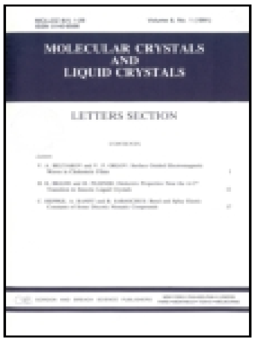

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Induced Polymorphism of Smectic Phases in Binary Mixture of Non-Mesogenic Compounds

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We report the results of our studies on the optical and thermal properties of the mixture of sodium dodecyl sulfate (SDS) and orthophosphoric acid (H_3PO_4), which exhibits very interesting induced polymorphic 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 differential scanning calorimetry (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

The importance of liquid crystals lies in their extensive use in display devises, as well as many other scientific applications [1]. However, the use of liquid crystals in different devices depends upon various properties owned by them like order parameter, dielectric constant, dielectric anisotropy, birefringent behavior, optical transmittance, elastic constants, etc. A particular application of liquid crystals requires a particular set of parameters of the liquid crystal in required range. Therefore, characterization of any liquid crystal sample is very important and a number of researchers are studying properties of different classes of liquid crystals [2, 3].

The liquid crystals' samples are characterized by their phase transition behavior, which can be studied both by dielectric as well as optical methods. The dielectric and optical studies have been very useful as they provide important information regarding molecular structure, molecular dynamics, and type of molecular interactions in the sample and hence the probable phases that could be shown by the molecules of sample [4, 5]. There are various tools for studying phase transition in liquid crystal. Optical polarizing microscopy is a standard tool for determining phase transitions in the liquid crystal samples [6, 7].

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Along with this method dielectric anisotropy and birefringence provide useful information about the order parameter (*S*) and activation energies of liquid crystal sample [8]. Most of the physical properties of the liquid crystal emerge from the order that exist in the sample and thus followed by the order parameter [9], which makes order parameter so important while studying liquid crystals. Various methods have been adopted by different workers to calculate the order parameter, like Neugebauer's anisotropic field model [10], Vuks isotropic internal field model [11], Saupe and Maier anisotropic model [12], etc.

In the present study, we have considered the mixture of non-mesogenic compounds, viz., sodium dodecyl sulfate (SDS) and orthophosphoric acid (H_3PO_4), which shows different liquid crystalline phases over a wide range of temperature. The polymorphic smectic modifications of the liquid crystalline phases were observed using microscopic technique and they have been verified from the results of differential scanning calorimetry (DSC), X-ray, and optical anisotropic techniques. Helfrich potential and elastic modulii have been estimated in the lamellar smectic phases using Helfrich model with approximation.

Experimental Studies

SDS used in this investigation was obtained from the Basic Pharma Life Science, Pvt. Ltd., India. They were further purified twice by re-crystallization in benzene. The melting point of the purified sample is in good agreement with the reported value. H_3PO_4 was supplied by M/s SISCO Research Laboratory, Mumbai, India. The H_3PO_4 was used after boiling it at 433 K for 6 hr. The mixture of 20 different concentrations of SDS (by wt%) in H_3PO_4 were prepared and kept in 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 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 phase diagram was obtained by plotting the phase transition temperatures of the mixtures, which were determined by the DSC studies as a function of concentrations of SDS in H_3PO_4. The phase diagram clearly indicates that the mesomorphism of the mixture is thermodynamically stable for lower and higher concentrations of SDS. X-ray diffraction (XRD) patterns were taken using a Jeol X-ray diffractometer at various temperatures for different concentrations in order to study the smectic phases [13–15]. The density and refractive indices of the mixtures were measured at different temperatures employing the technique described in our earlier paper [16].

Optical Studies

The induced polymorphic smectic modifications and the corresponding isotropic to liquid crystalline phase transition temperatures for the mixture with 40% of SDS in H_3PO_4 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 that 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

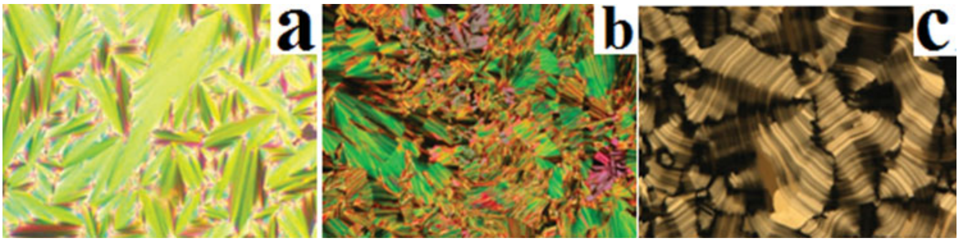

Figure 1. Microphotographs obtained in between the crossed polars. (a) Focal conic fan-shaped texture of SmA (Lamellar) phase (250X). (b) Paramorphotic fan-shaped texture of highly ordered smectic-B phase (250X). (c) Focal conic fans with radial striation of smectic-E phase (250X).

appears to be meta-stable and undergoes slow transformations to give a viscous smectic-D phase [17]. 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 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 [18] focal conic fan-shaped texture of ordered smectic-B phase and 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, is observed 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 SDS in H_3PO_4 exhibit wide variety of liquid crystalline phases. Here, it is pertinent to remark that the smectic-E phase exists at room temperature

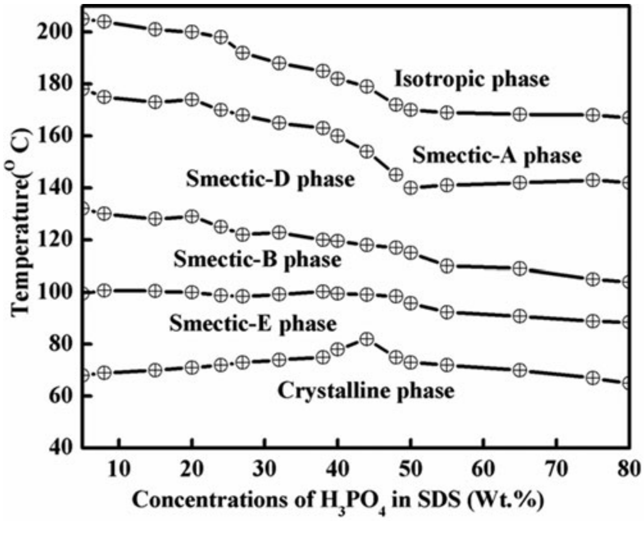

Figure 2. Partial phase diagram for the mixture of SDS in H_3PO_4.

for the concentrations from 5% to 80% of SDS. But above 80% of SDS, the mixture exhibits only a birefringent region and it is difficult to associate the texture with any of liquid mesophases. The most remarkable feature of these SDS 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 the limiting of the polymorphism for homogenous interfaces for higher concentrations of SDS.

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. [19] in which the mixture of a different compound with orthophosphoric acid has been studied. Hence, the interaction of orthophosphoric acid 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 [20]. 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 [20–22].

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 Precision Goniometer Spectrometer. The temperature variation of refractive indices for the mixture of 40% of SDS in H_3PO_4 is shown in Fig. 3. From this figure, it has been found that the mixture with small amount of SDS increases the required threshold of molecular orientation in given mixture. This phenomenon demonstrates the potential application in

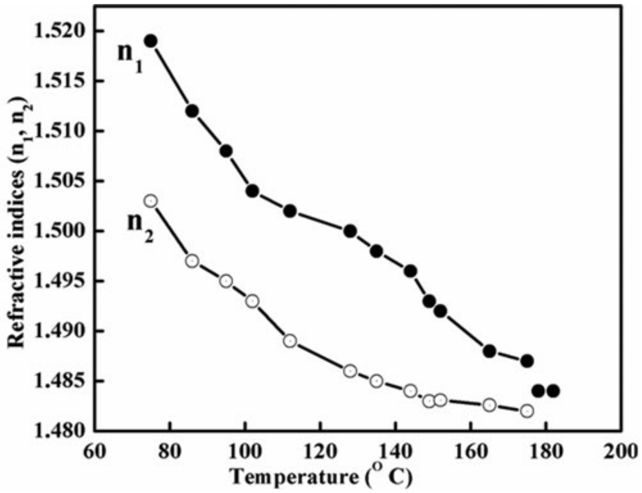

Figure 3. Temperature variations of refractive indices for the mixture of 40% SDS in H_3PO_4.

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 [23, 24]. The values of electrical susceptibility for 40% of SDS in H_3PO_4 have been calculated using Neugebauer relation [25] 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 various smectic modifications. Further, with increase in the concentration of SDS with the mixture of H_3PO_4, the value of electrical susceptibility decreases with temperature; because the effective optical anisotropy associated with the molecules of SDS also decreases.

X-Ray Studies

The X-ray diffractometer traces obtained for the mixture with 40% of SDS at temperatures 89°C and 109°C are as shown in 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 [26–28] 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

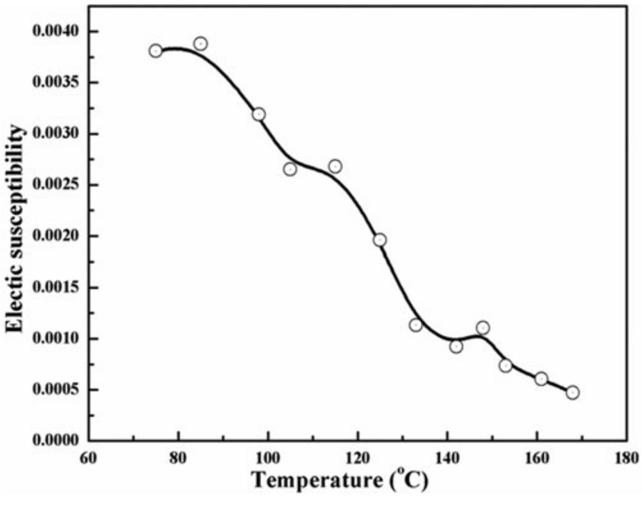

Figure 4. Temperature variation of electric susceptibility for the mixture of 40% SDS in H_3PO_4.

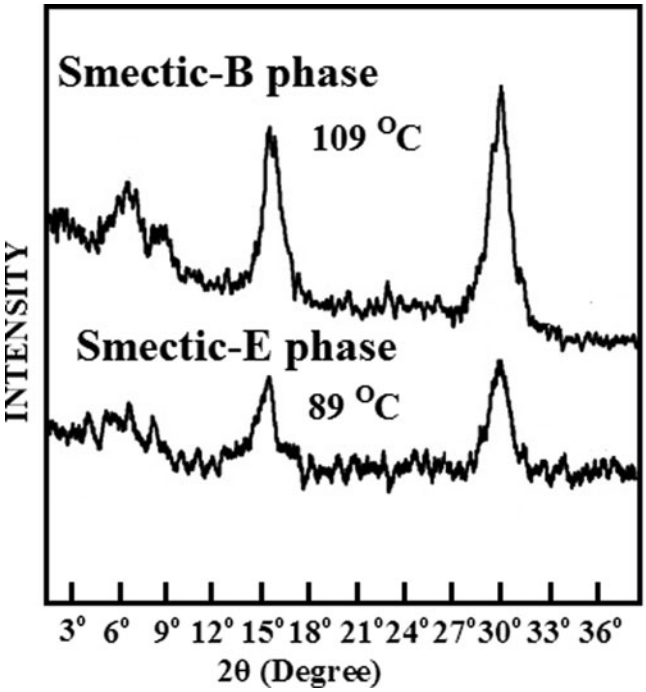

Figure 5. XRD traces obtained for the mixture of 40% SDS in H_3PO_4 at different temperature.

found that the phase transition temperature increases as we move from crystalline phase to amorphous region [29, 30], 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, which is 40.142 nm. The smectic-E phase is more stable for large crystallite, which is 53.1023 nm in size. 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 transforms into smectic-E phases, sequentially when the specimen is cooled from its isotropic phase, it clearly illustrates that the crystalline size of the materials is big enough to indicate that the molecular ordering [31] of layer structure increases as the temperature decreases.

Helfrich Potential and Elastic Modulus

The free energy of steric inter-membrane interactions exists between undulating neighboring membranes, when they are side by side in the multilayer systems [32]. The undulation modes in multilayer systems can be treated in terms of the de Gennes theory [33] of fluctuations in smectic phase, which invokes curvature elasticity and smectic compressibility. To estimate the Helfrich potential [$V(\xi)$], we consider the free energy per unit area

$$V(\xi) = \beta \frac{(k_B T)}{k_0 \xi^2}, \tag{1}$$

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

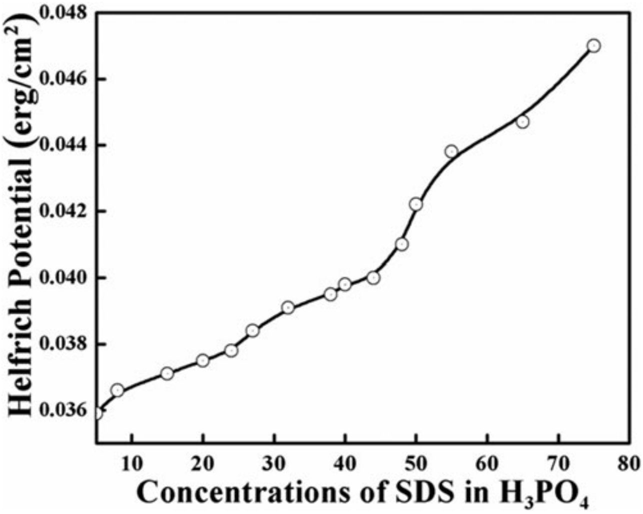

Figure 6. Variation of Helfrich potential with concentrations of SDS in H_3PO_4.

The $V(\xi)$ 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*" [34].

The variation of Helfrich potential along with the concentrations of SDS in H_3PO_4 is shown in Fig. 6 and hence it is very interesting to note that the Helfrich potential values increase as the concentrations of the SDS increase. This result invokes that in dilute region of the mixture, $V(\xi)$ value decreases. This is supported by the nature of variation exhibited by the elastic modulus.

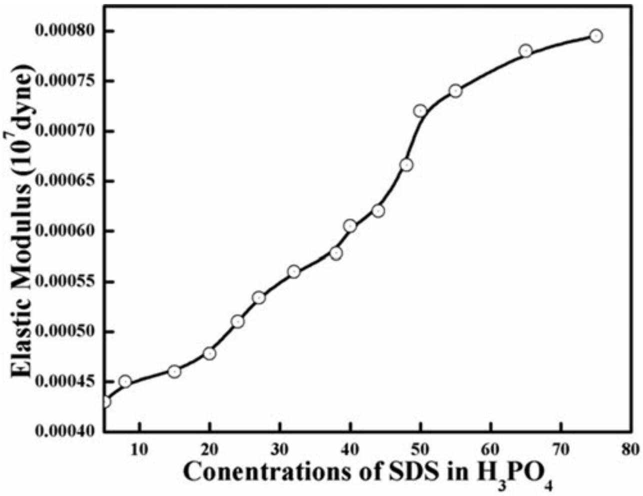

Figure 7. Variation of elastic modulus with concentrations of SDS in H_3PO_4.

The elastic modulus (K) [34] 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 SDS in H_3PO_4 is presented in Fig. 7. From the graph, it is observed that as the concentration of SDS decreases, value of the bulk modulus also decreases. The small values of electrical susceptibility, bulk modulus, and Helfrich potential 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 textures associated with various phases in mixture have enabled us to reach the following conclusions. Mixture with concentrations from 5% to 80% of SDS in H_3PO_4 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 are lending support to the grain size of the different liquid crystalline phases. This type of induced polymorphism is rare in the binary/ternary mixture of non-mesogenic compounds.

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