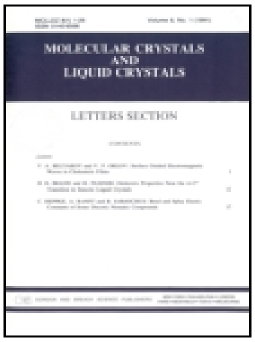

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Phase transition and thermal stability of reentrant smectic phase in mixture of liquid crystalline materials

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ABSTRACT
In the present work, our investigation is to study the optical and thermal properties of the binary mixture of cholesteric and nematic compounds namely, decyloxy benzoic acid (DBA), and cholesteryl chloride (ChCl), which exhibits different liquid crystalline phases with reentrant smectic-A phase. The reentrant smectic-A phase has been observed at different concentrations and at different temperatures. The existence of reentrant smectic-A phase has been observed by optical microscopic studies. The temperature variation of optical anisotropy, X-ray and helical pitch of the cholesteric (N*) phase has also been discussed.

KEYWORDS
Molecular orientation; phase transition; pitch; reentrant smectic phase

Introduction

The liquid crystalline phase of matter is one, in which the molecules retain some orientational order as they diffuse about in the typical fashion of liquids. For any pure substance, the transition from one phase to another occurs at a specific temperature, meaning that each phase possesses a range of temperature for which it is stable. The direction along which the molecules of a liquid crystal prefer to orient is called the director and is usually denoted by the unit vector. A liquid is isotropic, meaning that all properties of the liquid have the same value regardless of direction. Clearly liquid crystals are not isotropic, or in short, are anisotropic, meaning that the value of a parameter may depend on direction. The director breaks the material's isotropic symmetry and gives rise to properties such as optical birefringence, dielectric anisotropy, diamagnetic anisotropy, and orientational elasticity. The coupling of order and fluidity makes liquid crystals particularly intriguing materials because their orientation-dependent properties can be influenced by readily accessible fields [1–3].

In the present study, we have considered the mixture of two compounds viz., decyloxy benzoic acid (DBA) and cholesteryl chloride (ChCl). Different liquid crystalline phases such as cholesteric (N*), SmA, SmC*, ReSmA, SmC, and SmB phases were observed using microscopic technique and they have been verified from the results of X-ray and optical anisotropic techniques.

Experimental studies

In the present investigation, we have studied binary mixtures of liquid crystals, namely, decyloxy benzoic acid (DBA) and cholesteryl chloride (ChCl), which are obtained from M/s

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Eastman Organic Chemicals, USA. They were further purified twice by re-crystallization in benzene. The mixtures of different concentrations of DBA in ChCl were kept in desiccators for a long time. The samples were subjected to several cycles of heating, stirring and centrifuging to ensure homogeneity. The melting point of the purified sample is in good agreement with the reported value.

Polarizing microscopic studies

Polarizing microscopic technique is the most widely used method in identifying different phases. Liquid crystalline substance is placed between two glass cover slips. Depending on the boundary condition and the type of phase, various textures which are characteristics of a phase are observed. Usually the texture changes while going from one phase to another. Polarizing microscopy is a powerful tool when used in combination with miscibility of binary mixtures. Liquid crystalline phases possess characteristic textures when viewed under polarized light. These textures, which can often be used to identify phases, result from defects in the liquid crystals. Polarizing Microscopy is used for various phases like Nematic, Cho (N*), TGB and induced smectic phases such as SmA, SmB, SmC*, SmC, ReSmA, and SmE etc. As the liquid crystalline material goes from solid to liquid crystalline phase, the degree of order decreases. This is expressed by decrease in the value of order parameter. In case of orientational disorder it is possible to see changes between different liquid crystal phases during the heating and cooling cycles of liquid crystals.

Electrical conductivity measurements

The electrical conductivity measurements were carried out at different temperatures in the heating/cooling cycles, with the constant rate of scanning 2°C/min. The temperature was stabilized using a homemade thermoelectric cooler, based on Peltje elements and it was recorded by a Teflon-coated K-type thermocouple (±0.1°C) and it was connected to the data logger thermometer centre 309 (JDC Electronic SA, Switzerland). The un-oriented samples were used and the conductometric cell included two horizontal platinum electrodes of 14 mm in diameter, with 0.5 mm inter-electrode space. Before the measurements, the cell parts were washed in hexane and dried at 117°C. The electrical conductivity of the samples was measured by the inductance, capacitance, and resistance (LCR) meter 819 (Instek, 12 Hz–100 kHz). The measurements were done under the applied external voltage of 1 V and frequency of 500 Hz. This frequency was selected for avoidance of significant polarization effects on the electrodes.

Result and discussion

Phase diagram

The partial phase diagram is a very important method to determine the stability of liquid crystalline phase at different temperature. The partial phase diagram is as shown in Fig. 1 and is drawn by considering the phase transition temperatures against the concentrations of the given binary mixture of DBA in ChCl. Here, partial phase diagram shows very interesting cholesteric (N*), SmA, SmC*, ReSmA, SmC, and SmB phases, respectively, at different temperatures. The phase diagram clearly indicates that the mesomorphism of the mixture is thermodynamically stable for all concentrations of DBA. In the experimental studies, we have identified the different liquid crystalline phases on the basis of microscopic texture.

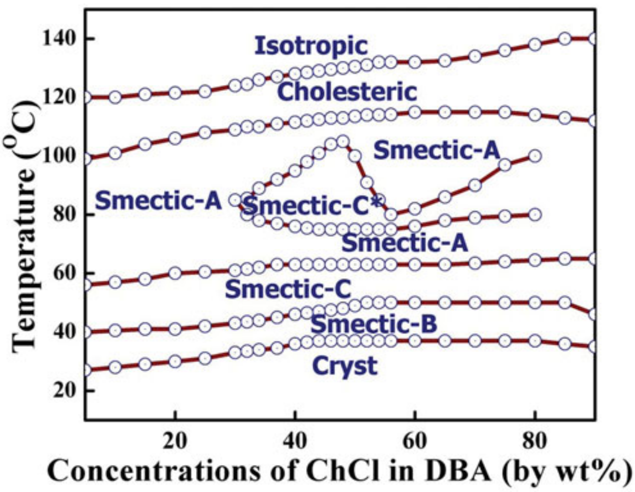
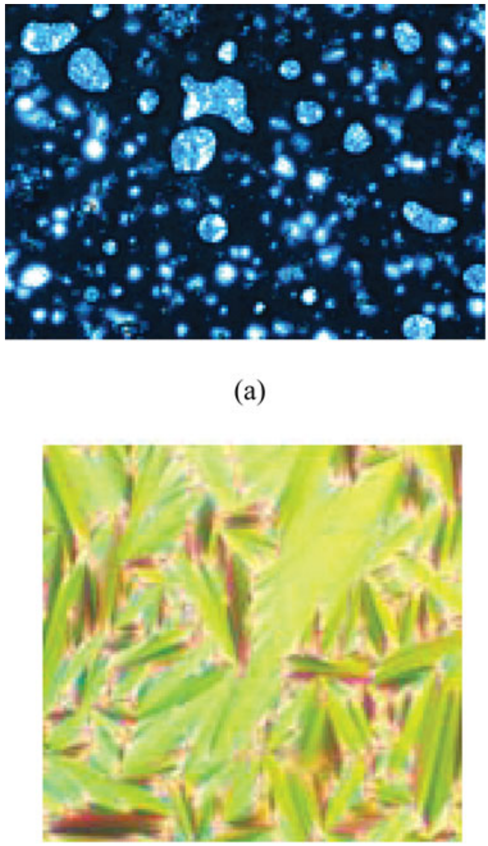


Figure 1. Partial phase diagram for the mixture of DBA in ChCl.

These observations clearly indicate that, the given mixture exhibits very interesting ReSmA phase [4]. The lowest temperature mesophase of some compounds exhibits two or more mesophases of the same type, over some different temperature ranges. Reentrant 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 [5]. In the given mixture, some of higher concentrations of DBA at lower temperatures did not show the aggregation of the molecules in preferred direction of alignment towards the crystalline phase, but it randomly oriented to form a reentrant smectic phase. The lower concentrations of DBA not show any of the reentrant phases, but the mixture with concentrations from 30% to 80% of DBA shows an ReSmA phase, respectively, at different temperatures. Mixtures with concentrations above 80% of DBA show only SmA, SmC, and SmB phase sequentially when they are cooled from isotropic to crystalline phase.

Optical texture studies

For the purpose of optical texture studies, the sample was sandwiched between a slide and a cover glass and then the optical textures were observed using a Leitz polarizing microscope in conjunction with a hot stage. When mixtures with concentrations in the range of 30% to 80% of DBA in ChCl are slowly cooled from their isotropic melt, nucleation starts in the form of a small bubble and slowly grows radially and forms a fingerprint pattern, which is characteristic of the cholesteric (N*) phase with large values of pitch [6, 7]. However, mixtures with concentrations from 20% to 45% exhibit a beautiful texture of cholesteric (N*) drops, as shown in Fig. 2(a) (Taken at 120°C). On further cooling, the cholesteric (N*) drops are slowly changed over to a well-defined focal conic fan-shaped texture, which is the characteristic of SmA phase and is shown in Fig. 2(b) (Taken at 105°C). The SmA phase is unstable and then changes over to the SmC* phase, which exhibits radial fringes on the fans of focal conic textures, which is characteristic of the chiral SmC* phase and then this phase is also not energetically stable, which changes over to ReSmA phase. On further cooling the specimen, this phase changes over to schlieren texture of SmC phase, sequentially this phase changes over to crystalline SmB phase, which remains stable till room temperature.



(a)

(b)

Figure 2. Microphotographs obtained in between the crossed polars, (a) Cholesteric drops (250X). (b) Focal conic fan-shaped texture of SmA phase (250×).

X-ray studies

To understand the change in layer spacings in SmA and SmC* phases with respect to temperature, X-ray diffractometer traces were taken. The traces obtained for the mixture of 42% DBA in ChCl at different temperatures correspond to SmA, SmC*, and ReSmA phases. It is observed that as the temperature increases the layer spacing also increases in SmC* phase. But in SmA and ReSmA phases, the layer spacing's are almost constant. These variations are as shown in Fig. 3 [8, 9].

Conductivity measurements

Electrical-conductivity measurements help in getting better idea on the phase behavior with temperature. An abrupt increase or decrease of electrical-conductivity with temperature relates to the phase behavior of the lyotropic and thermotropic systems [10]. The temperature variations of electrical conductivity are shown in Fig. 4, which clearly illustrates that there is some change in the value of electrical conductivity from 40°C to 120°C, while cooling from isotropic phase for the mixture of 42% DBA in ChCl. For the mixture of 42% DBA in ChCl, the sequence of phase changes from cholesteric (N*) to SmB phase. Here it has been

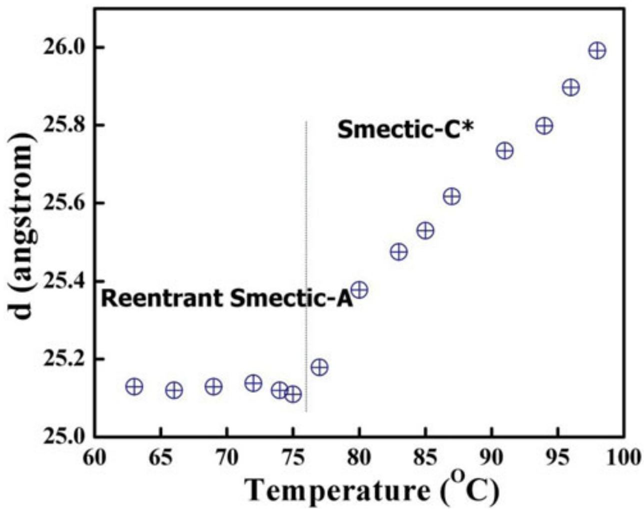


Figure 3. Variation of layer spacing with temperature for the sample of 42% DBA in ChCl.

found that the electrical conductivity goes on increasing as the temperature decreases. This suggests that aggregated molecular size start to grow towards lower temperatures and then the system becomes more ordered [11–16].

Helical pitch measurements in smectic and cholesteryl layers

The helical pitch measurements were performed on the cholesteric (N*) phase following the well-known Grandjean–Cano wedge method [17, 18]. The given 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°C min^{-1}) from isotropic cholesteric (N*) to smectic phase, which induces an array of equidistant Grandjean–Cano lines. The pitch of cholesteric (N*) phase was determined by measuring the distance between the Grandjean–Cano lines as a function of temperature. As the temperature was lowered the

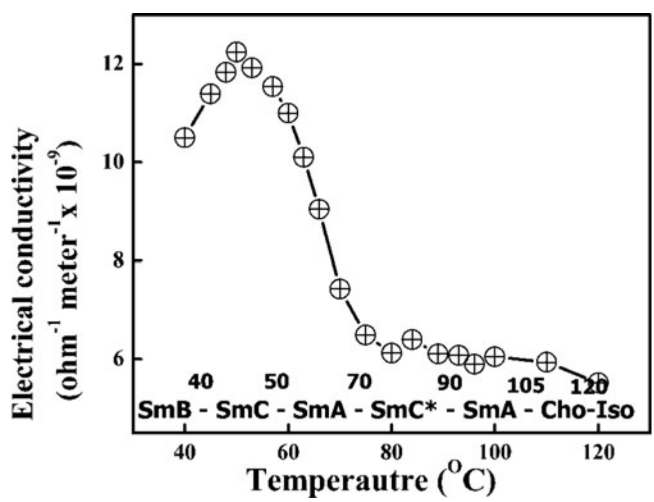


Figure 4. Temperature variation of electrical-conductivity σ (x 10^{-9} Ω^{-1} m^{-1}) for the sample 42% DBA in ChCl.

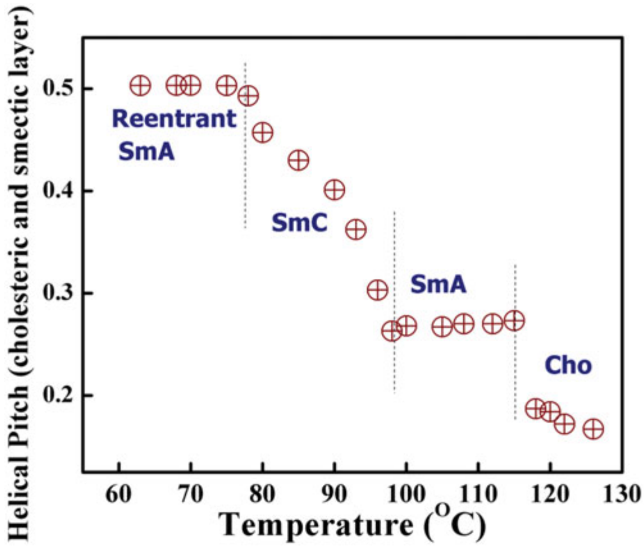


Figure 5. The temperature variations of pitch for the mixture of 42% DBA in ChCl.

mesophase changes from cholesteric (N*) to smectic phase, and the spacing between the lines are increased, indicating that the pitch in the cholesteric (N*) phase is also increasing. The temperature variation of pitch for the mixture of 42% DBA in ChCl is shown in Fig. 5. From this figure, it is evident that, the variation of pitch from cholesteric (N*) to smectic phase is smooth and continuous. But gradually, the value of pitch increases from 0.17 to 0.19 mm upon cooling the sample from cholesteric (N*) to smectic phase. The value of the pitch increases steeply and reaches a maximum of 0.52 mm at the cholesteric (N*) to smectic phase transition. In this study, we have noticed that, the sequence is Iso→(N*) →SmA→SmC*→ReSmA→SmC→SmB on cooling. Most of the data about the helical pitch are available in literature [19]. The pitch is continuous at the cho→smectic transition in spite of a rather energetic transition. It increases on cooling to smectic phase and diverges on approaching the SmA, SmC* and ReSmA phases. This divergence is related to the second-order nature of the transition. It exhibits a steep decrease, close to cholesteric (N*) phase which is usually the characteristics of second-order SmA, SmC*, and ReSmA phase transitions.

Conclusions

In light of the above results, we have drawn the following conclusions. The binary system of given mixture exhibits an unusual sequence of phases showing the formation of cholesteric (N*), SmA, SmC*, ReSmA, SmC, and SmB phases in different concentrations of DBA in ChCl. The phase behavior is discussed with the help of phase diagram. The X-ray results also lend support to the above observations. Changes in the values of electrical conductivity with temperature suggest that the size of aggregated molecules goes on increasing and the electrical conductivity is also increasing, while the mixture is cooled from the isotropic phase. The pitch of cholesteric (N*) phase is continuously increasing at the transition from cholesteric (N*) to smectic phase transition. But, it is very interesting to see that it increases on cooling to smectic phase, which evidently diverges on approaching the SmA, SmC*, and ReSmA phases, respectively, at different temperatures.

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