

Viscosity Measurement in Nematic/Lamellar Phase Transition of Lyotropic Liquid Crystal

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Viscosity of the binary perfluorosurfactant/water systems: i) Ammonium perfluoro-octanoate (NH_4PFO)+water and ii) Cesium perfluoro-octanoate (CsPFO)+water, has been measured using a simple capillary method. Both systems clearly show discontinuity in viscosity for high concentrations of surfactant (≥ 45 wt%) as the temperature decreases from the isotropic to the nematic phase transition temperature, and a collapse in the viscosity at the nematic to lamellar phase transition temperature for all concentrations, thus allowing us to determine the phase transition temperature which is consistent with that obtained by optical microscopic study. The reversal in activation energy, i.e., a higher activation energy in the nematic phase than in the isotropic phase is observed as the concentration of the surfactants decreases. The polymer effect on the viscosity of lyotropic liquid crystals is also discussed.

KEYWORDS: lyotropic liquid crystals, viscosity, phase transition

1. Introduction

Lyotropic systems are of interest for applications to detergents and food-emulsifiers in the petroleum industry, and for theoretical studies due to their similarity to thermotropic liquid crystals (LC).¹⁾ Several binary perfluoro-surfactant/water systems have been determined to form a nematic phase.²⁾ One of them is the NH_4PFO /water and CsPFO /water systems which have been determined to have isotropic (I), nematic (N), and lamellar (L_∞) phases over about 40–60 wt% of surfactant in water.³⁾ These binary systems form micelles which are illustrated in Fig. 1. The effect of polyethylene-oxide (PEO) on the phase diagram of a binary mixture of lyotropic LC has also been studied.⁴⁾ This study suggested that the replacement of water by PEO, up to 1.5 wt%, has no significant effect on the I/N transition, but the formation of the L_∞ phase is suppressed above a critical concentration.

Flow behavior of thermotropic liquid crystal (LC)⁵⁻⁷⁾ and lyotropic LC²⁾ has been studied for a long time. In previous studies, under the application of a magnetic field applied to fix the direction of the molecular director, Miesowicz viscosities (viscosities depending on the direction of a director and flow) for thermotropic LC were measured. Temperature dependence of the viscosity of the system of NH_4PFO with a surfactant content of 20 wt% using a Couette viscometer had been determined from the I phase to the N phase region, showing a peak at the I/N phase transition. Liquids with high fluidity, follow Arrhenius viscosity patterns, i.e. viscosity $\eta = \eta_0 \exp(\Delta E/k_B T)$ where ΔE is the activation energy for diffusion, k_B is the Boltzmann constant, and T is the temperature.⁸⁾ In this study, the viscosity, which is an important physical parameter for influencing the response time in the display device, is measured over the entire temperature range, including the N to L_∞ phase transition of the NH_4PFO /water and the CsPFO /water systems, using the Cannon-Ubbelohde Semi-Micro Vis-

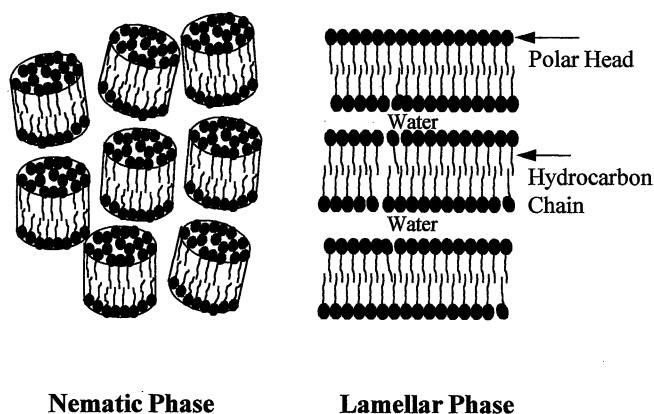


Fig. 1. The structure of nematic and lamellar phases in the surfactant+water binary mixtures. The symmetry axes of micelles have orientational ordering along one direction in the nematic phase and the bilayer is formed in the lamellar phase.

cometer which allows for the measure of kinematic viscosity. Experimental results show that the collapse of the viscosity at the N to L_∞ phase transition occurs and the activation energy in the N phase is higher than that in the I phase with a low concentration of surfactants.

2. Experimental Results and Discussion

The surfactants NH_4PFO and CsPFO were synthesized at the Liquid Crystal Institute at Kent State University. For polarizing microscopy observations with a Mettler heating stage, we placed our samples into commercially available flat microslides without special surface treatment, with an inner diameter of 0.2 mm (Vitro Dynamics Inc.). There may be a slight error in the measurement of the phase transition temperatures due to water loss while sealing the capillary using a torch. Solutions with 43(S1), 45(S2), and 49(S3) wt% CsPFO , and 50(S4) wt% NH_4PFO concentrations in water were prepared. The phase transition temperatures are determined by optical microscopy under crossed polarizers. With the temperature decreasing from the isotropic phase at a rate of $1^\circ\text{C}/\text{min.}$, small droplets with a schlieren tex-

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ture appear rapidly (I/N transition) and develop slowly to a large size of the schlieren texture. As the temperature decrease continues, the comb-shaped and brush-like textures appear in part (N/ L_α transition), and with continued cooling, they develop to throughout the entire whole area with no further change of texture occurring until the temperature approaches near the freezing point. Fast developing textures were only observed at both phase transition temperatures. The S1, S2, S3, and S4 show the I/N transition at 31.3, 33.8, 39.4, and 33.6°C, respectively, and additionally those of the N/ L_α transition at 24.5, 27.6, 34.1, and 27.4°C, respectively. Both systems form disk-like micelles in the nematic phase.³⁾ 43 wt% CsPFO solution in water containing 0.1 wt% PEO shows the same phase transition temperature as the S1.

The viscometer is immersed in a temperature bath and efflux time of the sample is measured. By multiplying the efflux time by the viscometer constant, we calculate the kinematic viscosity of the sample directly as given in Centistokes (cSt). In this case, since no external magnetic field is applied, the measured viscosity is a test of the flowing capability of the solution.

Figure 2 shows the temperature dependence of the vis-

cosity for the five solutions. The solid lines are a fit of equations η vs. T and the dashed lines are drawn as guides. The viscosity increases following Arrhenius viscosity patterns within the I region. However, as the temperature increases to the nematic phase from the isotropic phase, a sudden increase in the viscosity is observed for solutions S4, S3, and S2. This could be considered to be caused by the the orientational ordering between micelles as the temperature passes the I/N phase transition temperature. Within the nematic range, the viscosity again follows the Arrhenius viscosity pattern. Surprisingly, for all solutions as the temperature approaches the N/ L_α phase transition, the viscosity suddenly changes to the values of the high-temperature isotropic phase. At N/ L_α phase transition temperature, it was observed that small air bubbles appeared in most of the bulk solution while the solution was being placed at the desired position of the capillary tube before it was allowed to flow. At this transition temperature, the bulk of the solution also revealed an opaque color, indicating that strong light scattering was occurring due to the coexistence of the nematic and lamellar domains. Therefore, such a strong flow might be due to the weak interaction between the domains. For a 50 wt% NH_4PFO

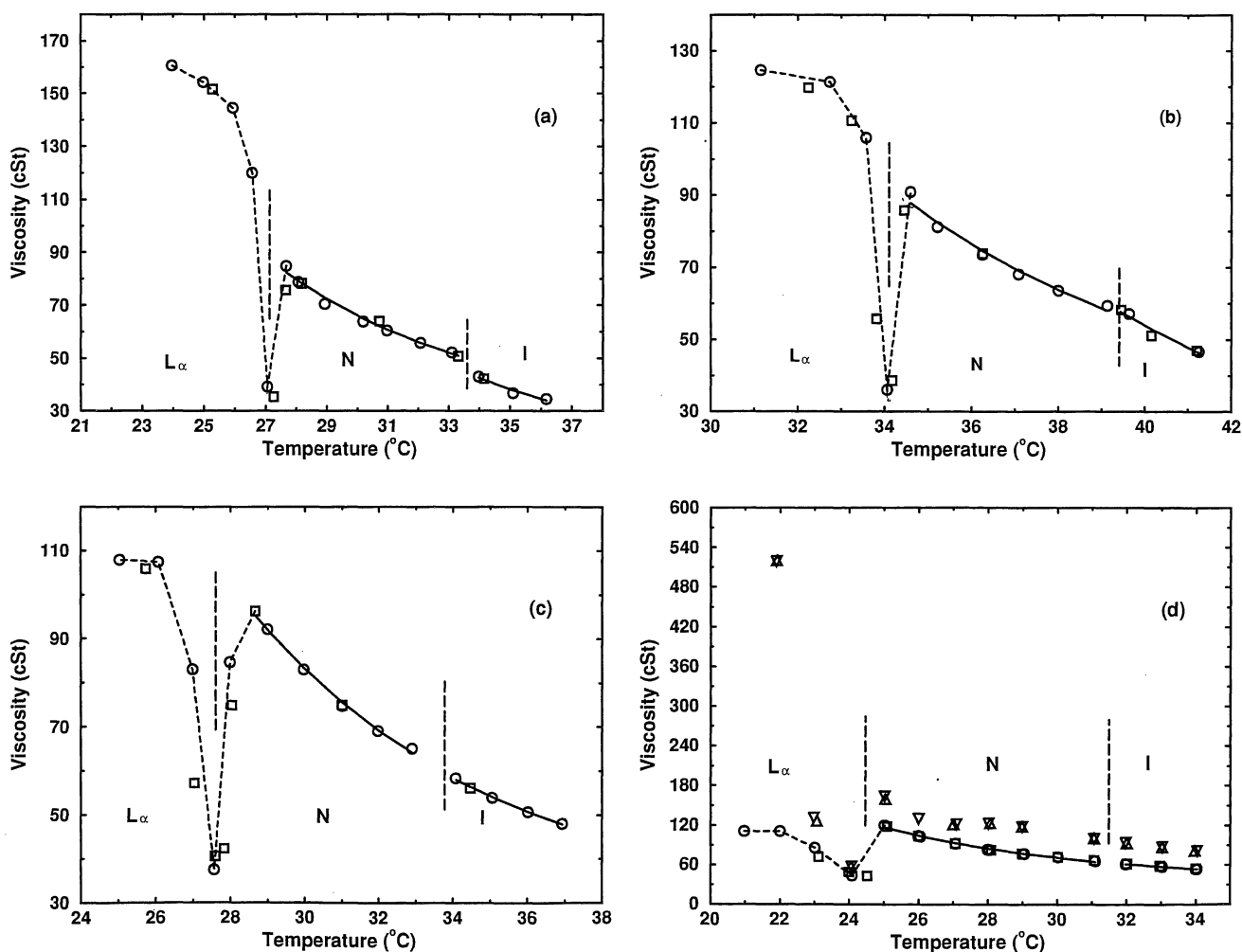


Fig. 2. Temperature dependence of the viscosity (a) for 50 wt% NH_4PFO , (b) for 49 wt% CsPFO, (c) for 45 wt% CsPFO, d) for 43 wt% CsPFO concentration in water (○: cooling data; □ heating data), and for 43 wt% CsPFO solution in water containing 0.1 wt% PEO ($M_w = 300,000$) (△: cooling data; ▽: heating data).

Table I. The calculated η_0 and activation energies in the isotropic and nematic phases for the samples S1, S2, S3 and S4.

	η_{0I} (cSt)	E_I (cal/mol)	η_{0N} (cSt)	E_N (cal/mol)
S1	6.8	139.9±1.6	6.8	150.2±6.4
S2	4.8	169.0±5.3	4.4	174.6±5.1
S3	0.4	390.6±42.8	2.5	245.1±15.7
S4	1.1	249.4±34.4	4.8	156.5±5.8

concentration in water as shown in Fig. 1(a), the absolute value of the viscosity in the L_α phase is much higher than that of the N phase and increases rapidly up to 160.1 cSt at 24°C (the efflux time is 321 s, compared with 71 s at the N/ L_α phase transition temperature (27.4°C)). The calculated η_0 in the I and N regions is clearly different, with higher E in the I phase than that in the N phase (see Table I). For a 49 wt% CsPFO concentration in water as shown in Fig. 1(b), a trend similar to that observed for the that of the S4 except that the increase in viscosity is relatively small in L_α . For a 45 wt% CsPFO concentration in water as shown in Fig. 1(c), the pretransitional range at the N/ L_α transition becomes wider than that of the S3 and the viscosity in the L_α phase becomes almost independent of the temperature. The absolute value of the viscosity in L_α phase is slightly higher than that of the maximum at the N phase. The calculated η_0 values in the N and I range are equal and the E in the N phase is slightly higher than that in the I phase. For a 43 wt% CsPFO concentration in water as shown in Fig. 1(d), the temperature dependence of the viscosity follows the Arrhenius viscosity pattern from the I to before the N/ L_α phase transition as indicated by the same η_0 values and by the absolute magnitude of the viscosity in the L_α phase which is about same as that of the maximum in the N phase. Replacement of the water by 0.1 wt% PEO caused the absolute value of the viscosity to increase over all temperature ranges but the collapse is still observed at the N/ L_α phase transition. Interestingly, the viscosity increases significantly at about 2°C below the N/ L_α transition temperature. The molecular weight of PEO is 300,000 i.e., the molecular motion of the polymer is much slower than that of water and surfactant. As a result, a small addition of PEO causes the viscosity to increase in all temperature ranges. Previous study⁴⁾ predicts that the PEO exists between the lamellar layers in the L_α phase, which is the water region between the polar heads. Therefore water-soluble PEO hinders translational motion of water molecules, resulting in high viscosity in lamellar phase. All experimental data agree well under conditions of both cooling and heating. Another viscometer which covers a different range of the viscosity was used to test whether the

observed data are affected by viscometer size. Results show exactly the same trends in viscosity but slightly different absolute values.

From these data one can infer that the spontaneous fluctuations of the positions of the lamellar layers decrease with increasing surfactant concentration, and in addition, are rapidly suppressed with an addition of a small amount of polymer. It is interesting that activation energy is higher in the N phase than that in the I phase at 43wt% of the surfactant concentration. This phenomenon is also observed for the side-chain liquid crystal polymer containing 30% mesogenic side chains in which the nematic phase ranges around 7°C.⁹⁾ Higher activation energy means that the viscosity is more sensitive to temperature changes in a given phase. A decrease in the concentration of surfactants or mesogenic units results in weak interactions between mesogenic units which makes the system more sensitive to temperature changes.

3. Conclusion

In summary, we have observed that the viscosity collapses at the N/ L_α phase transition temperatures are consistent with optical microscopic studies. Viscosity collapses at the N/ L_α phase transition might be due to the coexistence of the nematic and lamellar phases in weak interaction with each other. The degree of the decrease in viscosity on heating the lamellar phase increases with increasing surfactant concentrations and with a small wt% replacement of polymer in the water. A higher activation energy in the nematic phase than in the I phase with a decreased concentration of surfactant is observed. Unexpected observed phenomena at the N/ L_α phase transition require further investigation.

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