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Physical properties and intermolecular interactions of liquid crystalline materials

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ABSTRACT

Multi-component of 4-cyano-4'-heptyl biphenyl (7CB), 4'-n-octyloxy-4-cyanobiphenyl (8OCB) and Cholesteryl chloride (ChCl) exhibits cholesteric, twisted grain boundary (TGB) and re-entrant smectic-A (ReSmA) phases and these phases have been obtained sequentially when the specimen is cooled from its isotropic phase. Refractive indices, birefringence and optical transmittance have been measured by the optical technique. With the help of measured data, the macroscopic ordered parameter has been discussed. The temperature dependence of these parameters has also been discussed.

KEYWORDS

Optical anisotropy;
Phase transition;
Optical transmittance;
Temperature dependence;
Pitch.

INTRODUCTION

Liquid crystals are widely used in electro-optic display devices such as optical switches, light modulators, and image devices[1–4]. The use of liquid crystals in these devices depends on the kinds of mesophases exhibited by the liquid crystals, the transition temperature and optical anisotropies. The phenomenon associated with chiral liquid crystals has shown increasing importance with respect to both the crystals' fundamental scientific significance and their applicability to electro-optics and optoelectronics. The nature of chiral smectic phases that are exhibited in the mixture when there is a phase transition from cholesteric to smectic is clearly investigated. The existence of twisted grain boundary (TGB) and reentrant smectic-A phase in a binary mixture of liquid crystalline compounds[5-8] has been well investigated by earlier investigators.

In the present study, we have considered three compounds viz., (4-cyano-4'-heptyl biphenyl (7CB), 4'-n-octyloxy-4-cyanobiphenyl (8OCB) and Cholesteryl chloride (ChCl). The concentration of given mixture show Iso→Cho→TGB→SmA→SmC→ReSmA→SmB phases sequentially when they are cooled from its isotropic phase. Experimentally measured data of refractive index and its anisotropy have been discussed. The macroscopic order parameters have been evaluated by measured anisotropy of given mixture. Optical transmittance values have been measured with the variation of temperature in order to study the phase transition behavior of the system.

EXPERIMENTAL SECTION

In the present investigation, we have studied binary mixtures of liquid crystals, namely, Cholesteryl chloride (ChCl) and (4-cyano-4'-heptyl biphenyl (7CB), 4'-n-octyloxy-4-cyanobiphenyl (8OCB).

which are obtained from M/s Eastman Organic Chemicals, USA. The chemicals are purified twice with benzene. Concentrations of 32% ChCl in (7CB+8OCB) have been considered for the experimental studies and it was kept in desiccators for a long time. The samples were subjected to several cycles of heating, stirring and centrifuging to ensure homogeneity. The phase transition temperature of this concentration was measured with the help of Leitz-polarizing microscope in conjunction with hot stage. The samples were sandwiched between the slide and cover slip and were sealed for microscopic observations. Refractive indices values have been measured with the help of Abbe's Refractometer (MITTAL 1245) whereas optical transmittance measurements have been done on polarizing microscope (CENSICO 7626). The constant temperature has been maintained by microprocessor based temperature controller Julabo F-25 (Germany) in all studies. The X-ray broadening peaks were obtained at different temperatures using JEOL diffractometer. Electrical-conductivity measurements of the mixture at different temperatures were carried out using digital LCR meter and a proportional temperature control unit[9].

THEORTICAL STUDIES

The relation-ship between the refractive indices, parallel ((n_{II}) and perpendicular $n_{\perp}$ to the directions of molecular axis. The macroscopic order parameter can be obtained by modifying the equations[10] as

$$n_{II} = \bar{n} + \frac{2}{3}\mathbf{Q}\,.\,\mathbf{\Delta n} \quad (1)$$

$$n_{\perp} = \bar{n} - \frac{1}{3}\mathbf{Q}\,.\,\mathbf{\Delta n} \quad (2)$$

where $\bar{n}$ is the average refractive index and $\mathbf{\Delta n}$ is the birefringence corresponding to complete alignment $n_{II} = n_e$, $n_{\perp}$ =[11,12]. From both the equations (1) and (2), we get

$$\mathbf{Q} = \frac{n_{II} - n_{\perp}}{\Delta n} = \frac{n_e - n_o}{\Delta n} = \frac{\delta n}{\Delta n} \quad (3)$$

Where $\delta n = n_e - n_o$

The value of macroscopic order parameter equal to 1 represents complete order at absolute temperature that is at O K δn = $\mathbf{\Delta}n$. So the macroscopic order parameter (Q) has been obtained by extrapolating $\mathbf{\Delta}n$ for T = 0K. This extrapolation is done on the linear portion of the graph drawn between birefringence $\mathbf{\Delta}n$ against ln (1- T/T_C) as evaluated by others[10, 13], here T_C is the smectic to isotropic phase transition temperature.

RESULTS AND DISCUSSION

Optical texture studies

In the present study, optical textures exhibited by the samples were observed and recorded using Leitz polarizing microscope and constructed hot stage. The specimen was taken in the form of thin film and sandwiched between slide and cover glass. Concentrations of 32% ChCl in (7CB+8OCB) have been considered for the experimental studies. 32% of the given mixture slowly cooled from its isotropic melt, the genesis of nucleation starts in the form of small bubbles and slowly grow radially, which form a finger print pattern of cholesteric phase with large values of pitch[14, 15]. On further cooling the specimen, the cholesteric phase slowly changes over to mobile thread like filament texture, which is the characteristic of twisted grain boundary phase. The helical axes of twisted grain boundary phase lies in a direction parallel to the smectic layer planes[16, 17]. On further cooling, the twisted grain boundary phase of filamentary texture slowly changes over to focal conic fan-shaped texture of smectic-A phase and then this phase changes over to schlieren texture of smectic-C. On further cooling the specimen, unstable schlieren texture of smectic-C phase slowly changes over well defined focal conic fan texture of re-entrant smectic-A phase. In this system the microscopic observations clearly indicate that the given mixture exhibits a very interesting reentrant smectic-A phase[18]. The lowest temperature mesophase of some certain compounds exhibits two or more mesophases of the same type, over different temperature ranges. Re-entrant mesophases are most commonly observed when the molecules have strong longitudinal dipole moments. The sequences of reentrant mesophases have also been found in binary mixtures of non-polar liquid crystalline compounds[19]. In the given mixture, some of middle concentrations of ChCl in (7CB+8OCB) at lower temperatures did not show the molecular aggregates in preferred direction of alignment towards the crystalline phase, but it randomly oriented to form a re-entrant smectic-A phase and then this phase changes over to the crystalline smectic-B phase, which remains stable at room temperature .

Optical anisotropy

Temperature variations of refractive indices and optical birefringence studies for the sample 32% of ChCl in (7CB+8OCB) is presented in Figure 1 and 2. From the figure, it can observe that the value of ordinary refractive index increases where as the extraordinary refractive index decreases. Then the value of ordinary refractive index as well as extraordinary approaches sharply to isotropic refractive index and becomes same at smectic - isotropic transition after that the refractive index decreases almost linearly with the temperature like any liquid for given binary mixture. Optical birefringence value decreases slowly with increase in temperature and then its value decreases sharply with increase in temperature and becomes zero at smectic - isotropic transition for the mixture.

The temperature variation of macroscopic order parameter (Q) is presented in Figure 3. The value of order parameter shows degree of orderness of

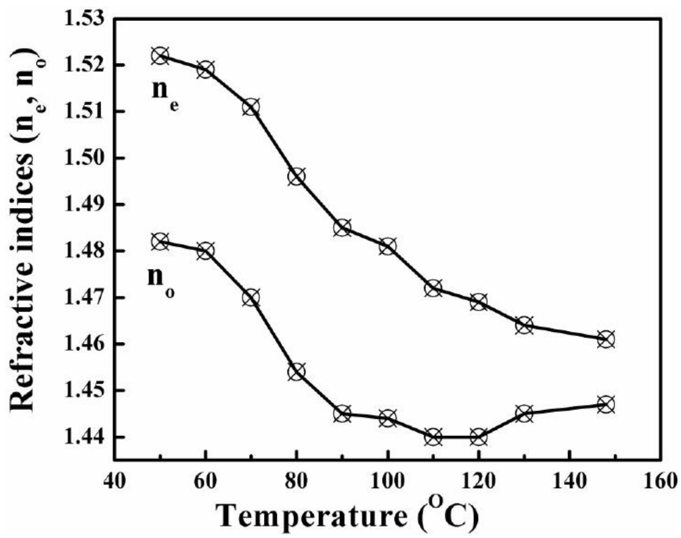

Figure 1 : Temperature variations of refractive indices for the given sample

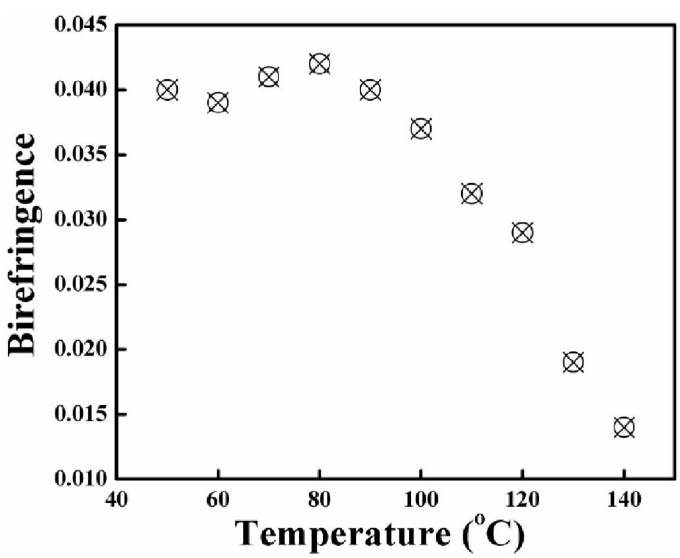

Figure 2 : Temperature variations of optical birefringence for the given sample

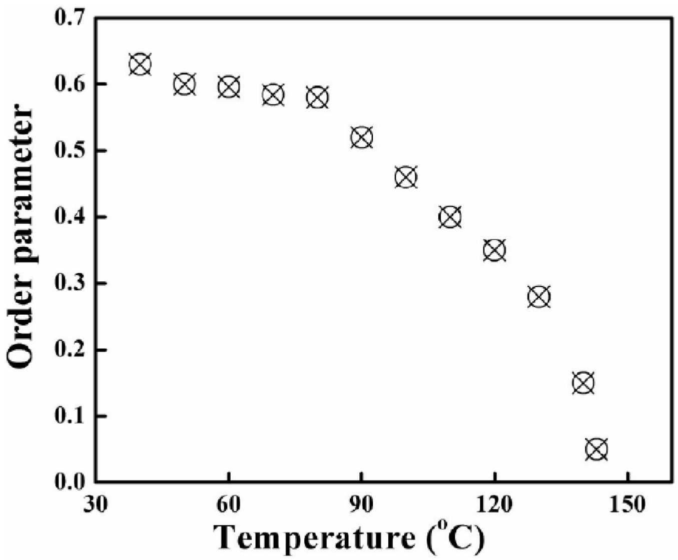

Figure 3 : Temperature variation of macroscopic order parameter (Q) for the given sample

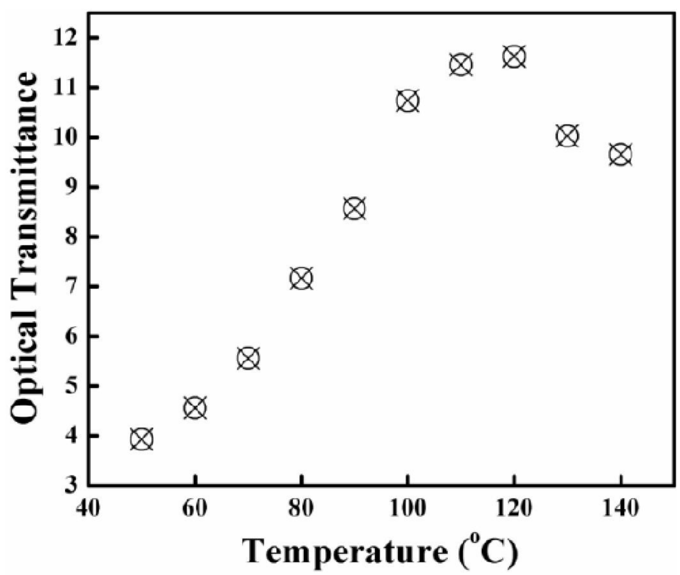

Figure 4 : Temperature variation of optical transmittance for the given sample

the molecule. Therefore, the decrease in value of order parameter indicates the increase in randomness of molecules finally at smectic - isotropic transition. The order parameter value reaches to zero shows highest degree of randomness i.e. the isotropic behaviour of sample, but some of lyotropic materials shows the order parameter becomes high at all temperatures and at different concentrations[20].

Optical transmittance

The temperature variation of optical transmittance as shown in Figure 4, which clearly illustrates that, the lower value of optical transmittance is almost constant in isotropic phase till 120 ^{0}C, and then its value increases abruptly by lowering temperature and hence it indicates the isotropic–smectic phase transition. The higher value of optical transmittance is almost unaffected with decreasing temperature up to 50 ^{0}C and after that its value decreases sharply which shows smectic-isotropic phase transition[21].

X-Ray studies

To understand the change in layer spacings in smectic-A and smectic-C phases with respect to temperature, X-ray diffractometer traces were taken. The traces obtained for the mixture of 32% ChCl in (7CB+8OCB) at different temperature corresponds

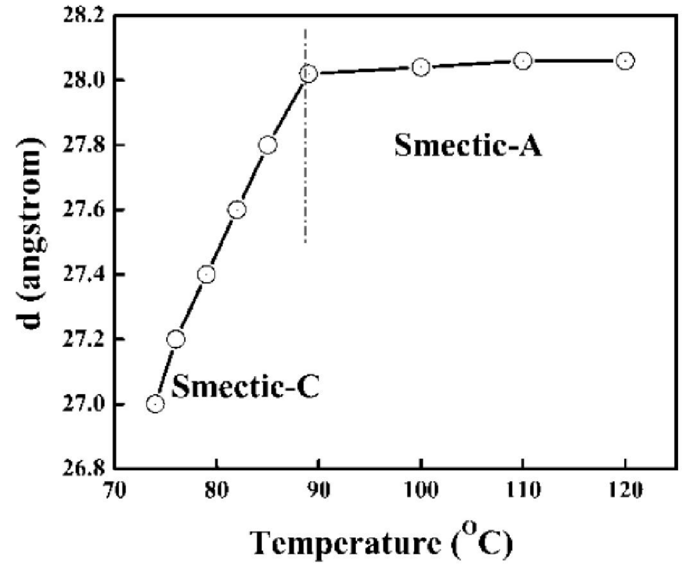

Figure 5 : Variation of layer spacings with temperature for the given sample

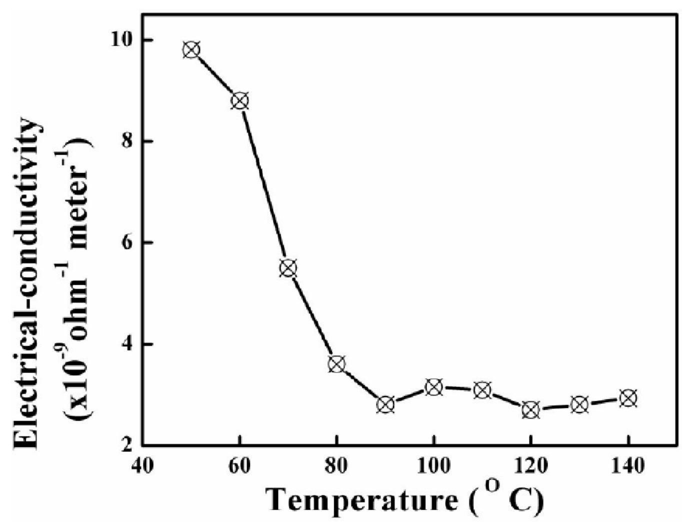

Figure 6 : Temperature variation of electrical-conductivity σ (x10^{-9} &!$^{-1}$ m^{-1}) for the given sample

to smectic-A and smectic-C phases. It is observed that as the temperature increases the layer spacing also increases in smectic-C phase, but in smectic-A phase the layer spacing is almost constant and this variation as shown in Figure 5[22–24].

Conductivity measurements

Electrical-conductivity measurements are helpful in the study of phase behavior with temperature. An abrupt increase or decrease of electrical-conductivity with temperature relates to the phase behavior of lyotropic, thermotropic and also chromonic systems[25]. The temperature variations of electrical-conductivity are as shown in Figure 6. The figure clearly illustrates that there is change in the value of electrical conductivity from 46 ^{0}C to 144 ^{0}C, while cooling from isotropic phase for the mixture of 32% ChCl in (7CB+8OCB). With further decrease in temperature, the electrical conductivity starts decreasing as we move towards the room temperature. The variation of electrical conductivity in the mixture of 32% ChCl in (7CB+8OCB) which shows the phase changes from Cho$\rightarrow$TGB, TGB$\rightarrow$SmA, SmA$\rightarrow$SmC,SmC$\rightarrow$ReSmA and ReSmA$\rightarrow$SmB phases, suggests that, the size of aggregates starts growing towards decreasing temperature and the system moves towards more orderliness. Finally, below 46 ^{0}C size of aggregates becomes so large that the specimen starts moving towards crystalline nature[26, 27].

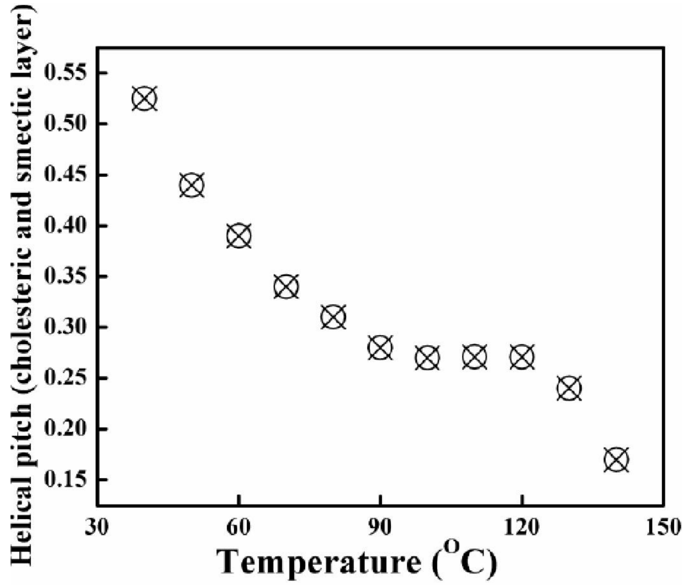

Figure 7 : Temperature variations of pitch for the mixture of 32% (7CB+8OCB) in ChCl

Helical pitch measurements

The helical pitch measurements were performed on the cholesteric phase after the well known Grandjean–Cano wedge method[28, 29]. The mixture was taken in a wedge-shaped cell treated for homogeneous alignment. The two glass plates formed a small angle at the wedge. The mixture was cooled slowly (0.2 ^{0}C min^{-1}) from the isotropic phase to the smectic phase, which induced an array of equidistant Grandjean–Cano lines. Pitch of the cholesteric phase was determined by measuring a distance between the Grandjean-Cano lines as a function of temperature. As the temperature was lowered from the cholesteric phase to smectic phase, the spacing between the lines increased, indicating that the pitch in this phase was increasing. The temperature variation of pitch for the mixture of 32% ChCl in (7CB+8OCB) is shown in Figure 7. From this figure, it is evident that, the variation of pitch from the cholesteric phase to smectic phase is smooth and continuous. The value of pitch gradually increases from 0.17 mm to 0.19 mm while cooling the sample from cholesteric phase towards TGB phase. The value of pitch increases and reaches a maximum value 0.28 mm at the TGB phase to SmA phase transition with a constant value in SmA phase and then steeply increases upto 0.52 mm as it moves towards crystalline phase at room[30].

CONCLUSIONS

The multi-component system of 32% ChCl in (7CB+8OCB) exhibits an unusual sequence of phases showing the formation of Cho, TGB, SmA, SmC, ReSmA and SmB phases when the specimen is cooled from its isotropic phase. The measured and calculated values of Refractive indices, birefringence, optical transmittance and macroscopic ordered parameter are decreases sharply with increases in temperature and become zero at smectic - isotropic transition.

The drastic changes in the value of electrical conductivity with the variation of temperature unambiguously correspond to Cho, TGB, SmA, SmC, ReSmA and SmB phases. The values of pitch increase steeply and reach 0.52 mm as it moves towards crystalline phase at room temperature.

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