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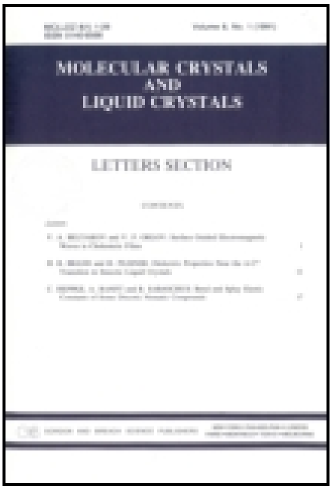

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Induced Thermotropic Smectic Phases in Binary/Ternary Mixture of Nonmesogenic Compounds

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We report the results of our studies on the optical and thermal properties of the mixture of Sodium Lauryl Sulfate (SLS) and Dodecyl trymethyl ammonium bromide + Ethylene glycol (DTAB + EG) exhibits very interesting induced thermotropic smectic phases such as smectic-A, smectic-D, smectic-B, and smectic-E phases, 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 temperature variation of optical anisotropy has also been discussed. Helfrich potential and elastic moduli have been estimated in the smectic phase using Helfrich model.

Keywords Binary mixture; Helfrich potential; molecular orientation; optical texture and optical anisotropy; phase diagram

Introduction

A material designated as a liquid crystal has a liquid crystal phase. This is a phase between solid and liquid which only appears in certain materials, also called mesogenic materials. The liquid crystalline phases can be subdivided by the amount of order they posses. This is possible because the molecules show a certain orientational order, while they show no or limited positional order in various degrees. Apart from the liquid crystal phase, there is a mesophase called plastic crystal phase or disorder crystal phase [1]. In such a phase, the molecules do have positional order but lack of orientational order. The name plastic crystal phase originates from the ease with which such materials can be deformed. One can also differentiate between two main types of liquid crystalline materials: the lyotropic and the more known thermotropic kinds. The lyotropic liquid crystals are often simply obtained by mixing rod or disk shaped molecules in an isotropic solvent [2]. Besides the temperature also, the concentration determines the stability of the mesophase. For thermotropic liquid crystals, the stability of the phase depends only on the temperature. Thermotropic liquid crystals are used in most cases of “technological” applications such as displays, temperature, and pressure sensors. On the other hand, lyotropic liquid crystals are responsible for countless “biological” processes. The liquid crystal phases are usually divided in nematic and smectic. The former term is used when only orientational order is

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*Address correspondence to Dr. T.N. Govindaiah, Asst. Professor, P.G. Department of Physics, Government College (Autonomous), Mandya-571401, India. E-mail: tngovi.phy@gmail.com present in the material. The latter is used when next to orientational order also positional order is a characteristic of the material. The smectic liquid crystals themselves then are further subdivided according to their degree of order.

In the present study, we have considered the mixture of nonmesogenic compounds viz., Sodium Lauryl Sulfate (SLS) and Dodecyl trymethyl ammonium bromide + ethylene glycol (DTAB + EG) shows different liquid crystalline phases over a wide of range temperature. The polymorphic smectic modifications of the liquid crystalline phases were observed using microscopic technique and they have been verified from the results of DSC, X-ray, and optical anisotropic techniques. Here, SLS serves as building blocks of the unit. In this unit, EG and Dodecyl trymethyl ammonium bromide molecules are attached to the SLS molecule. For the experimental investigation of the mixture (SLS in DTAB + EG), we have kept the concentration of DTAB at 50% in the mixture of DTAB + EG and the concentrations of SLS and EG have been varied. Helfrich potential and elastic modulii have been estimated in the lamellar smectic phases using Helfrich model with approximation.

Experimental Studies

The compound DTAB used in this investigation was 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. EG was supplied by M/s Reechem Research Laboratories, Mumbai, and it was used directly without any further purification. The SLS was supplied by M/s SISCO Research Laboratory, Mumbai, India. The EG was used after boiling it at 433K for 6 hours. The mixture at different concentrations of DTAB +EG (by wt%) in SLS were prepared and kept in a desiccators for a long time. Phase transition temperatures of the mixtures 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 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 [3–5]. The density and refractive indices were determined at different temperatures by employing the techniques described earlier [6,7].

Optical Studies

The induced polymorphic smectic modifications and the corresponding isotropic to liquid crystalline phase transition temperatures for the mixture with 40% of SLS in DTAB+EG are given below.

Iso-182 °C, Sm A-160 °C, Sm D-119.5 °C, Sm B-99.5 °C, Sm E-78 °C.

On cooling, the specimen from its isotropic melt, the setting point is marked by the genesis of nucleation at several points which appear as minute bubbles initially, but which progressively grow radially and form a focal conic fan texture of smectic-A phase in which the molecules are arranged in layers and the texture is shown in Fig. 1(a). This phase appears to be metastable and undergoes slow transformations to give a viscous smectic-D phase [8]. When the optically extinct smectic-D phase is submitted to the external pressure or stress by touching the cover slip over the sample, no flash or change in the birefringence was observed. This is one of the basic tests to identify the smectic-D phase. The isotropic

Figure 1. Microphotographs obtained in between the crossed polars. (a) Focal conic fan-shaped texture of smectic-A (Lamellar) phase (250×). (b) Paramorphotic fan-shaped texture of highly ordered smectic-B phase (250×). (c) Focal conic fans with radial striation of smectic-E phase (250×).

viscous smectic-D phase is also meta-stable and transforms to focal conic fan-shaped texture on cooling the specimen. This texture corresponds to the paramorphotic [9] focal conic fan-shaped texture of ordered smectic-B phase is shown in Fig. 1(b), in which the molecules are arranged in hexagonal close-packed structure. On further cooling, focal conic fan texture with radial striation on the fans, which is the characteristics of smectic-E phase and it is shown in Fig. 1(c). At this phase transition, i.e., from smectic-B phase to smectic-E phase, it is observed that there is a drastic change in the values of density, refractive index, and electro-conductivity of the sample. This anomalous behavior is presumably associated with high degree of order of the molecular arrangement in smectic-E phase. The phase diagram is shown in Fig. 2. It clearly illustrates that, the lower and higher concentrations of SLS in DTAB+EG exhibit wide variety of liquid crystalline phases. Here, it is pertinent to remark that, the smectic-E phase exists at room temperature for the concentrations from 5% to 45% of SLS. But above 45% of SLS, the mixture exhibits only a birefringent region and it is difficult to associate the texture with any of liquid crystalline mesophases. The most remarkable feature of the SLS molecules is the tendency of their constituent parts to segregate in space with the creation of interfaces. Evidently, the polymorphism seems to be entirely depending on the interfacial behavior and this behavior ultimately leads to

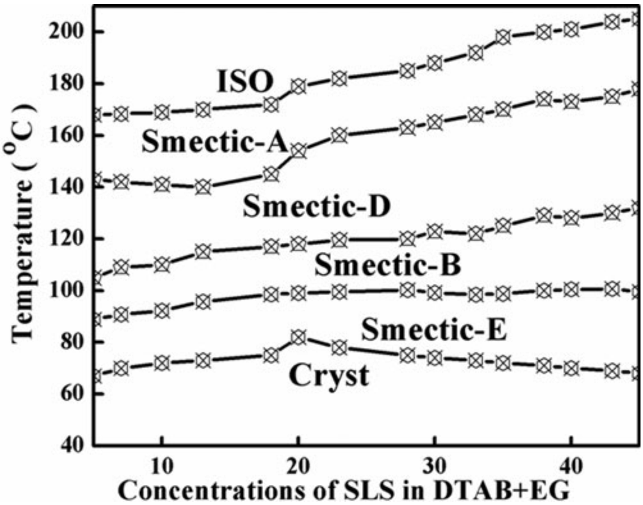

Figure 2. Partial phase diagram for the mixture of SLS in DTAB+EG.

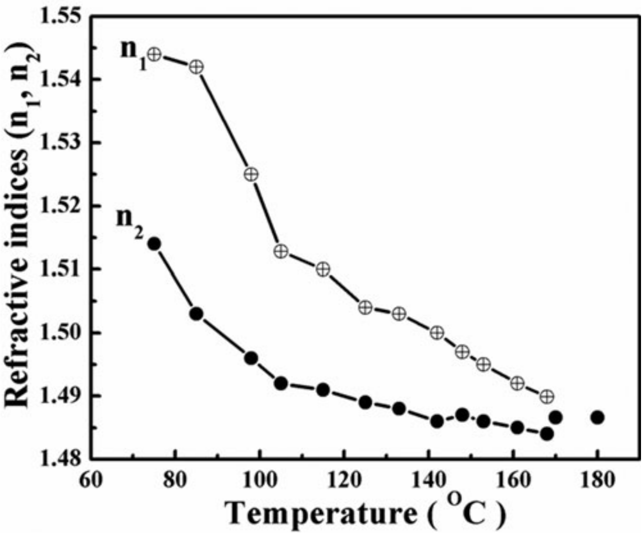

Figure 3. Temperature variation of refractive indices for the mixture of 23% SLS in DTAB+EG.

the limiting of the polymorphism for homogeneous interfaces for higher concentrations of SLS.

It can be noticed that the phase transition temperatures observed in the present study are different from the values observed in a similar type of study by T.N. Govindaiah et al. [10] in which the mixture of a different compound with EG has been studied. Hence, the interaction of EG looks to be different with different compounds.

Optical Anisotropy

Liquid crystals demonstrate a nonlinear response and are sensitive to their optical environments. Many of nonlinear mechanisms have been revealed the promising character of these 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 [11]. 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 [11–13].

In 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 23% of SLS in DTAB+EG is shown in Fig. 3. From this figure, it has been found that, the mixture with small amount of SLS increases the required threshold of molecular orientation in given mixture. This phenomenon demonstrates that, 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 [14,15]. The values of electrical susceptibility for 23%

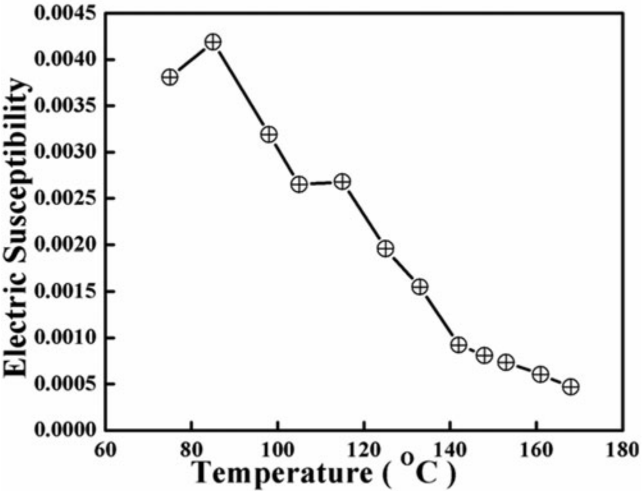

Figure 4. Temperature variation of electric susceptibility for the mixture of 23% SLS in DTAB+EG.

of SLS in DTAB + EG has been calculated using Neugebauer relation [16] at different temperatures. The variation of electrical susceptibility as a function of temperature for the mixture is as shown in Fig. 4. From the figure, it can be observed that wherever there is an isotropic-liquid crystalline phase transition, the value of electrical susceptibility changes appreciably, which indicates that the changes correspond to different smectic modifications. Further, with increase the concentration of SLS in the mixture of DTAB+EG, the value of electrical susceptibility decreases with temperature; because the effective optical anisotropy associated with the molecules of SLS also decreases.

X-Ray Studies

The X-ray diffractometer traces obtained for the mixture with 23% of SLS at temperatures 89 °C, and 109 °C are as shown in the Fig. 5. The diffraction peaks at these temperatures correspond to smectic-E, and smectic-B phases, respectively. They were obtained using JEOL diffractometer with the settings: TC4, CPS400, channel width 100 for $\lambda = 1.934$ Å. XRD method appears to be only the practical and reliable way to find the crystallite size measurement [17–19] of the liquid crystalline materials. Perfect liquid crystals would extend in all directions to infinity, so we can say that no crystal is perfect due to its finite size. The deviation from perfect liquid crystallinity leads to a broadening of the diffraction peaks. In order to estimate the crystallite size of materials from the broadening of corresponding X-ray diffraction peaks can be done using Scherrer's formula

$$L = K\lambda/\beta\cos\theta$$

where L is the crystallite size, λ is the wavelength of X-radiation, K is usually taken as 0.89, β is the line width at half maximum, and θ is the diffraction angle. It has been found that the phase transition temperature increases as we move from crystalline phase to amorphous region [20,21], which clearly illustrates that, the crystallite size of the liquid crystalline materials decrease with increasing the temperature. Here in the present study; the smectic-B phase is metastable for a small value of crystalline size is 40.142 nm. The

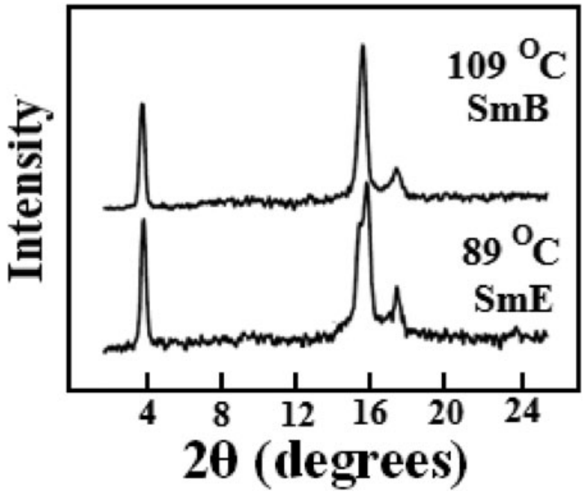

Figure 5. (a) X-ray broadening spectrum for the mixture of 23% of SLS in DTAB+EG.

smectic-E phase is more stable for large crystallite is 53.1023 nm. From the X-ray studies, we have been observed that molecular ordering of the liquid crystalline phase increases with decreasing toward room temperature. The smectic-B phase transform into smectic-E phases, sequentially when the specimen is cooled from its isotropic phase, it clearly illustrate that, the crystalline size of the liquid crystalline materials are big enough to indicate that, the molecular ordering [22] of layer structure increases as well as decrease the temperature.

Helfrich Potential and Elastic Modulus

The free energy of steric intermembrane interactions exists between undulating neighboring membranes, when they are side by side in the multilayer systems [23]. The undulation modes in multilayer systems can be treated in terms of the de Gennes theory [24] of fluctuations in smectic phase, which invokes curvature elasticity and smectic compressibility. To estimate the Helfrich potential [V (ξ)], we consider the free energy per unit area

$$V(\xi) = \beta \frac{(k_B T)^2}{ko\xi^2}, \tag{1}$$

where $\beta = 3\pi^2/128$, $(k_0/k_B\, T) = 0.75$ (The repulsive force between the membrane), $k_0 =$ bare bending constant, k_B is the Boltzman constant.

The V (ξ) of membrane varies with inverse square of the membrane spacing assumed that the local tilt of the membrane induced by undulations remains in effect well below $\pi/2$. ξ is the mean membrane separation. Here, it has been considered that the value of "ξ " is equal to the value of "*d*" [25].

The variation of Helfrich potential along with the concentrations of SLS in DTAB+EG is shown in Fig. 6 and hence it is very interesting to note that, the Helfrich potential values increase as the concentrations of the SLS increase. This result invokes that in dilute region of the mixture V (ξ) value decreases. This is supported by the nature of variation exhibited by the elastic modulus.

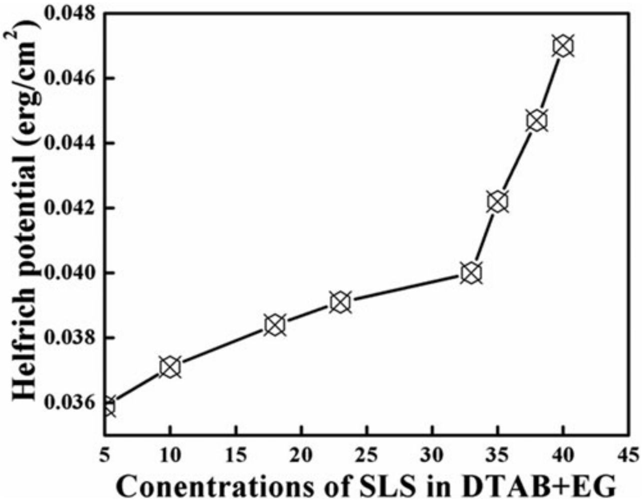

Figure 6. Variation of Helfrich potential with concentrations of SLS in DTAB+EG.

The elastic modulus (K) [25] of smectic compressibility is calculated using the relation

$$K = \frac{3\pi^2}{64}\frac{(k_B T)^2}{k_c d}, \tag{2}$$

where k_c is curvature elastic modulus.

The elastic modulus is also estimated for the mixture of different concentrations at various temperatures. The graph obtained by plotting the elastic modulus as a function of the concentrations of SLS in DTAB+EG is presented in Fig. 7. From the graph, it is observed that, as the concentration of SLS decreases, value of the bulk modulus also decreases. The small values of electrical susceptibility, bulk modulus, and Helfrich potential

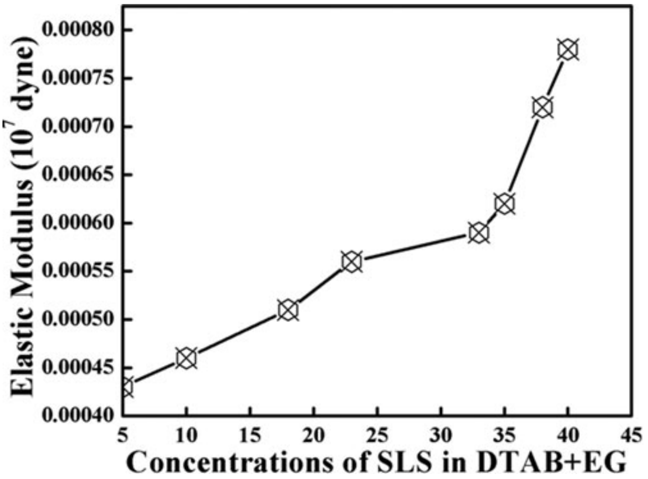

Figure 7. Variation of Elastic modulus with concentrations of SLS in DTAB+EG.

in low concentrations are due to the lesser value of density in which the interaction of smectic layers with the neighboring layers appears to be very less.

Conclusions

The above studies apart from revealing numerous optical textures associated with various liquid crystalline smectic phases in the given mixture have enabled us to reach the following conclusions. Mixture with concentrations from 5% to 45% of SLS in DTAB+EG exhibits induced polymorphic smectic modifications at different temperatures. The drastic changes in the values of density, refractive index, and anisotropy of polarizability with the variation of temperature suggest that, the size of aggregates goes on increasing and the electrical conductivity also goes on increasing, while the mixture is cooled from its isotropic phase,. But below a particular temperature, the size of aggregates becomes so large, that the specimen moves toward crystalline nature. X-ray studies lend support to the grain size of the different liquid crystalline phases. This type of induced polymorphism is rare in the binary/ternary mixture of nonmesogenic compounds.

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