

Liquid Crystals



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Experimental studies on the phase diagram and physical properties of mixture of calamitic and discotic nematic liquid crystals

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ABSTRACT

Physical studies on mixture of calamitic and discotic nematic liquid crystals are meagre although they are potential for optimising physical properties. Here, we report experimental studies on the phase diagram and physical properties of mixtures of ambient temperature discotic and calamitic nematic liquid crystals. A substantial decrease in several physical properties such as birefringence, dielectric anisotropy and elastic constants are observed with increasing wt% of discotic compound. On the other hand a large increase in the rotational viscosity is observed. Based on the experimental results a simple model of mutual orientation of the rod-like and disc-like molecules is proposed.



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1. Introduction

Liquid crystals (LCs) used in display devices are mostly the calamitic nematic, which are composed of rodshaped molecules. For a desired electro-optic response, the physical properties are required to be optimised, and that is usually achieved in the mixture of several single component liquid crystals. Here we concentrate on the studies of mixture of a calamitic and a discotic liquid crystals, which are interesting from several aspects. First, they have the opposite sign of the birefringence and dielectric anisotropy, which makes it possible to tune the electro-optic response and elasticity. Second, there may be a region of immiscibility of rod-like and disk-like nematics, resulting in a liquid dispersion of one phase in another. This should result in a dispersion of microdroplets of one liquid crystal phase in another liquid crystal phase, which could be of great interest for applications in topological micro-photonics [1] and for the fundamental studies of topology in liquid crystals. In such a liquid crystalliquid crystal dispersion, individual nematic droplets might function as tunable optical microcavities [2,3] and microlasers [4], which could be elastically bound by topological defects [5,6] of the other nematic carrier fluid (continuous phase). Third, immiscible liquid crystalline phases could provide a novel testbed for studying topological defects in both phases, as well as their interrelation across the interfaces. Understanding and tailoring of mixtures of rod-like and disc-like nematic materials is therefore not only of high interest, but could also lead to new research directions.

There are a very few reports on the phase diagram and physical properties of mixture of calamitic and discotic nematic liquid crystals. For example, Pratibha et al. experimentally studied the phase diagram and defect structure in the binary mixture of a calamitic and a discotic nematic LCs [7,8]. Apreutesei et al. experimentally showed a complete miscibility of disclike and rod-like compounds [9]. Andrzej et al. theoretically studied the elastic constants in the binary mixture and reported a discontinuous change of elastic anisotropy from disc-like to rod-like properties [10]. A possibility of getting biaxial nematic and smectic phases in such binary systems was discussed by G J Vroege [11]. Recently, Parthasarathi et al. measured several physical properties of binary mixtures of a calamitic and a columnar discotic liquid crystals [12]. They also observed an anchoring transition driven by short-range ordering in the calamitic-discotic composites. In the above mentioned reports (experimental), the compounds studied exhibit nematic phase above the ambient temperature. To the best of our knowledge, there are no reports on the phase behaviour and physical studies on the mixture of ambient temperature discotic and calamitic nematic LCs. In this paper, we report experimental studies on the phase diagram, and physical properties such as birefringence (Δn) , dielectric anisotropy ($\Delta \epsilon$), curvature elastic constants $(K_{11} \& K_{33})$ and rotational viscosity (γ_1) of the mixture of a calamitic and a room temperature discotic nematic liquid crystals.

2. Experimental

The experimental cells were made of two indium-tinoxide (ITO)-coated glass plates with circularly patterned electrodes. These plates were spin coated with polymide AL-1254 and cured at 180°C for 1 hour and rubbed antiparallel way for homogeneous alignment of the sample. Cells were made by placing two plates together such that the active electrode area overlaps. The cell gap was controlled by glass-bead spacers of average diameter of 8 μ m. The thickness of the empty cell was measured within ± 1% accuracy by an interferometric technique using a spectrometer (Ocean Optics, HR-4000). The empty cell was heated and filled with the sample in the isotropic phase. The phase transition of the samples was observed using a

polarising optical microscope (OLYMPUS BX51) and a temperature controller (Instec, mK 1000). The temperature-dependent birefringence of a planar cell was measured by using a phase modulation technique [13] with the help of a Helium-Neon laser, a photoelastic modulator (PEM-100) and a lock-in amplifier. The perpendicular component of the static dielectric constant (ϵ_{\perp}) was measured in a planar cell and the parallel component of the dielectric constant (ϵ_{\parallel}) was measured by applying a sinusoidal voltage with a frequency of 10 kHz from 0.02 to 20 V in steps of 0.02 V using a LCR meter (Agilent E4980A). The linear part of the dielectric constant is plotted against 1/V and extrapolated to 0 (1/V = 0) to obtain ϵ_{\parallel} at various temperatures. The splay elastic constant (K_{11}) was measured directly from the Freedericksz threshold voltage (V_{th}) of the voltage dependent retardation data using the relation, $K_{11} = \epsilon_0 \Delta \epsilon (V_{th}/\pi)^2$, where $\Delta \epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$, is the dielectric anisotropy. The bend elastic constant (K_{33}) was obtained from the fitting of voltage dependent optical retardation with theoretical variation [14–17]. The rotational viscosity (y_1) was measured in a planar cell by a phase-decay-time measurement technique [18,19].

3. Results and discussion

The sample E-18 (a room temperature calamitic nematic mixture) exhibits the following phase transitions: Cr. 10° C N 60°C I. The discotic nematic was synthesised in our laboratory (Figure 1(a)) and it has the following phase transitions: N 83°C I. It also exhibits a glass transition much below the room temperature [20,21]. We prepared three different mixtures with increasing concentration of discotic compound, namely; E-18+disc(2.5 wt%), E-18 +disc(5 wt%), E-18+disc(7.5 wt%). Physical appearance of the mixtures is shown in Figure 1(b) and the phase diagram is shown in Figure 1(c). From turbid and white, it becomes brownish in colour with increasing wt% of discotic compound. In pure E-18, there exists an isotropic-nematic coexistence (I + N) range of approximately 3°C and this range increases with increasing wt% of discotic compound. In case of mixture with 7.5 wt% discotic compound, while cooling, the I + N coexistence range exists nearly up to 30°C. Below this temperature, it exhibits a monodomain (no coexistence) nematic sample. During heating, the coexistence reappears at 43°C. Thus, larger temperature range of monodomain nematic is obtained during heating. Hence we performed all the measurements while heating and the physical measurements in the I + N coexistence region are excluded.

The temperature variation of birefringence (Δn) of E-18 and various mixtures is shown in Figure 2(a). The



Figure 1. (colour online) (a) Chemical structure of the disc-like molecule. (b) Physical appearance of the samples with increasing wt % of the discotic compound in E-18. (c) Phase diagram of the mixtures along with a few representative photomicographs. The transition temperatures are measured while heating the samples from the room temperature.



Figure 2. (colour online) Variation of (a) birefringence (Δn) and (b) dielectric anisotropy ($\Delta \epsilon$) as a function of shifted temperature. Continuous lines are drawn as a guide to the eye. The shaded region indicates the nematic–isotropic (N + I) coexistence range. The downward arrows indicate the decrease of the respective quantities with increasing wt% of the discotic compound.

birefringence of E-18 is large and positive whereas in discotic nematic it is large but negative. For example, at room temperature, in E-18, $\Delta n \simeq 0.21$ and this is consistent with the previous measurement [22]. In pure discotic nematic, at room temperature, Δn is negative and large ($\simeq -0.2$) [23]. In the mixtures, Δn decreases with increasing wt% of discotic compound. For example, at a fixed temperature (e.g. $T - T_{NI} = -26^{\circ}$ C), Δn of the mixture (E-18 + 7.5 wt%) decreases by 13% compared to the pure E-18. This suggests that the mutual orientation of the rod and disc-like molecules is such that the polarisability anisotropies are antithetically related.

The variation of dielectric anisotropy ($\Delta \epsilon$) of various mixtures as a function of shifted temperature is shown

in Figure 2(b). In pure E-18, $\Delta\epsilon$ is positive and relatively large whereas in discotic nematic it is small and negative [23]. For example, at room temperature in E-18, $\Delta\epsilon =$ 13.5 and in pure discotic nematic, $\Delta\epsilon = -0.18$ [23]. It is observed that $\Delta\epsilon$ decreases with increasing wt% of discotic compound. For example, at a fixed temperature $(T - T_{NI} = -30.5^{\circ}\text{C})$, $\Delta\epsilon$ of the mixture, E-18 + 7.5 wt% decreases by 12% compared to the pure E-18. Though $\Delta\epsilon$ of pure discotic compound is very small and negative, it has a significant contribution in reducing the dielectric anisotropy of the mixtures.

The optical phase difference $(\Delta \phi)$ of the samples was measured as a function of applied voltage to measure splay (K_{11}) and bend elastic constants (K_{33}) simultaneously. The temperature variation of K_{11} and K_{33} is shown in Figure 3. K_{33} is always greater than K_{11} and both the elastic constants decrease with increasing wt% of discotic compound. At room temperature, $(T - T_{NI} = -30^{\circ}\text{C})$, K_{11} and K_{33} decreases by 25% and 30%, respectively. According to the mean-field theory, $K_{ii} \propto S^2 \propto \Delta n^2$. Since Δn decreases by about 13% (see Figure 2(a)), the decrease of the elastic constants is consistent with the prediction of the mean-field theory. However, it may be noted that the relative decrease of K_{33} is slightly larger (about 5%) than K_{11} . This is due to the fact, that in pure discotic nematic, the elastic anisotropy is negative i.e. K_{33} is less than K_{11} [23], and this is opposite to the behaviour observed in pure E-18.

We also measured the rotational viscosity (y_1) of the mixtures with temperature (see Figure 4). y_1 increases with increasing wt% of the discotic compound. For example, near the room temperature $(T - T_{NI} = -30^{\circ})$ C), γ_1 of the mixture, E-18 + 7.5 wt% is 73% larger than that of the pure E-18. The rotational viscosity is given by; $\gamma_1 = \tau_o K_{11} \pi^2 / d^2$, where *d* is the sample thickness and τ_0 is the relaxation time. In the mixtures, γ_1 increases significantly in spite of the decrease of K_{11} . So the increase of y_1 is mainly due to the increase of relaxation time of the system. This is expected as the relaxation time of the pure discotic nematic is very large [23]. The birefringence, dielectric anisotropy and the elastic properties clearly suggest that the plane of the disc molecules is parallel to the director as shown schematically in Figure 5.



Figure 3. (colour online) Variation of splay (K_{11}) and bend (K_{33}) elastic constants of the mixtures as a function of shifted temperature. Continuous lines are drawn as a guide to the eye. The downward arrows indicate the decrease of the respective quantities with increasing wt% of the discotic compound.



Figure 4. (colour online) Variation of rotational viscosity (γ_1) of the mixtures as a function of temperature. The upward arrow indicates the increase of γ_1 with increasing wt% of the discotic compound.



Figure 5. (colour online) Schematic representation of mutual orientation of rod-like and disc-like molecules in the nematic phase.

4. Conclusion

In conclusion, we have determined the phase diagram, and measured several physical properties such as birefringence, dielectric anisotropy, curvature elastic constants and the rotational viscosity of mixture of E-18 and a discotic nematic liquid crystals. We find rather broad temperature range of coexistence of the isotropic and nematic phases. The temperature range of nematic-isotropic coexistence increases with increasing wt% of discotic nematic compound. At room temperature, with a small (7.5 wt%) addition of discotic compound, the birefringence and dielectric anisotropy decreases by about 13%. The splay and bend elastic constants decrease by 25% and 30%, respectively. On the other hand rotational viscosity increases by about 73%. We have shown that the physical properties of the calamitic nematic liquid crystals can be changed significantly by adding a small amount of discotic nematic compound. This is therefore a very efficient method of tuning the electro-optic parameters of nematic mixtures. The experimental results suggest that the planes of the disc-like molecules are oriented parallel to the nematic director. Future studies should focus on the high concentration range of discotic component in the phase diagram (Figure 1), where a coexistence region of two immiscible nematic phases was observed in preliminary experiments above 10 wt% of discotic component.

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Disclosure statement

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