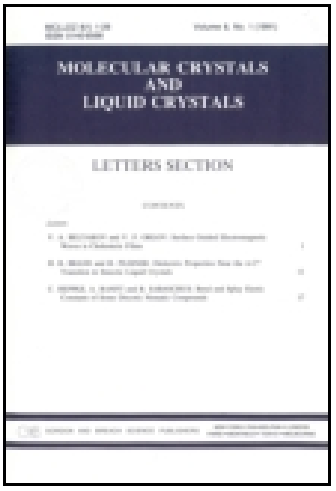

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Anisotropic Molecular Orientation of Micellar Nematic Phase in a Binary Mixture of Two Nonmesogenic Compounds

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Anisotropic Molecular Orientation of Micellar Nematic Phase in a Binary Mixture of Two Nonmesogenic Compounds

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We report the results of our studies on the optical and thermal properties of two non-mesogenic compounds, namely, Cetyl-dimethyl-ethylammonium bromide (CDEAB) and Glacial acetic acid. The mixture exhibits very interesting schilieren texture of micellar nematic phase, SmA, SmC, and SmE phases, respectively, at different concentrations of CDEAB sequentially when the specimen is cooled from its isotropic phase. The order parameter (S) of the micellar nematic phase is estimated with the help of temperature dependence of optical anisotropy from the measured values refractive index and density data. The temperature variation of order parameter of the experimental curve is very well fitted with the Mayer–Saupe theoretical curve. X-ray studies have been discussed. The formation of above phases has been confirmed by optical and DSC studies.*

Keywords Binary mixture; lyotropic phase; molecular orientation; optical anisotropy; phase formation

Introduction

The importance of liquid crystals lies in their extensive use in display devices, 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, optical and dielectric anisotropy, birefringent behavior, elastic constants, etc. A particular application of liquid crystals requires a particular set of parameters of the liquid crystal in required range. Studies on physical properties of lyotropic/thermotropic liquid crystals are of importance because of their layered structure. It is very interesting to study the binary and ternary mixture of some nonmesogenic compounds exhibit a lyotropic and thermotropic mesophases [2, 3]. The lyotropic micellar nematic phase was observed by Lawson and Flautt [4, 5] in the mixture of higher concentrations of some surfactant solutions of isometric micelles, which possess long-range orientational order [6]. The micellar nematic phase was identified on the basis of microscopic texture and the fact that they spontaneously orient in a strong magnetic field. The nematic phases of disc-shaped micelles N_D and cylindrical micelles N_C occur in some lyotropic systems. The nematic

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phases of disc (N_D) and cylindrical (N_C) shaped micelles have been observed by earlier investigators in a lyotropic system of mixtures. For example, a cesium pentadecafluoro octanoate/water systems [7] exhibit a nematic phase (N_D), which occurs between lamellar (L) phase and isotropic micellar solution [8]. Occasionally, the phase transition of lyotropic systems exhibits isotropic, micellar nematic, and lamellar phases sequentially when the specimen is cooled from isotropic liquid phase. Generally, the lyotropic phase transitions I–N_D–L correspond to isotropic (I)–nematic (N)–smectic A (SmA), exhibited by rod-shaped molecules. A similar correspondence symmetry exists between the phase involved in the lyotropic I–N_C–H transitions (H = hexagonal phase) and those in the thermotropic I–N_C–L transitions exhibited by disc-shaped molecules.

In the present investigation, we have shown the existence of micellar nematic phase, SmA, and SmE phases in the binary mixture of Cetyl-dimethyl-ethylammonium bromide (CDEAB) and Glacial acetic acid (GAA). We have discussed the results of X-ray diffraction (XRD) studies of SmC* phase at different temperatures, birefringence, and optical texture studies have been carried out for the micellar nematic (N_D) phase at higher temperatures. In light of the above investigations, we have tried to understand the coupling between aggregate structure and the mesophase order.

Experimental Section

The compound CDEAB used in this investigation was obtained from the Basic Pharma Life Science Pvt., Ltd., India, and it was further purified twice by a recrystallization method using benzene as a solvent. GAA was supplied from Kodak, Ltd., Kodak house, Mumbai, India. Mixtures of twenty different concentrations of CDEAB in GAA were prepared and were mixed thoroughly. These concentrations of the mixture were kept in desiccators for a long time. The samples were subjected to several cycles of heating, stirring, and centrifuging to ensure homogeneity. The phase transition temperatures of these concentrations were measured with the help of Leitz-polarizing microscope in conjunction with a hot stage. The samples were sandwiched between the slide and cover slip and were sealed for microscopic observations. The sample whose refractive indices have to be determined is introduced between two prisms of the Abbe refractometer. The combination of prisms containing liquid crystalline material is illuminated by a monochromatic light ($\lambda = 5893$ Å). The refractometer is in conjunction with a temperature bath from which hot water can be circulated to maintain the sample at different temperatures. In the field of view, two lines of demarcation of slightly different polarization are observed. The horizontal polarization corresponds to the ordinary ray and vertical polarization is due to the extraordinary ray. By matching the cross-wire, the refractive indices of the ordinary ray and extraordinary ray are read directly. Measured refractive indices of mixtures using Abbe refractometer are compared with the results obtained by measurement using goniometer spectrometer developed by Chatelain [9]. The density and refractive indices in the optical region are determined at different temperatures by employing the techniques described by the earlier investigators [10, 11]. The differential scanning calorimetry (DSC) thermograms were taken for mixtures of all concentrations using the Perkin-Elmer DSC II Instrument facility available at Raman Research Institute, Bangalore, India. The DSC thermogram for the sample of 50% CDEAB is shown in Fig. 1. The sequence of occurrence of different phases as follows:

$$\mathrm{I} - 145^{\circ}\mathrm{C}, \mathrm{N_D} - 119^{\circ}\mathrm{C}, \mathrm{SmA} - 101.25^{\circ}\mathrm{C}, \mathrm{SmC^*} - 72.8^{\circ}\mathrm{C}, \mathrm{SmE} - 48.31^{\circ}\mathrm{C}$$

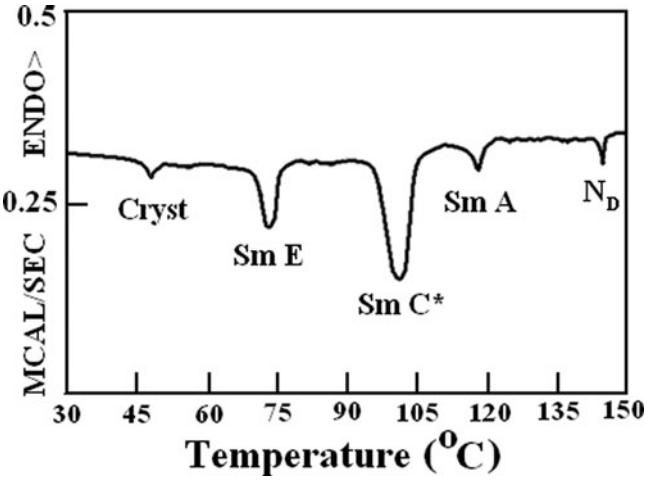

Figure 1. DSC thermogram for the sample of 50% of CDEAB in GAA.

The X-ray broadening peaks were obtained at different temperatures using JEOL diffractometer.

Results and Discussion

Phase Diagram

The partial phase diagram shown in Fig. 2, which is drawn by considering the phase transition temperatures against the concentrations of mixture, clearly illustrates that all concentrations of CDEAB exhibit a schlieren texture, which is the characteristic of micellar nematic lyophase (N_D). Raja et al. [12] have also carried out experimental studies on nematic

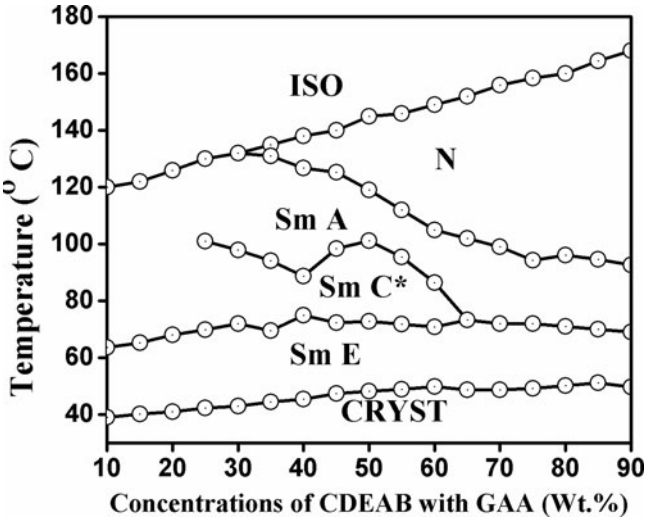

Figure 2. Partial phase diagram for the mixture of CDEAB and GAA.

to SmA transition in nematic mixtures and located the tricritical point, where the change of phases occurs from first-order to second order. In the present study, Fig. 1 clearly illustrates that the I–N_D transition is of first order. We propose the micellar nematic to lamellar transition to be of first order, looking into following considerations. During the phase transition in DSC thermograms, we observe the enthalpy change at SmA – Nematic transition is higher than at Nematic – SmA transition, which is usually observed for this type of phase transition [13]. It is well known that, the transition between isotropic liquid and SmA phase is of first order, whereas transition between nematic and SmA phase may be either first order or second order depending upon the coupling between the orientational order and positional order, which, in turn, depends on the width of the nematic phase. It is also known that a liquid crystal with a nematic phase is more likely to exhibit a first-order nematic to SmA transition [14]. Since the width of the nematic phase in the present case is not wide, here in the present case nematic to SmA transition appears to be of first order. The second-order transition of SmC^* phase indicates that there is continuity in the structure of the amphiphile aggregate, therefore, it infers that at SmA – SmC^* transition, the nematogenic disc-shaped micelles condense on the smectic layer planes instead of aggregate into infinitely extending molecular orientation of the smectic planes [15, 16].

Optical Texture Studies

The optical textures exhibited by the samples were observed and recorded using the Leitz polarizing microscope and specially constructed hot stage. The specimen was taken in the form of thin film and sandwiched between the slide and cover glass. The concentrations from 10% to 90% of binary mixture of CDEAB and GAA have been considered for the experimental studies. When the specimen of 50% CDEAB is cooled from isotropic liquid phase, it exhibits I–N_D–SmA–SmC^*–SmE–K phases sequentially. While the sample is cooled from isotropic liquid phase, the genesis of nucleation starts in the form of small bubbles growing radially, which are identified as nematic drops as shown in Fig. 3(a). The nematic drops change over to schlieren texture, which is the characteristic of micellar nematic phase. This is shown in Fig. 3(b). On further cooling the specimen, the micellar nematic (N_D) phase changes over to lamellar (L) phase and it is characterized by a focal conic fan texture of SmA phase as shown in Fig. 3(c). Before crystallizing the specimen, SmA phase change over to SmC^* phase, which exhibit a radial fringes on the fans of focal conic textures, which are the characteristics of chiral Smc^*phase as shown in Fig. 3(d). On further cooling the specimen, Smc^* phase changes over to SmE phase and the same texture is retained up to room temperature. Whereas the concentrations from 30% to 90% of CDEAB exhibit a micellar nematic phase and this phase appears to be stable, and finally change over to SmA, SmC^*, and SmE phase, respectively, at different temperature and at different concentrations. The phase behavior is also discussed with the help of a phase diagram given in Fig. 2. Similar results have been reported by our group in the mixture of N-Cetyl-N, N, N, trimethyl ammonium bromide, and GAA [17].

Birefringence Studies

The Micellar nematic phase in lyotropic system is generally formed by amphiphilic aggregation with bilayer structure [18]. As in nematic phase of thermotropic system, the bilayer micelles show some degree of parallel orientation, which is responsible for the macroscopic anisotropy of the phase. The birefringence study helps us to understand the optical

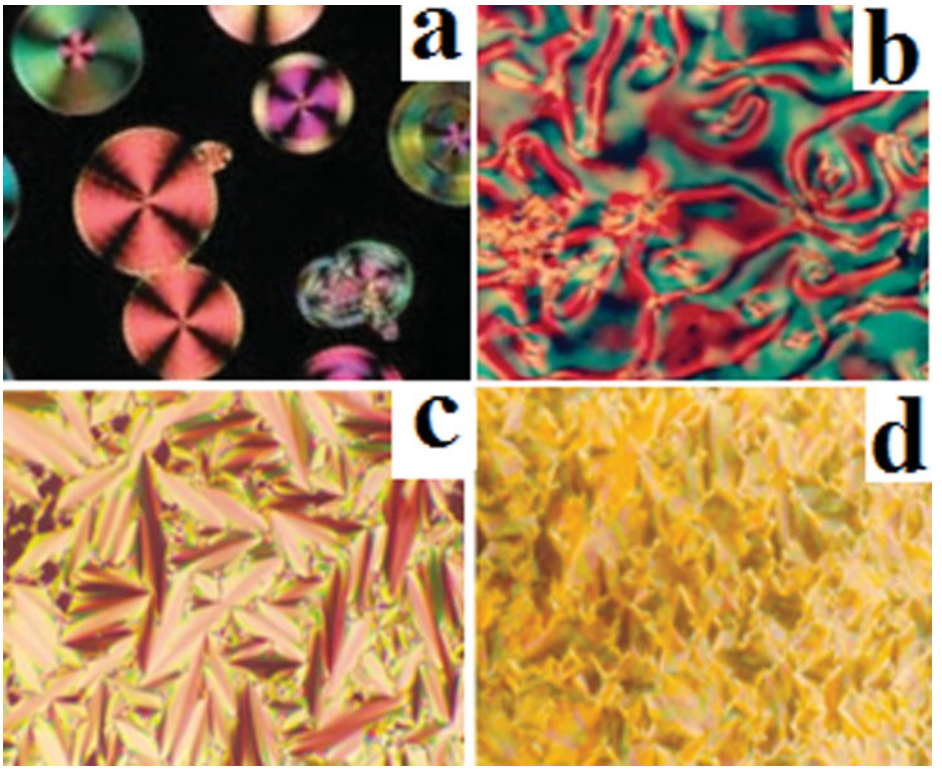

Figure 3. Microphotographs showing: (a) Nematic Drops (180×). (b) Schlieren texture of nematic phase (180×). (c) Focal conic fan shaped texture of SmA phase (180×). (d) Chiral SmC* phase (180×).

anisotropic properties of the samples. The orientational order parameter of the nematic phase is essential to understand the degree of orientations of the micelles [19].

In the present investigation, we have measured the temperature variation of the refractive indices (n_1 and n_2) and densities for the mixture CDEAB at different concentrations by using Abbe refractometer and precision Goniometer spectrometer using the wavelength 589.3 nm in the nematic and smectic phases, the refractive index n_1 due to extraordinary ray and n_2 due to ordinary ray respectively have been determined. Saupe [20] used the modified Lorentz-Lorentz [21] formula for the calculation of orientational order parameters of the lyotropic mixture. The refractive indices n_1 and n_2 are given by

$$\frac{n_1^2-1}{n_2^2+2}=4\frac{\pi}{3N}\left[W_{\mathrm{GAA}}\alpha_{\mathrm{GAA}}+W_{\mathrm{CDEAB}}\alpha_{\mathrm{CDEAB}}-\left(\frac{2}{3}\right)W_{\mathrm{CDEAB}}\Delta\alpha_{\mathrm{CDEAB}}S\right], \quad (1)$$

$$\frac{n_1^2-1}{n_2^2+2}=4\frac{\pi}{3N}\left[W_{\mathrm{GAA}}\alpha_{\mathrm{GAA}}+W_{\mathrm{CDEAB}}\alpha_{\mathrm{CDEAB}}-\left(\frac{1}{3}\right)W_{\mathrm{CDEAB}}\Delta\alpha_{\mathrm{CDEAB}}S\right], \quad (2)$$

where, N is the number of molecules per unit volume of the mixtures and W_{GAA} and W_{CDEAB} are the mole fractions of GAA and CDEAB, respectively, α is the mean polarizability of the respective compounds. For the estimation of orientational order parameter of the

micellar nematic phase, we assume only the birefringence Δn of the CDEAB molecules [18]. Because the polarizability tensor of CDEAB can be approximated with principle polarizability α_1 parallel to the long axis of the molecule and α_2 is perpendicular to it. The optical anisotropy ($\Delta\alpha$) contribution from acetic acid is neglected. Therefore, only $\Delta\alpha$of CDEAB molecules is considered, $\Delta\alpha = (\alpha_1 - \alpha_2)$and S = $\frac{1}{2}[3\cos^2\theta - 1]$ is the degree of order of the CDEAB molecules, where θ is the angle between the long molecular axis and optic axis of the molecular disc in the micellar nematic phases and $\cos^2\theta$ is the average over the molecular motion.

From the equations 1 and 2, and using $\Delta n = (n_e - n_o) << 1$ we obtain

$$\Delta n = \frac{\left[2\pi (n_2^2 + 2)^2 N \Delta\alpha W_{\text{CDEAB}} S\right]}{9 n_2}. \tag{3}$$

In order to estimate the value of optical anisotropy ($\Delta\alpha$) of CDEAB molecule, the value of $(\alpha_\parallel)_{\text{eff}}$ i.e., the polarizability along the axis of the molecules and $(\alpha_\perp)_{\text{eff}}$ the polarizability perpendicular to the long axis of the molecule, the value of $(\alpha_\parallel)_{\text{eff}}$ of each methylene group is calculated from the optical anisotropy of bond polarizability data for the wavelength 5893 ' [22] assuming that the molecules have all trans-configuration and hence $(\alpha_\perp)_{\text{eff}}$ may also calculated. Using the values of $(\alpha_\parallel)_{\text{eff}}$, $(\alpha_\perp)_{\text{eff}}$ and α the mean polarizability, the value of $\Delta\alpha$ is estimated [23]. The value of ($\Delta\alpha$) for CDEAB molecules turns out to be 4.981×10^{-24} cm^3. The order parameter (S) of the micellar nematic phase is calculated with the help of ($\Delta\alpha$) value. The order parameter (S) value of the mixture was estimated at different temperatures for different concentrations. Boden et al. [8] have pointed out in their study that the variation of birefringence with temperature is dependent upon both the size and shape of the micelles, in addition to their dependence on the orientational order. However, we also notice that the order parameter varies with mole percent of CDEAB in the micellar nematic phase. It is observed that the order parameter (S) decreases with decreasing the concentrations of CDEAB. The temperature variations of order parameter of the micellar nematic phase are as shown in Fig. 4, the experimental values of the order parameters are compared with the Maier–Saupe theoretical curve. It is observed that, the trend of the variation of order parameter (S) values agrees with the Maier–Saupe theoretical curve. The values of birefringence are in good agreement with the values measured using the interference techniques [24].

X-Ray Diffraction Studies

The X-ray diffraction broadening peaks were obtained for the mixture with 50% of BBE at temperatures 80 °C, 85 °C, and 93 °C are as shown in the Fig. 5. The diffraction broadening peaks at these temperatures corresponds to SmC* phase only. 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 [25–27] 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 Scherer's formula

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

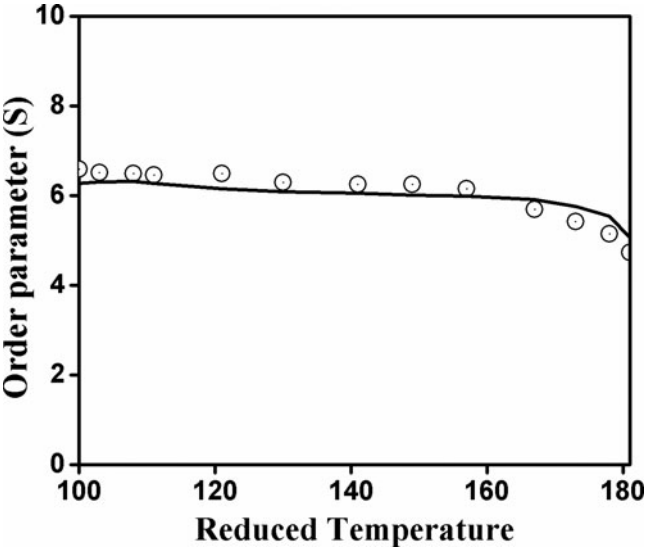

Figure 4. Temperature variation of order parameter of micellar nematic phase.

where L is the crystallite size, λ is the wavelength of X-ray radiation (1.934 Å), 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

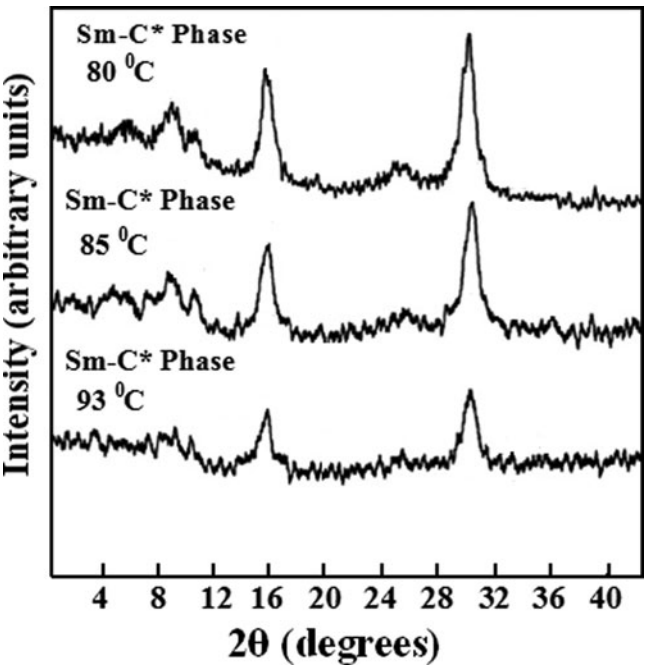

Figure 5. XRD peaks for the mixture of 50% of CDEAB in GAA at different temperature in SmC* phase.

amorphous region [28, 29], which clearly illustrates that, the crystallite size of the liquid crystalline materials decrease with increasing the temperature. In present case, we observed that, SmC* phase is stable energetically for different concentrations of CDEAB mixture, respectively, at different temperature. The crystallite size of SmC* phase is (21.6 nm, 20.3nm, 15.9nm) at temperature 80°C, 85°C, and 93°C, respectively. The crystallite size of this phase is different for different temperature. Evidently which indicates that crystallinity increases with decreasing temperature, i.e., the phase transition from higher temperature to lower temperature, when the crystalline size of the liquid crystalline materials are big enough to indicate that the molecular ordering [30] of layer structure increases as well as decrease the temperature.

Conclusions

Microscopic investigation of the binary mixture of CDEAB and GAA shows the existence schilieren texture of micellar nematic phase, SmA, SmC*, and SmE phases for different concentrations of CDEAB molecule. The phase behavior is discussed with the help of phase diagram. The birefringence study shows that the contribution of birefringence of the mixture is mainly due to CDEAB. X-ray studies helps to understand the aggregate structure and mesophase order, DSC studies also lend support to these observations. It is observed that the variation of order parameter values is in good agreement with the Maier–Saupe theoretical curve.

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