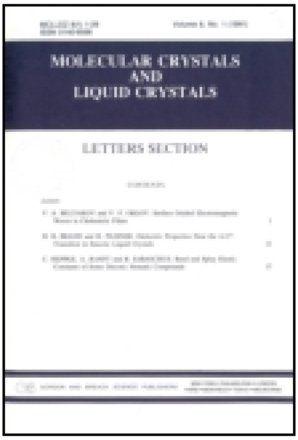

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Induced Reentrant Smectic-A Phase in Binary Mixtures of Liquid Crystals

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We report the results of our studies on the optical and thermal properties of the mixture of cholesteryl chloride (ChCl) and sodium dodecyl sulphate/water (SDS/water), which exhibits very interesting liquid crystalline mesophases, such as cholesteric (N_*) phase and induced reentrant smectic-A phase, sequentially when the specimen is cooled from its isotropic liquid phase. Different liquid crystalline phases observed in the mixture were studied using DSC, X-ray, and optical microscopic techniques. The pitch of the cholesteric phase and the temperature variation of optical anisotropy have also been discussed.

Keywords Binary mixture; cholesteric; molecular orientation; optical texture; optical anisotropy

Introduction

Liquid crystals are a special class of soft materials characterized by so called mesophases, where they flow like an isotropic liquid yet possess a long-range orientational order and a complete or partial absence of positional order of building units that can either be individual molecules or their aggregates [1]. The two main types of liquid crystals are thermotropic liquid crystals and lyotropic liquid crystals. Thermotropic liquid crystals show mesophases depending on temperature and pressure. Their basic building units are usually individual molecules that have a feature of pronounced shape anisotropy, such as rods, disk, etc. Thermotropic liquid crystals have been successfully used in display devices. Lyotropic liquid crystals are formed on the dissolution of lyotropic liquid crystal molecules in a solvent (usually water). A feature of lyotropic liquid crystals distinguishing them from thermotropic liquid crystals is the self-assembly of molecules into supermolecular structures that represent a basic unit of these mesophases [2,3]. The most common lyotropic liquid crystalline system is those formed by water and surfactants (amphiphiles), such as soaps, synthetic detergents, and lipids. Surfactant molecules are formed by a hydrophilic part

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chemically bound to a hydrophobic part. Mixtures of these surfactant molecules with a solvent under certain conditions of temperature and relative concentrations produced the different types of liquid crystalline mesophases such as cholesteric, nematic, lamellar, discotic, twisted grain boundary (TGB) phase, blue phase [2,3], etc.

In the present study, we have considered the mixture of two compounds viz., cholesteryl chloride (ChCl) and sodium dodecyl sulphate/water (SDS/water). The polymorphic smectic modifications of the different liquid crystalline phases were observed using microscopic technique and they have been verified from the results of DSC, X-ray, and optical anisotropic techniques.

Experimental Studies

The compounds SDS and ChCl used in this investigation were obtained from the Basic Pharma Life Science, Pvt. Ltd., India. They were further purified twice by recrystallization in benzene. The melting point of the purified sample is in good agreement with the reported value. The mixture of 20 different concentrations of ChCl (by wt%) in SDS/water were prepared and kept in desiccators for a long time. Phase transition temperatures of the mixture with different concentrations were measured using Leitz-polarizing microscope and conventional hot stage. The sample was sandwiched between the slide and cover slip, which was sealed for microscopic observation. The DSC thermograms were taken for different concentrations of the mixture using the Perkin-Elmer DSC II Instrument facility available at Raman Research Institute, Bangalore, India. The X-ray diffraction studies were undertaken by using JEOL-X-ray diffractometer. The density and refractive indices of the mixtures were measured at different temperatures employing the technique described in our earlier paper [4].

Phase Diagram

The partial phase diagram as shown in Fig. 1, which is drawn by considering the phase transition temperatures against the concentrations of the given mixture, clearly illustrates

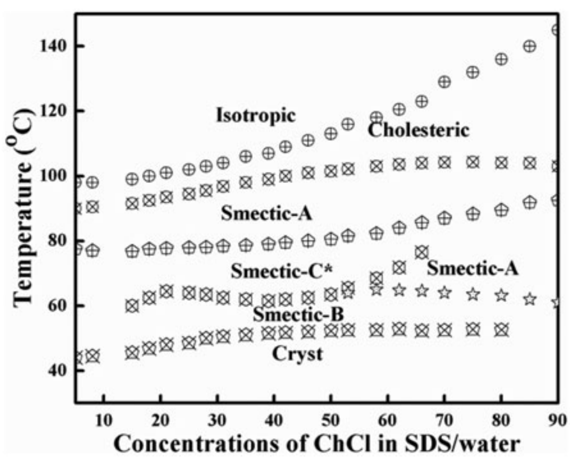

Figure 1. Partial phase diagram for the mixtures of ChCl in SDS/water.

the presence of ChCl in SDS/water. Here, partial phase diagram shows a very interesting cholesteric (N*), smectic-A, smectic-C*, smectic-A, and smectic-B phases, respectively, at different temperatures. The phase diagram clearly indicates that the mesomorphism of the mixture is thermodynamically stable for all concentrations of ChCl. In our experimental studies, the different liquid crystalline phases have been identified on the basis of microscopic texture. These observations clearly indicate that the given mixture exhibits a very interesting reentrant smectic-A phase [5]. The lowest temperature mesophase of some certain compounds exhibits two or more mesophases of the same type, over 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 nonpolar liquid crystalline compounds [6]. In the given mixture, some of higher concentrations of ChCl 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 reentrant smectic phase. The lower concentrations of ChCl did not show any of the reentrant phases, but the mixture with concentrations from 53% to 66% of ChCl showed a reentrant smectic-A phase, respectively, at different temperatures. Above 66% of ChCl showed only smectic-A phase sequentially while it 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 specially constructed hot stage. When mixtures with concentrations in the range of 5% to 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 cholesteric phase with large values of pitch [7, 8]. However, mixtures with concentrations from 20% to 40% exhibit a beautiful texture of cholesteric drops, as shown in Fig. 2(a). On further cooling, the cholesteric drops are slowly changed over to a well-defined focal conic fan-shaped texture, which is the characteristic of smectic-A phase and is shown in Fig. 2(b). The smectic-A phase is unstable and then changes over to the smectic-C* phase, which exhibits radial fringes on the fans of focal conic textures, which is characteristic of the chiral smectic-C* phase, as shown in Fig. 2(c). On further cooling, this phase changes over to the crystalline smectic-B phase, which remains stable at room temperature.

Study of Refractive Indices

Liquid crystals demonstrate a nonlinear response and are sensitive to their optical environments. Many of nonlinear mechanisms have revealed the promising character of these

Figure 2. (a) Microphotographs of cholesteric drops (185×). (b) Microphotographs of focal conic fan-shaped texture of smectic-A phase (180×). (c) Microphotographs of schlieren texture of chiral smectic-C* phase (180×).

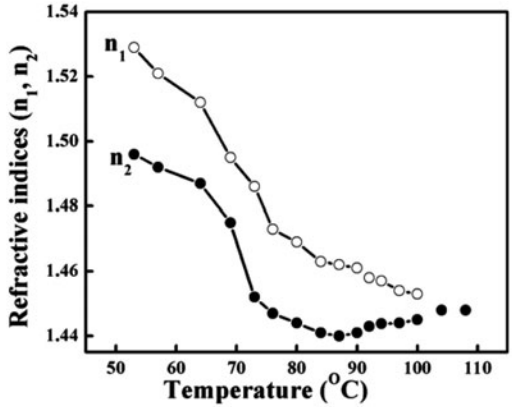

Figure 3. Temperature variation of refractive indices for the mixture of 42% ChCl in SDS/water.

materials. The difference in refractive indices measured along perpendicular to the director axis brings the property of birefringence from the visible to the infrared region. This property provides an opportunity for various potential applications [9]. Director axis reorientation-based effects causing a change of refractive index and observations of several interesting dynamic and storage wave-mixing effects have also been extensively studied [9–11].

The present investigations are further supported by the optical studies. The refractive indices for extraordinary ray (n_e) and ordinary ray (n_o) of the mixture were measured at different temperatures for the different concentrations using Abbe Refractometer and Precission Goniometer Spectrometer. The temperature variation of refractive indices for the mixture of 42% of ChCl in SDS/water is shown in Fig. 3. From this figure it has been found that the mixture with small amount of cholesteric material increases the required threshold of molecular orientation in the given mixture. This phenomenon demonstrates the potential application in areas such as holographic data storage. Birefringence property and its dependency on molecular orientation play an important role in understanding the molecular mechanism. Moreover, birefringence enhancement is of primary importance for the innovation of different electro-optic applications [12,13].

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 35% ChCl in SDS/water at different temperatures correspond 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 spacings are almost constant. These variations are shown in Fig. 4 [14,15].

Spiral Pitch and Helical Twisting Power

The cholesteric phase is regarded as twisted nematic phase, wherein the molecules are orientationally ordered, but at the same time they are rotationally disordered with respect to long axis [16]. It is well known that when a cholesteric compound is added as impurity to a SDS/water molecule, the pitch of the cholesteric phase increases in dilute limit of

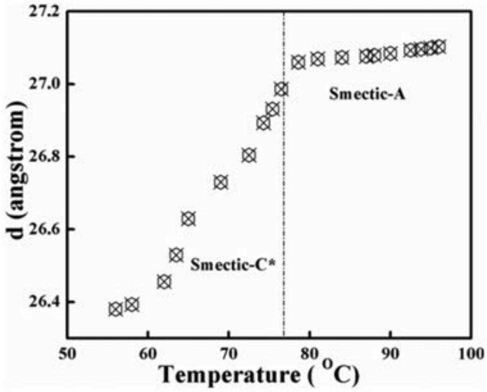

Figure 4. Variation of layer spacing with temperature for the sample of 35% of ChCl in SDS/water.

the mixture; indeed, if the pitch is sufficiently large it is possible to observe stripes under the Leitz-polarizing microscope. When the pitch is comparable to the wavelength of light, the phase becomes iridescent because of the selective reflection of light. The stripes are associated with the helicoidal structures, which clearly indicate that the mesophase is cholesteric. The mixtures with concentrations from 8% to 18% of the mixture exhibit a stripped pattern when they are cooled from isotropic phase at the respective temperatures, which corresponds to cholesteric phase. Microscopic twisting power β of the solute in the mixture of 5% to 15% of ChCl is calculated using the formula:

$$4\pi\beta C = \frac{2\pi}{P}$$

where, P is the pitch of the helix, C is the concentration of ChCl, and

$$\beta = \frac{1}{2PC}.$$

The pitch of the cholesteric phase against concentration is drawn and shown in Fig. 5, which illustrates that at low concentrations of the cholesteric compound, the pitch is

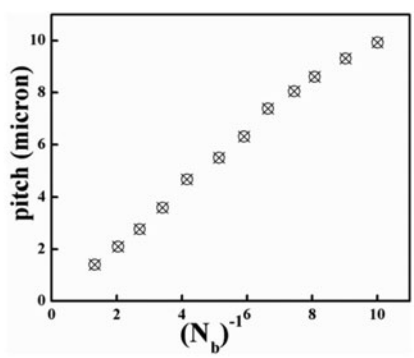

Figure 5. Variation of pitch of cholesteric phase with $(N_b)^{-1}$. Here N_b represents the number of molecules of ChCl per unit volume of the mixture.

inversely proportional to the concentrations of the cholesteric compound. The parameter β characterizes a helical twisting power value for the induced cholesteric phase. This result is in conformity with the rule for a small concentration of cholesteric compounds in SDS/water molecules.

Conclusions

The above studies, apart from revealing numerous textures associated with various phases in mixture, have enabled us to reach the following conclusions. Mixture with concentrations from 53% to 66% of ChCl in SDS/water exhibits a reentrant smectic-A phase at different temperatures. The phase behavior is discussed with the help of phase diagram. Variation of layer spacing with temperature has been studied. The pitch of the cholsteric phase has been also discussed. This type of polymorphism is rare in the binary mixture of liquid crystalline compounds.

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