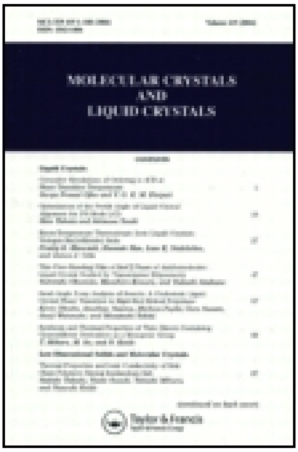

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Induced Chiral Smectic Phase in Mixtures of Mesogenic and Non-Mesogenic Compounds

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The mixture of cholesteryl chloride (CCl), cetyl pyridinium chloride, and ethylene glycol exhibits very interesting liquid crystalline mesophase cholesteric (N^*) and induced smectic phases, such as Sm A, Sm C^*, and Sm E, sequentially when the specimen is cooled from its isotropic liquid phase. These phases have been characterized by using differential scanning calorimetric (DSC), X-ray diffraction, nuclear magnetic resonance (NMR), infrared (IR), and optical texture studies.

Keywords Chiral smectic phase; NMR, IR, and XRD; optical texture studies; phase diagram

Introduction

Studies on physical properties of lyotropic liquid crystals are of importance because of their layered structure. Investigations of multi-component systems containing an amphiphile with water, cholesterol, ethylene glycol, and/or alcohol are of particular interest. Every component of such systems, with a degree of freedom, can modify not only the types and structures of the phases but also their various physical properties, such as electric susceptibility, dielectric constant, and optical anisotropy [1–6]. After adding certain additives into a binary mixture of amphiphilic compounds, a non-uniform distribution of their molecules takes place within the system, and therefore, these molecules can affect both short-range intramicellar interactions determining the micellar sizes and shape, and long-range intramicellar interactions determining the mutual orientation of micelles. It is well established that some of the mixtures of amphiphilic substances form nematic liquid crystal phases. The building block of those lyotropic mesophases have rod-like (sphero-cylindrical) or disk-like (lamellar) shapes. The molecules in aggregates (or building blocks) are called micelles, and the spontaneous aggregation of these micelles depends on the balance of hydrophilic–hydrophobic interactions between the molecules present in the solution [7–14].

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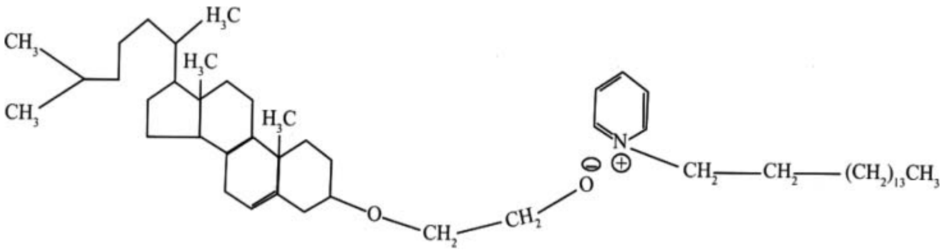

Figure 1. Sheet-like structure observed from the NMR spectra.

In the present study, the mixture of cholesteryl chloride (CCl) and cetyl pyridinium chloride + ethylene glycol (CpCl + EG) exhibits thermotropic and lyotropic liquid crystalline mesophase N* and induced smectic phases, such as Sm A, Sm C*, and Sm E, sequentially when the specimen is cooled from its isotropic liquid phase. These phases are characterized using differential scanning calorimetric (DSC), X-ray diffraction (XRD), nuclear magnetic resonance (NMR), infrared (IR), and optical texture studies. Here, cholesteryl chloride (CCl) serves as building blocks of the unit. In this unit, ethylene glycol (EG) and cetyl pyridinium chloride (CpCl) molecules are attached to the CCl molecule, which is as shown in Fig. 1. For the experimental investigation of the mixture (CCl in CpCl + EG), we have kept the concentration of CpCl at 40% in the binary mixture of CpCl + EG and the concentrations of CCl and EG have been varied.

Experimental Studies

The compound cetyl pyridinium chloride was obtained from M/s Lobo Chemicals, Mumbai, India. It was further purified twice by re-crystallization from benzene. Ethylene glycol was supplied by M/s Reechem Research Laboratories, Mumbai, and it was used directly without any further purification. The cholesteryl chloride was obtained from M/s East Mann Organic Chemicals, USA. The structural formulae for these compounds are shown in Figs 2(a)–(c). Mixtures of these three materials have been prepared with 30 different concentrations. The DSC and microscopic studies were carried out for the mixtures of all concentrations. The phase transition temperatures were compared with the values obtained from DSC at the Raman Research Institute, Bangalore, India. XRD patterns were taken using a Jeol X-ray diffractometer at various temperatures for different concentrations in order to study the smectic phases [15–17].

The ^{1}H-NMR spectroscopic studies were carried out using a Bruker 300-MHz NMR spectrometer at 299 K to understand the layer structure and intermolecular interaction. IR spectra were recorded using a Perkin–Elmer IR spectrometer. The density and refractive indices were determined at different temperatures by employing the techniques described earlier [18,19].

Results and Discussions

Phase Diagram

The partial phase diagram shown in Fig. 3 illustrates that mixtures with concentrations from 10% to 15% and 20% to 40% of CCl in (CpCl + EG) exhibit an N* phase and also induced smectic phases (Sm A, Sm C*, and Sm E phases) sequentially when the specimen is cooled

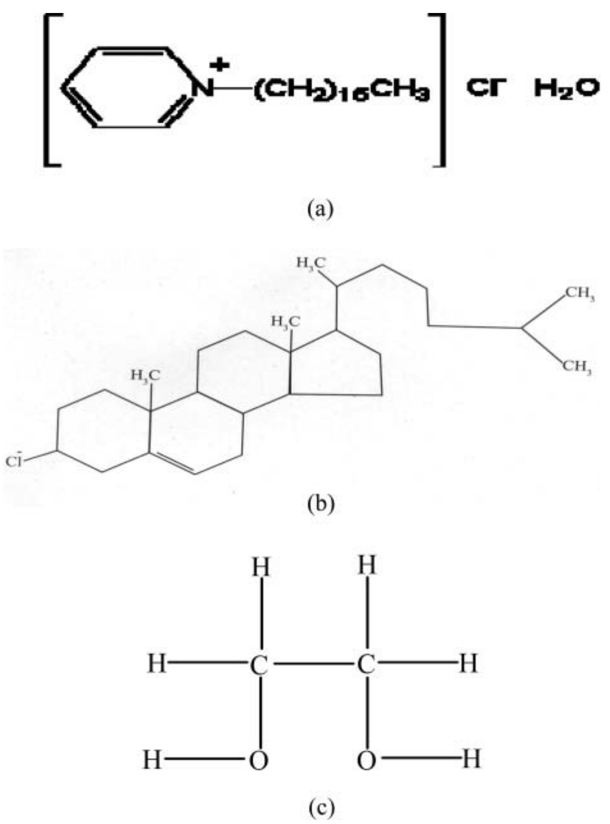

Figure 2. (a) Structural formula of the cetyl pyridinium chloride (CpCl) molecule. (b) Structural formula of the cholesteryl chloride (CCl) molecule. (c) Structural formula of the ethylene glycol (EG) molecule.

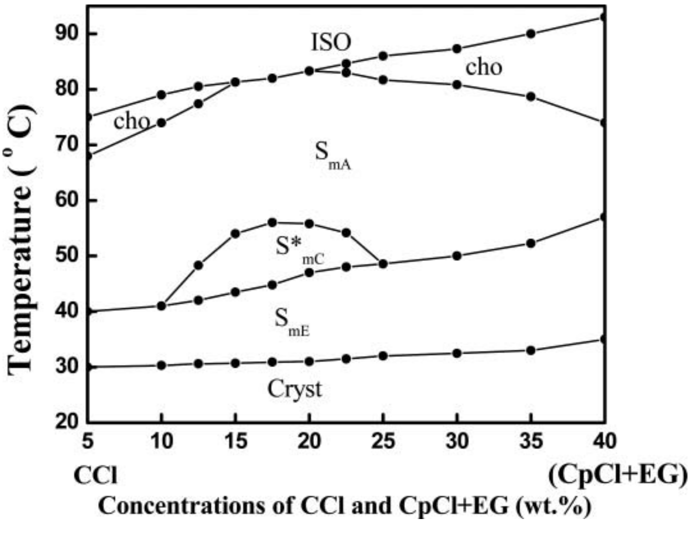

Figure 3. Partial phase diagram for the mixture of CCl and CpCl + EG.

Figure 4. Microphotographs showing (a) cholesteric (N*) drops (180X), (b) focal conic fan-shaped texture of Sm A phase (180X), and (c) chiral Sm C* phase (180X).

from its isotropic melt. The isotropic liquid-to-crystalline phase transition temperature increases on increasing the concentration of CCl. The mixture with 12.5% of CCl exhibits Iso – N* – Sm A – Sm C* – Sm E phases sequentially. Mixtures with concentrations from 15% to 20% of CCl do not exhibit a cholesteric (N*) phase but exhibit smectic phases only. The interesting feature of the phase diagram of the present mixture is that it exhibits an unusual sequence of phases and shows the presence of induced chiral smectic phase in the mixture with concentrations in the range of 10%–25% of CCl in the temperature range of 55°C–40°C.

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 specially constructed hot stage. When mixtures with concentrations in the range of 5%–15% 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 N* phase with large values of pitch [20, 21]. However, mixtures with concentrations from 20% to 40% exhibit a beautiful texture of cholesteric drops, as shown in Fig. 4(a). On further cooling, the cholesteric drops are slowly changed over to a well-defined focal conic fan-shaped texture, which is characteristic of the Sm A phase and is shown in Fig. 4(b). The Sm A phase is unstable and then changes over to the Sm C* phase, which exhibits radial fringes on the fans of focal conic textures, which is characteristic of the chiral Sm C* phase, as shown in Fig. 4(c). Further on, this phase changes over to the crystalline Sm E phase, which remains stable at room temperature.

X-Ray Studies

XRD patterns were taken for the mixture with concentration of 12.5% of CCl for the Sm A and chiral Sm C* phases at different temperatures. The temperatures were controlled by the special heaters provided in the diffractometer. It is observed that as the temperature increases, the layer spacing also increases in Sm C* [22–24]. However, the layer spacings are almost constant in the Sm A phase. The XRD patterns of the Sm C* phase which have been observed in the mixture at two different temperatures are shown in Figs. 5(a) and (b).

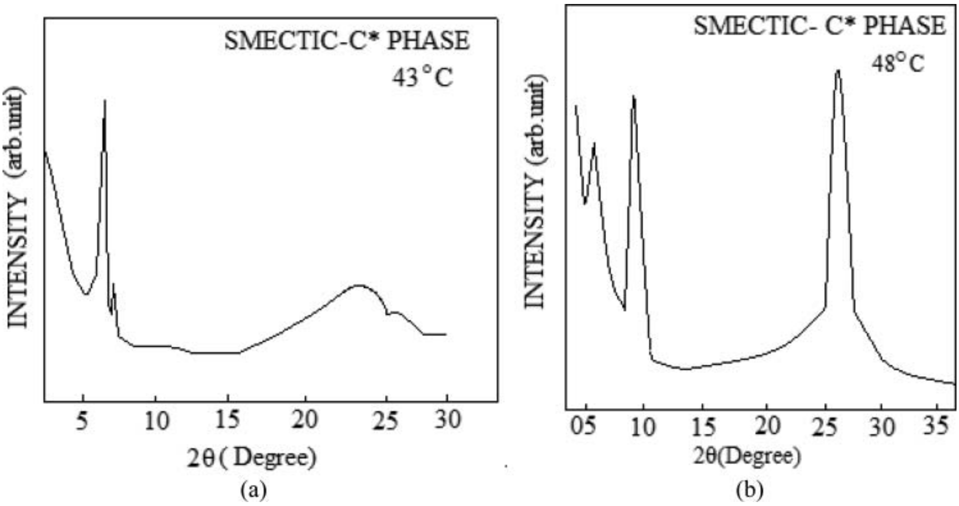

Figure 5. (a) XRD traces obtained for the mixture of 12.5% of CCl in (CpCl + EG) at 43°C. (b) XRD traces obtained for the mixture of 12.5% of CCl in (CpCl + EG) at 48°C.

^{1}H-NMR and IR Studies

The ^{1}H-NMR spectrum of 12.5% CCl in (CpCl + EG) mixture shows the absence of peak at $\delta = 2.7$ due to CCl and the presence of a new multiplet peak at $\delta = 3.80$, which is attributed to CHO—. This new peak may be due to the nucleophilic attack of glycol OH on CCl with the elimination of HCl. The absence of OH peak clearly indicates that the present multi-component system will arrange as shown in Fig. 1.

This was further confirmed by IR spectroscopy. The IR peak at 3450 cm^{-1} due to the presence of OH in EG is missing in the present mixture. This clearly shows that (CCl + CpCl) is associated with EG and helps to form the columnar and lamellar phases.

Conclusions

In light of the above results, we have drawn the following conclusions. The multi-component system of CCl, CpCl, and EG exhibits an unusual sequence of phases, showing the formation of an induced chiral smectic phase in the concentration range of 10%–25% of CCl in (CpCl + EG) in the temperature range of 55°C–40°C. The arrangement of molecules in the present mixture is in the form of a sheet-like structure. It has been confirmed from IR studies that the OH bond, which is present in one of the components, is missing in the mixture and its absence is resulting in the formation of the different phases observed in the present case.

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