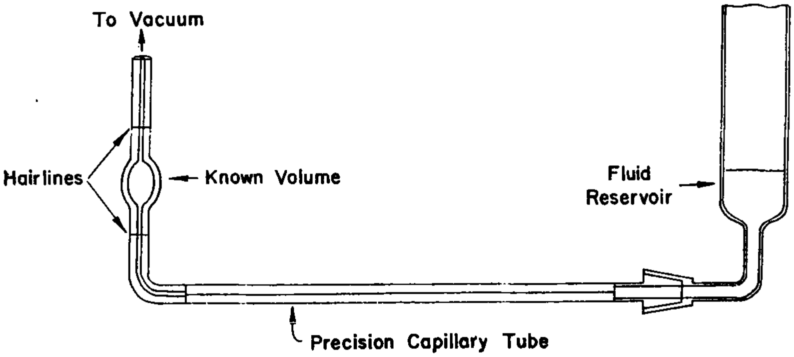


Figure 1. Diagram of a typical viscometer.

Their critical dimensions are listed in Table 1. Tube diameters were chosen so that the smallest diameter used (77.6μ) would be of the same order of magnitude as the 20μ oriented layer thickness mentioned by Gray.[6] It would have been desirable to use still smaller tubes, but these were not readily available.

Table 1 Dimensions of Capillary Tube Viscometers. Diameters determined as described in text

Tube No.	Diameter (μ)	Length/Diameter
1	77.6	1090
2	130.9	1040
3	253.6	1030
4	516	260

With the large length-to-diameter ratios used, entrance and exit effects were judged to be unimportant, as were kinetic energy effects.[16] Thus, the pressure gradient used in calculating the viscosity was simply the reading of the manometer on the vacuum line divided by the length of the capillary tube.

It was not possible to determine the diameters—and the uniformity of diameters—by the usual technique of filling the tubes to various lengths and weighing for the amount of fluid contained. Hence, the tubes were calibrated with two fluids of known viscosity: water and a viscosity standard oil ($S - 3$) supplied by the Cannon Instrument Co. Calibration runs were made at 38.7 °C, at which temperature the viscosity of water is[10] 0.68 cp. and that of the oil, according to the supplier, is 2.32 cp. It was assumed that these fluids follow the Hagen-Poiseuille law, and tube diameters were calculated from flow data using this law. The diameters calculated from data on the flow of water agree closely with diameters calculated from data on the flow of oil. Diameters given in Table 1 are averages of the data obtained. Runs with *p*-azoxyanisole were made at 121.8 °C and 140.6 °C, but the thermal expansion coefficient of the glass tubes is so low that the dimensions given in Table 1 are still valid at the higher temperatures.

The apparatus was immersed in a constant temperature bath filled with mineral oil. The bath had a glass front for observation of liquid levels in the viscometers. Temperature could be controlled to ± 0.1 °C.

MATERIAL

The only nematic mesophase studied was that of *p*-azoxyanisole. This was purified by three or sometimes four recrystallizations from absolute ethyl alcohol. The C—N transition temperature was in the range 117.8–118.2 °C; the N—I transition temperature was in the range 134.2–135.0 °C.

PROCEDURES

The interior surfaces of the capillary tubes were pretreated in two different ways. In order to produce what was hoped to be a perpendicular orientation of *p*-azoxyanisole molecules at the interface, the tubes were washed in sulfuric acid-dichromate cleaning solution for twenty minutes, rinsed with distilled water, and dried with air when the tubes were in the hot oil constant temperature bath (121.8 °C). In order to produce what was hoped to be a parallel orientation of *p*-azoxyanisole molecules at the interface, a human hair or bundle of hairs was passed through the cleaned tube and drawn to-and-fro 150 times. This procedure was suggested by Mr. James Fergason of the Liquid Crystal Institute, Kent, Ohio. Only tubes 2 and 3 were treated in this way.

The last phase change seen by a nematic *p*-azoxyanisole sample being studied was the crystalline solid to nematic liquid transition. Results obtained were independent of the thermal history of the sample prior to this transition. It would have been of interest to see what results were obtained when the last phase change was the isotropic liquid to nematic liquid transition. However this was not studied.

Results

ISOTROPIC LIQUIDS

Presumably, water and oil S-3 at 37.8 °C and *p*-azoxyanisole at 140.6 °C are all isotropic liquids. They should therefore exhibit Newtonian (constant) viscosities and moreover, their viscosities should be independent of tube diameter (no interfacial effects). Figure 2 shows that this expectation is fulfilled in all three cases.

The viscosity found for isotropic *p*-azoxyanisole was 2.9 cp. at 140.6 °C. The results of Peter and Peters[11] indicate a viscosity of 2.92 cp. at this temperature; those of Porter and Johnson[13] indicate a viscosity of about 3 cp. Agreement with previously published results therefore is satisfactory. The data on water and oil in Fig. 2 are not included to show that their viscosities are 0.68 and 2.32 cp., respectively, since that was assumed for these materials. Instead, the data are included to indicate the absence of non-Newtonian and interfacial effects on their viscosity.

NEMATIC *p*-AZOXYANISOLE; PERPENDICULAR ORIENTATION AT THE INTERFACE

The foregoing heading may be somewhat misleading in that we do not know the precise situation at the interface. Nevertheless,

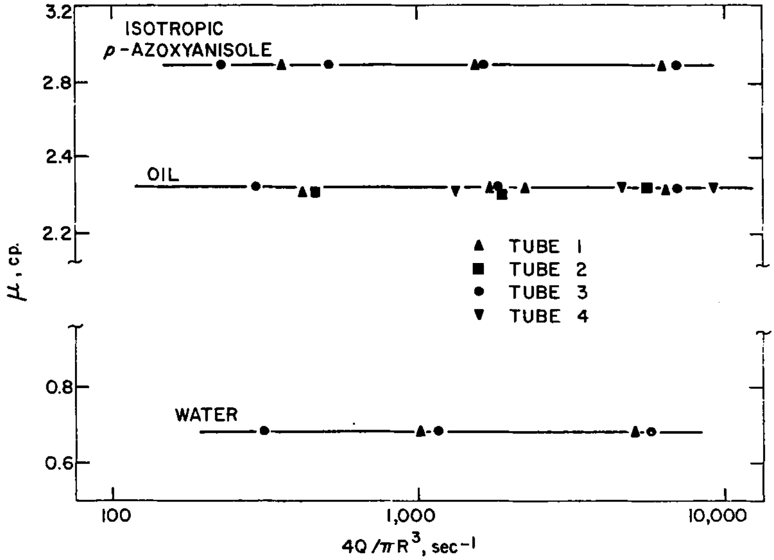


Figure 2. Viscosity behavior of water and oil S-3 at 37.8 °C, and of *p*-azoxyanisole at 140.6 °C (i.e., above the N–I transition temperature).

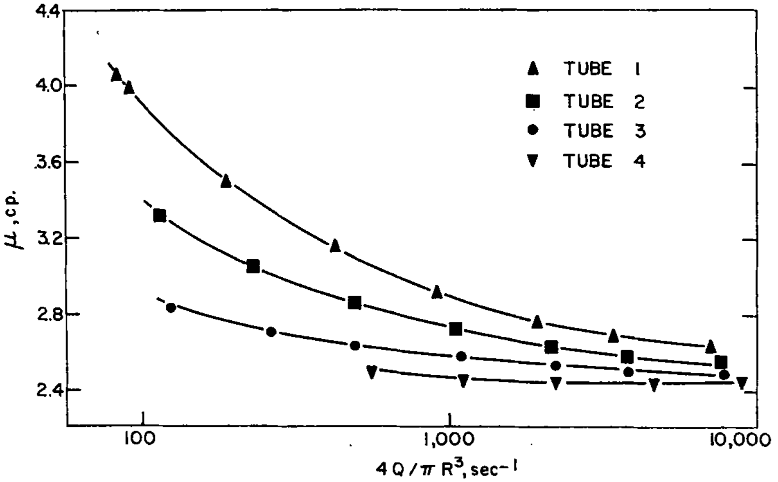


Figure 3. Viscosity behavior of nematic *p*-azoxyanisole at 121.8 °C; surface treated so as to produce a perpendicular orientation of mesophase molecules there.

some short way of referring to the experiments performed when the glass surfaces of the capillaries were cleaned but not rubbed is necessary, and so we adopt the terminology used in the heading. The same qualifying statement applies to the experiments done with " Parallel Orientation at the Interface ".

The results of the perpendicular orientation experiments are shown in Fig. 3. The quantity μ—the apparent viscosity—is computed from the Hagen-Poiseuille equation:

$$\mu = \frac{PR/2}{4Q/\pi R^3} \tag{1}$$

where R is the tube radius, P the pressure gradient, and Q the volumetric flow rate through the tube. The quantity $PR/2$ is the shear stress at the wall of the tube. If the fluid is Newtonian and if there is no wall effect, μ is constant and $4Q/\pi R^3$ is the shear rate at the wall of the tube. If the fluid is non-Newtonian or if there is a wall effect, $4Q/\pi R^3$ is an " effective shear rate " inasmuch as it is the value of the shear rate at some radius *inside the tube.*[5]

If the material being studied is homogeneous, that is, if its properties are everywhere the same, then one can show[5] that μ must be a unique function of $4Q/\pi R^3$. In other words, the relation between μ and $4Q/\pi R^3$ must be independent of tube diameter. It is not necessary here that the fluid be Newtonian (i.e., μ consant). Indeed, very general non-Newtonian but homogeneous materials called by Noll[9] *simple fluids* can be shown to exhibit a unique relation between μ and $4Q/\pi R^3$. If on the other hand, the fluid is not homogeneous, in particular, if its viscous behavior is altered in the vicinity of the wall, then the relation between μ and $4Q/\pi R^3$ will not be unique but will be dependent on tube diameter.

Figure 3 shows that nematic *p*-azoxyanisole is not a homogeneous fluid, since there is a marked dependence of the relation between μ and $4Q/\pi R^3$ on tube diameter. Hence, nematic *p*-azoxyanisole is not a simple fluid in the sense that that term is used by Noll.[9]

The increase of apparent viscosity as the tube diameter is decreased, with $4Q/\pi R^3$ the same, shows that the material near the interface must have a higher viscosity than the material near the axis of the tube. This is what is expected for a perpendicular orientation at the wall. In addition, all curves appear to be approaching the same asymptote at high shear rates, and the viscosity here is close to the high shear rate value of 2.4 + cp. found by various investigators (see graph given by Porter and Johnson[14]) at 121.8 °C.

Nematic *p*-Azoxyanisole; Parallel Orientation at the Interface

The results of these experiments are shown in Fig. 4. One sees that there is a slight interfacial effect as well as a slight non-Newtonian effect, but that these are by no means as pronounced as the corresponding effects in the perpendicular orientation experiments.

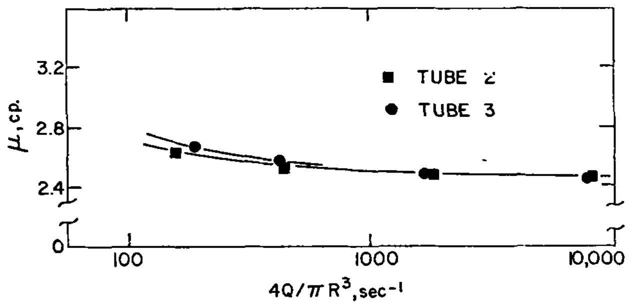


Figure 4. Viscosity behavior of nematic *p*-azoxyanisole at 121.8 °C; surface treated so as to produce a parallel orientation of mesophase molecules there.

The slight decrease of apparent viscosity as the tube diameter is decreased, with $4Q/\pi R^3$ the same, suggests that the material near the interface has a lower viscosity than the material near the axis of the tube. This is precisely the opposite of what was found in the perpendicular orientation experiments. At high shear rates, the two curves seem to approach a common asymptote 2.4 + cp. This is the same asymptote found in the perpendicular orientation case, and also reported by previous investigators for high shear rate experiments.

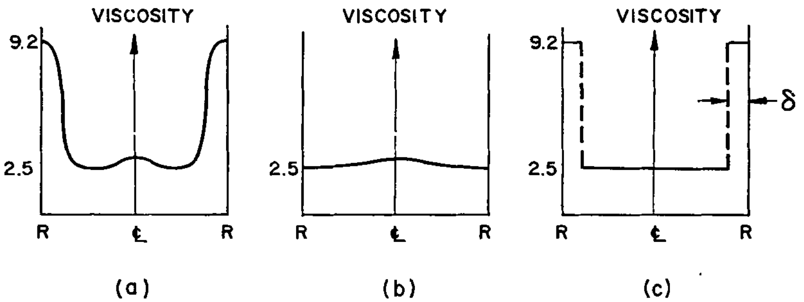
Discussion of Results

ISOTROPIC LIQUIDS

The data obtained here demonstrate that the apparatus gives results free from artifact. Thus, the demonstration of non-Newtonian viscosity behavior and diameter effects in the experiments with nematic *p*-azoxyanisole must be regarded as genuine, and is not to be attributed to some artifact of the apparatus or technique.

NEMATIC *p*-AZOXYANISOLE; PERPENDICULAR ORIENTATION AT THE INTERFACE

A very simple model from which one can extract useful results can be constructed for the flow of nematic mesophases. The actual situation, insofar as viscosity is concerned, is probably as shown in Fig. 5a. Near the interface, the viscosity is high owing to the perpendicular orientation of the molecules there. In fact, if we assume that orientation is essentially complete and truly perpendicular, then the viscosity at the wall is known; it should



(a) (b) (c)

Figure 5. Profiles of viscosity in the capillary tube for various situations: (a) Perpendicular orientation at the interface; (b) parallel orientation at the interface; (c) idealization of (a) used to calculate the wall layer thickness, δ.

be the 9.2 cp. value found by Miesowicz[8] when he oriented *p*-azoxyanisole molecules perpendicular to the flow and parallel to the velocity gradient with a strong magnetic field. At the tube center, the shear rate is zero, and orientation due to the interface is probably negligible (at least if the tube is no smaller than those used here). Hence, the viscosity should be the 3.0 cp. viscosity of a " disoriented fluid " given by Becherer and Kast.[1] At intermediate radii, interfacial effects are probably still negligible, but the shear rate is assumed to be large enough to produce essentially complete alignment in the direction of flow. The viscosity here must be the 2.5 cp. found in high shear rate flows. Of course, the viscosity does not change abruptly, but follows the smooth curve shown in Fig. 5a. In addition, the shape of the curve must be dependent on flow rate, obviously.

Let us replace this situation with the idealized situation shown in Fig. 5c. Here we divide the fluid into a wall layer of Newtonian fluid and a core of Newtonian fluid. We neglect the rise of viscosity near the tube axis; in very low shear rate experiments, or in experiments with parallel orientation at the interface, this could not be done. The thickness (δ) of the wall layer is assumed to be shear rate dependent. Let η_w be the viscosity of the wall layer and η_0 be the viscosity of the core. We shall assume complete orientation perpendicular to the wall in the wall layer, and take η_w to be Miesowicz' value of 9.2 cp. We assume complete orientation parallel to the flow in the core and choose η_0 such that the wall layer thickness is least dependent on tube radius. The value satisfying this criterion is 2.42 cp., in good agreement with the previously quoted figure (2.4 + cp.) for the viscosity of fully flow-oriented *p*-azoxyanisole.

An elementary calculation shows that the thickness δ must be related to the apparent viscosity μ by the formula

$$\frac{R-\delta}{R} = \left[\frac{\eta_0}{\mu} \cdot \frac{\eta_w - \mu}{\eta_w - \eta_0}\right]^{1/4} \tag{2}$$

Hence, since μ is known in any specific case and η_w and η_0 have been assumed, δ can be calculated.

Figure 6 shows values of δ calculated from Eq. (2) and the data of Fig. 3. One sees that there is indeed little systematic dependence of δ on tube radius so that the thickness of the oriented layer is determined almost entirely by the effective shear rate, $4Q/\pi R^3$.

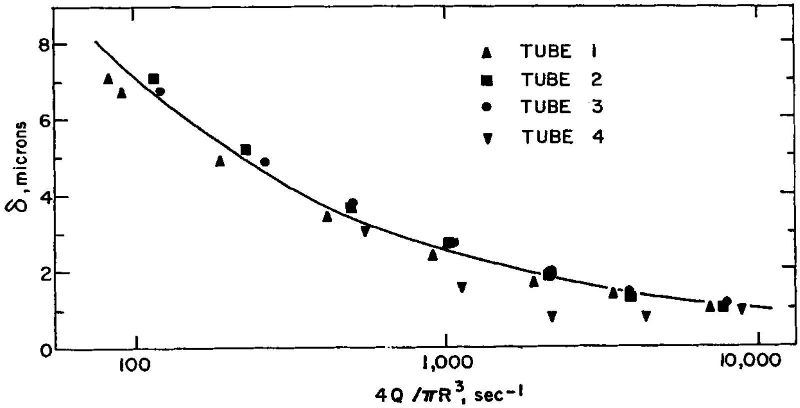


Figure 6. Variation of wall layer thickness with effective shear rate for the case of perpendicular orientation at the interface; nematic p-azoxyanisole at 121.8 °C.

The results shown in Fig. 6 exhibit the following gratifying features: First, the thickness of the wall layer decreases as the shear rate increases. This is expected since shear must become relatively more important as an orienting influence than is proximity to an interface as the shear rate increases. Second, the thickness of the wall layer is of the same order of magnitude, but less than, the figure of 20μ mentioned by Gray[6] for static orientation on a glass surface. Third, δ probably approaches zero at high shear rates, indicating that shear alignment prevails in all but a minute fraction of the tube. Unfortunately, the zero shear rate limit of δ cannot be found from the data, but we believe that it would be finite, and probably not far from 20μ.

During the course of the Second International Liquid Crystal Conference in August, 1968, at which some of the data of this paper were presented, one of us (AGF) was made aware of the prediction of the continuum theory of mesophases[3,7] respecting

Poiseuille flow in a tube. According to information presented by Prof. J. L. Ericksen, Dr. R. J. Atkin has applied the theory to Poiseuille flow of a nematic mesophase, and he predicts that

$$Q = Rf(R^3P) \tag{3}$$

where the (unstated) function f depends on the orientation at the wall of the tube (i.e., orientation perpendicular to the wall would produce a different function f than would orientation parallel to the wall). If Equation (3) is true, then μ should be a unique function of $R^2(4Q/\pi R^3) = 4Q/\pi R$. Let it be noted that neither μ nor $4Q/\pi R$ is dimensionless, so that the prediction is not made on the grounds of dimensional analysis. Let it be noted further that the prediction conflicts with Noll's theory[9] of simple fluids, for which μ is a unique function of $4Q/\pi R^3$.

Figure 7 shows a plot of μ vs. $4Q/\pi R$. One sees that the result is not systematically dependent on tube diameter, so that the prediction of the continuum theory is in agreement with our observations.

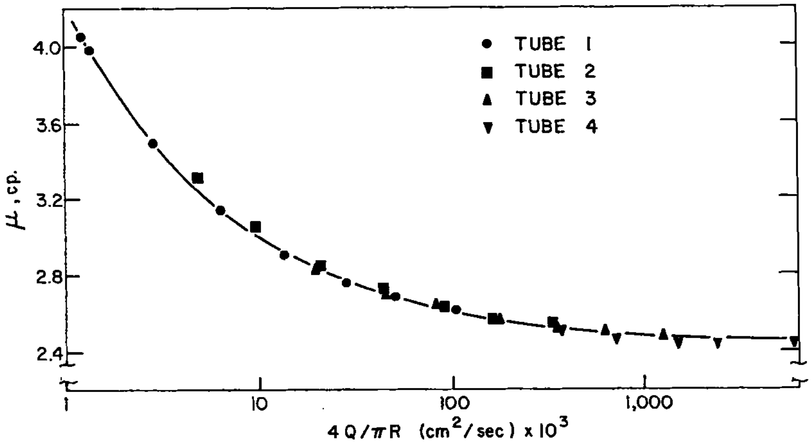


Figure 7. Correlation of flow data on nematic *p*-azoxyanisole at 121.8 °C provided by the continuum theory of liquid crystals. Perpendicular orientation at the interface.

NEMATIC *p*-AZOXYANISOLE; PARALLEL ORIENTATION AT THE INTERFACE

The results obtained in this set of experiments are consistent with the following model: Near the wall, rubbing of the surface produces a layer of molecules essentially completely aligned parallel to the wall and to the tube axis. The viscosity of this layer should be the same as the fully shear-oriented viscosity of about 2.4+ cp. In the center of the tube, interfacial affects are unimportant (unless of course one used tubes somewhat smaller than those used here) as are shear effects. Hence, the viscosity here should be the 3.0 cp. viscosity of a " disoriented fluid " given by Becherer and Kast.[1] The postulated situation is shown in Fig. 5b. The model is consistent with the observed direction of change of viscosity (decrease) as tube diameter is decreased, as well as with the amount of change of viscosity. One could apply Eq. (2) in this case as well, with $\eta_w \approx 2.4$ cp. and $\eta_0 = 3.0$ cp., in order to calculate a wall layer thickness. However, the concept seems to have less utility in this case—where shear and interfacial effects augment rather than oppose—so we have not done the calculations.

The continuum theory predicts that again μ should be a unique function of $4Q/\pi R$, though not, of course, the same function that was found for the perpendicular orientation case. Figure 8 shows the plot of μ vs $4Q/\pi R$ for the parallel orientation case. One sees

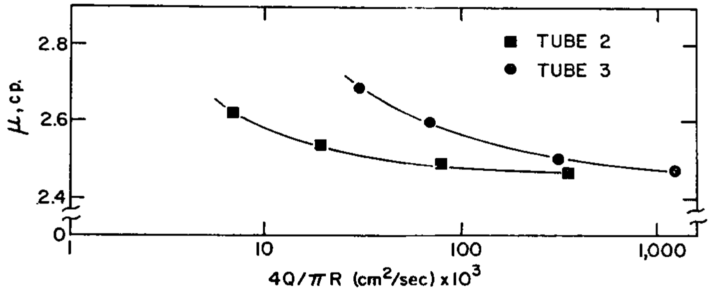


Figure 8. Correlation of flow data on nematic *p*-azoxyanisole at 121.8 °C provided by the continuum theory of liquid crystals. Parallel orientation at the interface.

here that the prediction of the continuum theory is not valid at lower shear rates.

Conclusions and Suggestions for Further Work

The results reported above confirm the hypothesis that the viscosity of *p*-azoxyanisole is affected by factors, including proximity to an interface, that influence orientation. These results and others reported in the literature are consistent with a model that views the orientation at a point as a balance between all orienting influences. The effect of shear is to align the molecules in the direction of flow. The effects of proximity to an interface are various, depending on the prior treatment of the interface. Acid cleaning produces an orientation perpendicular to the interface, whereas acid cleaning followed by rubbing with a fiber in the direction of flow produces an orientation parallel to the direction of flow. There is a tendency for orientation, whatever its source, to spread, but the magnitude of this effect decreases with distance. Thus, an orientation at one point tends to promote a similar orientation at other points remote from it. For this reason, nematic liquid crystals are not simple fluids in Noll's sense.[9] Orientation parallel to flow leads to a viscosity of about 2.4 cp. (in *p*-azoxyanisole at the experimental temperature). Orientation perpendicular to the flow but parallel to the velocity gradient leads to a viscosity of 9.2 cp. In the absence of external orienting influences, viscosity is supposed to be[1] about 3.0 cp.

Not all of these statements are firmly established by the data presented here or by other data reported in the literature. We offer them as reasonable working hypotheses for work on transport phenomena in nematic mesophases. The element of conjecture involved could be reduced by further studies on viscosity, particularly at low shear rates and at both small and large tube diameters (or gap widths if a Couette viscometer is used). Specific experiments that should be done include studies on the perpendicular orientation case to see if μ approaches Miesowicz' value of 9.2 cp. and δ approaches the value of 20μ found by Riwlin for static orientation, at vanishingly small values of $4Q/\pi R$. In addition, studies should be conducted with low shear rates and large tube diameters to see if μ approaches the limit of 3.0 cp. that the data of Becherer and Kast[1] would lead one to expect. Finally, a repetition of these studies at a different temperature or on a different nematic mesophase would be useful to provide confirmation (or negation) of the generality of the results obtained and a new set of viscosity constants that might be exploited in further experimental studies.

It should be noted that the foregoing qualitative model is not in complete agreement with the concepts embodied in the continuum theory,[3,7] in spite of the fact that our data for perpendicular orientation at the interface agree with the prediction of that theory. The continuum theory describes the local structure of mesophases in terms of a single vector of unchanging length. This unit vector gives the direction in which, on the average, the mesophase molecules are oriented at the point in question. However, the direction of mean orientation does not give a complete specification of the local structure of the mesophase. A more complete picture of local structure would include a specification of the amount of dispersion of molecular orientations about the direction of mean orientation and a specification of the dispersion of domain (" swarm ") orientations about the direction of mean orientation. If we refer to a dispersion of domain orientations about the mean as " fractional orientation ", then it is clear that the continuum theory as currently developed cannot account for any phenomena associated with fractional orientation. Some of our results, in particular, the increase of viscosity with decreasing shear rate in the parallel orientation case, seem to us to be effects of fractional orientation.

The effects of fractional orientation should be most apparent when external orienting influences are small; e.g., when the shear rate is small or when the distance from an interface is large. As $4Q/\pi R^3 \rightarrow 0$ and $R^2 \rightarrow \infty$, the model that we advance requires μ to approach the viscosity of a disoriented fluid (i.e, domains oriented at random) and this should be the 3.0 cp. value of Becherer amd Kast.[1] However, as $4Q/\pi R^3 \rightarrow 0$ but $R^2 \rightarrow 0$, μ should approach a different limit (the 9.2 cp. value of Miesowicz[8] for perpendicular wall orientation, but the 2.5 cp. value of high shear rate experiments for the parallel orientation case). According to the continuum theory, μ should be a unique function of $4Q/\pi R$ so that the theory does not allow μ to approach *both* of the limits required by our model. Figure 8 suggests that μ is not a unique function of $4Q/\pi r$ at low shear rates in the parallel orientation case. This figure also suggests that as $4Q/\pi R^3 \rightarrow 0$, μ will approach a higher value (3.0 cp.?) in large tubes than it does in small tubes. This is, of course, in accord with our model. Presumably, diameter effects on the relation between μ and $4Q/\pi R$ were not observed in the perpendicular orientation case (Fig. 7) because in the range of shear rates studied, wall orientation exerts a much larger influence on viscosity in this case (cf. Figs. 5a and 5b). In fairness to the continuum theory, it should be pointed out that we do not have the same degree of confidence in the data shown in Fig. 8 as we have in the data shown in Fig. 7. This is because fewer data points were taken, only two tubes were used, and it is not certain that the rubbing process produced the same degree of parallel surface orientation in both of the tubes used.

The findings reported herein suggest a word of caution for those workers attempting to elucidate the structure of mesophases. If experiments for structure elucidation are done on thin sections (say 100μ or less in *p*-azoxyanisole), any interpretation of results that ignores the orienting influence of interfaces is likely to be incorrect. Hence, if one wishes to isolate the effect of an orienting influence, say a magnetic field, he should use a rather thick sample of material in order to avoid the complications of interfacial orientation. Insufficient attention to this consideration has probably caused a good deal of confusion in the past.

Acknowledgment

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