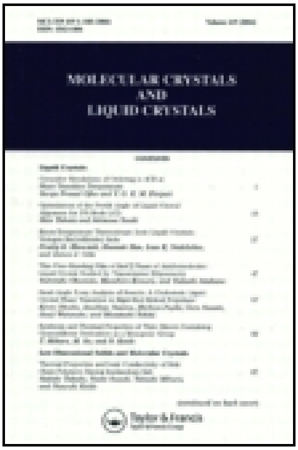

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Capillary Viscometry of Some Lyotropic Nematics

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Capillary Viscometry of Some Lyotropic Nematics

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Capillary viscometry measurements as a function of temperature were made on two lyotropic nematic liquid crystals involving the surfactants potassium laurate and sodium decylsulfate. The transitions between rod-like, disc-like, and biaxial phases are clearly seen, and the origins of the anomalies are discussed.

INTRODUCTION

The flow behavior of lyotropic nematics is not as well characterized as thermotropics. At least two factors contribute to this situation: (1) at the present time lyotropics have not found practical applications in display technology; (2) theoretically the flow behavior of dense strongly interacting flexible anisometric particles is not well evolved.

Recently, the dynamical properties of lyotropic nematics are coming under more intense scrutiny; for example, quasielastic light scattering,[1] and birefringence relaxation measurements[2] have been performed. Also, along with these examples, the dynamics of particulate suspensions (i.e. lyotropic ferrofluids[3]) depend intimately on the viscosity and viscosity anisotropy.

In this note we report the results of capillary viscometry measurements for two lyotropic nematic systems: potassium laurate (KL) and sodium decylsulfate (SDS). Both of these systems form disc-like (N_D) and rod like (N_C) micellar nematic phases along with hexagonal and lamellar smectic phases. Phase diagrams of the above systems have been published elsewhere.[4–6]

EXPERIMENTAL

SDS (Research Plus, Inc.) was purified by recrystallization from 95% and 100% ethanol several times before use and then mixed with 1-decanol (99+%, Aldrich Chemical Co.) and triply distilled water. The concentrations of SDS used were 35 wt% and 36 wt% respectively with 7 wt% decanol. They all formed nematic mesophases at room temperature. In order to prevent the hydrolysis of SDS into decanol, samples were kept below 50° at all times during preparation. KL was synthesized from lauric acid (BDH Chemical Ltd.) by neutralization with potassium hydroxide and was further purified by recrystallization from hot anhydrous ethanol several times. The liquid crystal system was prepared by mixing 27.5% by weight of KL in water, with the amount of decanol held at 6.29% by weight.

Samples were made at the same time for microscope and viscosity studies. In the rheological study, the sample was injected into a Cannon-Manning semi-micro calibrated viscometer. The viscometer was calibrated with standards of known viscosities. The length and diameter of the capillary of the viscometer were 15 cm and 0.038 cm respectively. Measurements were performed in the customary manner of timing the passage of the meniscus past the engraved lines above and below the drainage bulb, which had a volume of 0.40 ml. The shortest time measured for this passage was 60 seconds, the longest 242 seconds. For flow times greater than ~100 sec, kinetic corrections to the viscosity were negligible. Due to the relatively high viscosity of our systems, the subjective nature of judging when the meniscus passed an engraved line introduced negligible error. Temperature control of the system was achieved by the immersion of the viscometer in a constant temperature

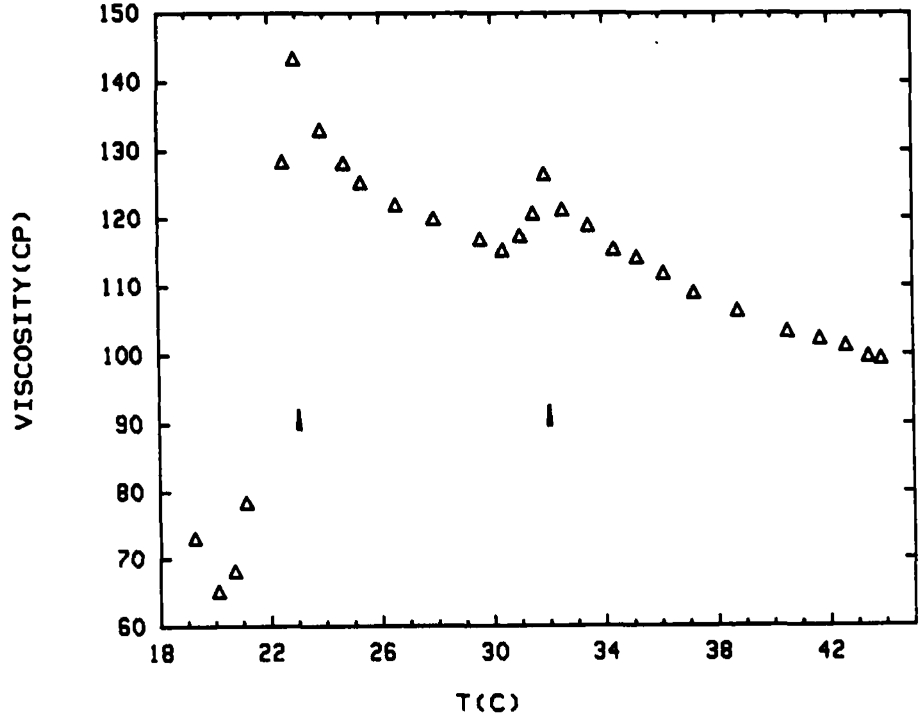

FIGURE 1 Viscosity of 35/7/58 wt% SDS/decanol/water solution. On descending temperature the first arrow indicates the Isotropic–N_C transition. The second arrow shows the onset of the N_C to N_D transition.

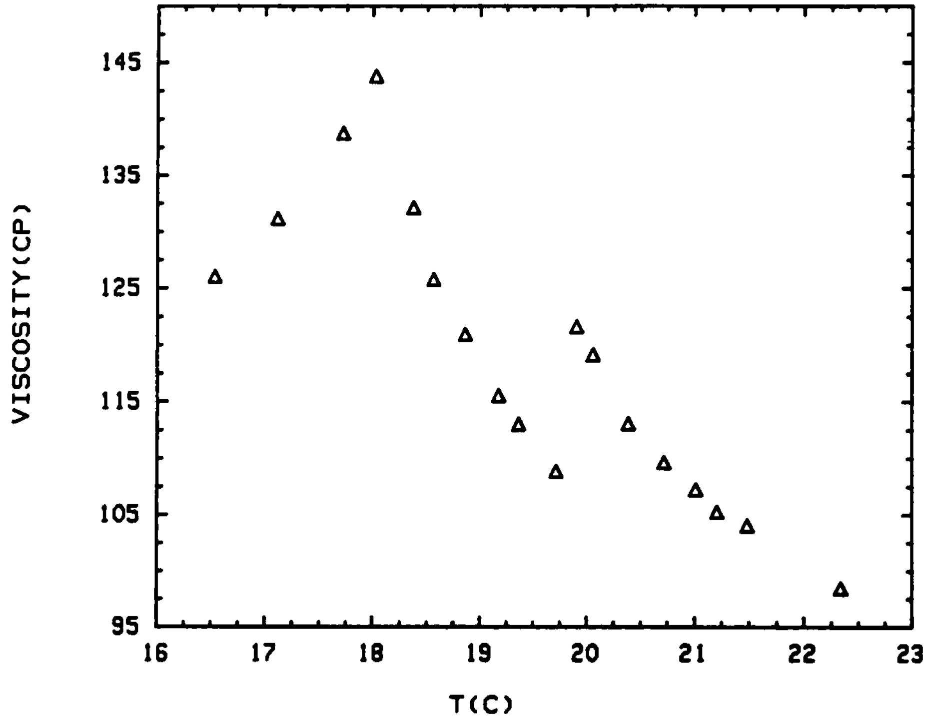

FIGURE 2 Viscosity of 36/7/57 wt% SDS/decanol/water solution. On descending temperature the first peak corresponds to the Isotropic-N_C transition, while the second peak shows the onset of the N_C to N_D transition.

water bath calibrated with an iron-constantan thermocouple (Omega Engineering, Inc.) with an accuracy of ±0.05°C.

Figure 1 shows the behavior of the viscosity of the 35 wt% SDS solution. Above 32°C two phases, isotropic plus batonnets of middle soap, coexist. From 32°C to 23°C an N_C phase is stable, and upon decreasing temperature from 23°C to 20°C a direct N_C to N_D transition is observed. Figure 2 displays the same sequence of events for a 36 wt% SDS solution.

The behavior of the viscosity vs. temperature of the 27.5 wt% KL system which shows a biaxial phase between N_C and N_D is shown in Figure 3. The following discussion, however, pertains only to Figures 1 and 2. Our study complements a previous capillary measurement of viscosity by Hochapfel, Boidart and Vivoy[7] on a (35.9/7.2/56.9) wt% solution of (SDS/decanol/water) solution.

DISCUSSION

For the N_C phase, with the laminar flow velocity parallel to the director, the viscosity for steady state Poiseuille flow is[8]

$$\eta_c = 1/2(\alpha_3 + \alpha_6 + \alpha_4) \tag{1}$$

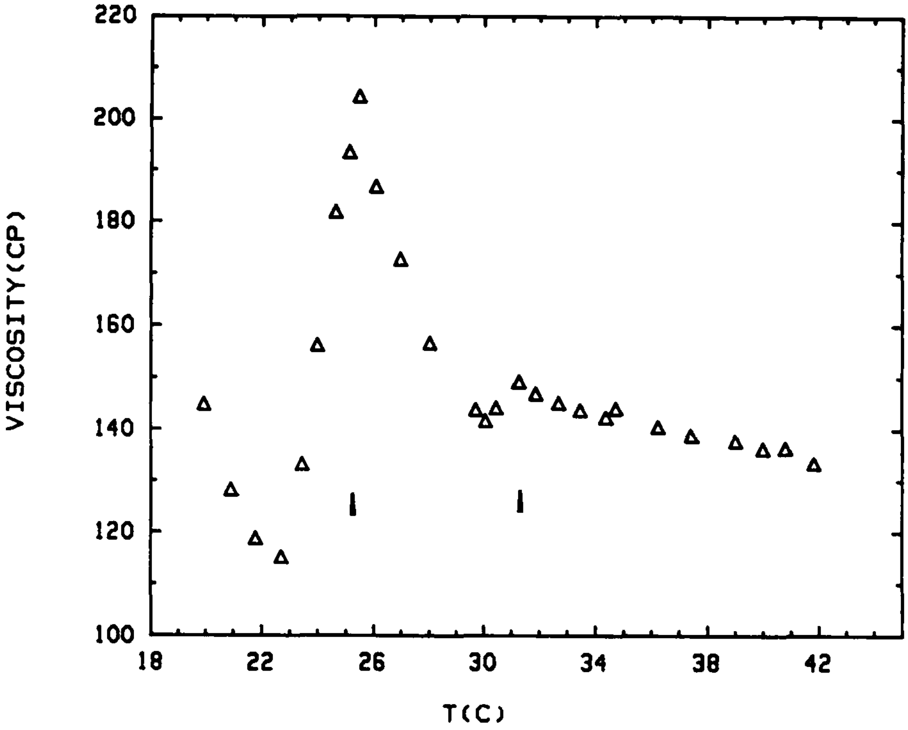

FIGURE 3 Viscosity of 27.5/6.24/66.26 wt% KL/decanol/water solution. On descending temperature the first peak corresponds to the N_C–$N_{biaxial}$ transition, the second to the $N_{biaxial}$–N_D transition.

Here the α_i's are the Leslie-Ericksen viscosities. The viscosity α_4 is a pure shear viscosity and is therefore the only α_i present in the isotropic phase. On approaching the nematic–isotropic transition from the isotropic phase we observe the usual pretransitional enhancement superimposed upon the conventional Arrhenius behavior of the viscosity.[8,9] For the N_D phase the problem is complicated by the fact that the director now prefers to orient perpendicular to the capillary walls. Thus there is a strong coupling between flow and orientation. In this case the governing equations were studied by Atkin[10] and later by Tseng *et al.*[11] for typical rod-like thermotropics. Optical observations on equilibrium samples of the N_D phase show the well-known "escape to the third dimension" structure. During flow this structure deforms. The amount of deformation depends on the elastic constants, viscosities and flow rate.[11]

One qualitative feature of the data which appears to be preserved is the magnitude of the discontinuity in viscosity through the N_C–N_D transition (Figures 1 and 2). The viscosity decreases by about a factor of two when passing from the N_C to the N_D phase. It is tempting to interpret the discontinuity as a geometric effect, similar to the discontinuities observed in deuterium magnetic resonance spectra.[12] However, this is not necessarily correct, since the sign and magnitude of the α_i's may also change through the N_C–N_D transition in addition to the reorientation of the director field. Further experiments and theory are required to elucidate the above behavior.

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