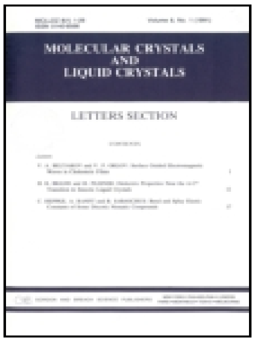

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Formation of Lyotropic Micellar Nematic Phase in Binary Mixture of Liquid Crystals

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We report the results of our studies on optical and thermal properties of two nonmesogenic compounds namely, dodecyl trimethylammonium chloride (DTAC) and Glacial acetic acid (GAA). The mixture exhibits very interesting schlieren texture of lyotropic micellar nematic phase, SmA and SmG phases, respectively, at different concentrations of DTAC sequentially when the specimen is cooled from its isotropic phase. The order parameter (S) of the lyotropic 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. Electrical conductivity has been discussed. The formation of above phases has been confirmed by optical and DSC studies.

Keywords: Molecular orientation; nematic phase; optical anisotropy; phase formation

Introduction

Liquid crystals are the share features of both crystal and melt, i.e., with partial order/disorder of atomic species. The ordering may be purely orientational, with no spatial order (nematic and cholesteric) or spatial. Spatial order in the liquid crystal can occur on the atomic scale (with melting of some atoms in the molecule, while the others remain frozen) or on longer length scales, such as mesoscale ordering found in many solvent-induced liquid crystals. In the latter case, the material may exhibit no atomic ordering, so that material is a pure melt on the atomic scale. Collective order of the molecular aggregates leads to well-defined structure on a larger length scale. Like crystals, liquid crystals are sometimes optically isotropic (cubic phase) or otherwise optically anisotropic (Lamellar, hexagonal, smectic, and intermediate phases).

Many pure molecular substance form liquid crystals during the melting process. Where the chemically pure material is found to melt over a temperature range, rather than abrupt first order transition expected for the solid-melt transformation, the formation of liquid

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crystals within that range is certain. Such substances exhibit thermotropic liquid crystals, whose stability is a function of temperature. A good overview of thermotropic phases is that of Seddon [1]. Materials that form liquid crystals by the addition of solvents are called lyotropic liquid crystals. Many materials exhibit both thermotropic and lyotropic liquid crystalline transition, i.e., mesomorphism. Liquid crystals are typically organic molecules, ranging from polyelectrolytes (examples DNA, vegetable gums etc.) to small molecules (membrane lipids, detergent, etc.) in the presence of (sometimes aromatic) hydrocarbons oils and water. Other solvents, including glycerol, form amide, etc., result in the lyotropic mesophases in the absence of water. The hydrophobic chemical moieties are not limited to hydrocarbons: perflourinated spieces—both as amphiphiles and solvent and also exhibit lyotropic liquid crystalline mesophases.

The lyotropic micellar nematic phase was observed by Lawson and Flautt [2, 3] in the mixture of higher concentrations of some surfactant solutions of isometric micelles, which possess long-range orientational order [4]. 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 [5]. The nematic 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 (CSPFO)/water systems [6] exhibit a nematic phase (N_D), which occurs between lamellar (L) phase and isotropic micellar solution [7]. Occasionally, the phase transition of lyotropic systems exhibits lyotropic micellar nematic and lamellar smectic 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 lyotropic micellar nematic (N_D) phase, SmA and SmG phases in binary mixture of dodecyl trimethylammonium chloride (DTAC) and glacial acetic acid (GAA). We have discussed the results of X-ray diffraction studies of SmG phase at different temperatures. Birefringence and optical texture studies have also been carried out for the lyotropic micellar nematic (N_D) phase at higher temperatures. In light of the above investigations, we have tried to understand the coupling between aggregated structure and order of mesophase.

Experimental Section

The compound dodecyl trimethylammonium chloride (DTAC) used in this investigation was obtained from the Basic Pharma Life Science Pvt., Ltd., India, and it was further purified twice by a re-crystallization method using benzene as a solvent. Glacial acetic acid (GAA) was supplied from Kodak, Ltd., Kodak house, Mumbai, India. Mixtures of different concentrations of DTAC in GAA were prepared and were mixed thoroughly. These mixtures of various concentrations of DTAC in GAA 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 differential scanning calorimetry (DSC) thermograms were taken for the

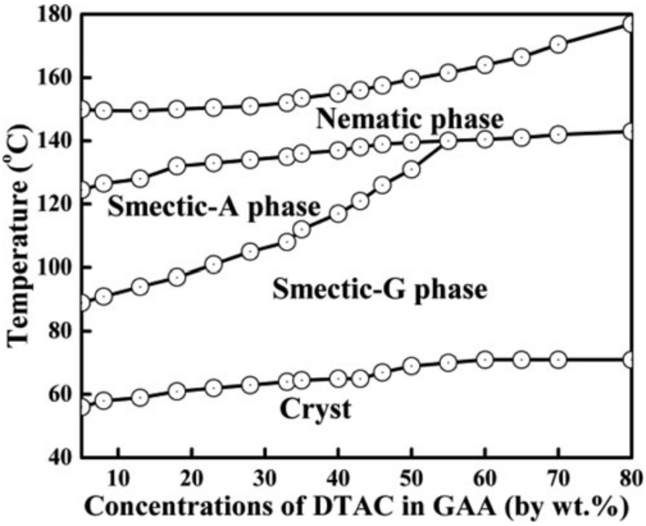

Figure 1. Partial phase diagram for the mixture of DTAC and GAA.

mixtures of all concentrations using Perkin–Elmer DSC II Instrument facility available at Raman Research Institute, Bangalore, India. The X-ray broadening peaks were obtained at different temperatures using JEOL diffractometer. The density and refractive indices in the optical region are determined at different temperatures by employing the techniques described by the earlier investigators [8, 9].

Results and Discussion

Phase Diagram

The partial phase diagram shown in Figure 1, which is drawn by considering the phase transition temperatures against the concentrations of mixture, clearly illustrates that all concentrations of DTAC in GAA exhibit a schlieren texture, which is the characteristic of lyotropic micellar nematic (N_D) phase. Raja et al. [10] have also carried out the experimental studies on nematic 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, Figure 1 clearly illustrates that the I–N_D transition is of first order. We propose the lyotropic micellar nematic (N_D) phase to lamellar smectic phase transition to be of first order, looking into following considerations. During the phase transition in DSC thermograms, we observe that the enthalpy change at SmA–Nematic phase transition is higher than that at Nematic–SmA phase transition, which is usually observed for this type of phase transition [11]. 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 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 phase transition [12]. 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 SmG phase indicates that there is continuity in the structure of the amphiphile aggregate. Therefore it infers that at SmA–SmG phase transition, the nematogenic disc-shaped micelles condense on the smectic layer planes instead of aggregate into infinitely extending molecular orientation of the smectic planes [13, 14].

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 binary mixtures of DTAC and GAA with concentrations of DTAC ranging from 5% to 80% of have been considered for the experimental studies. When the specimen of 35% DTAC is cooled from isotropic liquid phase, it exhibits I-N_D–SmA–SmG–K phases sequentially. When the sample is cooled from isotropic liquid phase, the genesis of nucleation starts in the form of small bubbles which grow radially and were identified as nematic drops and then the nematic drops change over to schlieren texture [15, 16], which is the characteristic of lyotropic micellar nematic (N_D) phase as shown in Figure 2(a). On further cooling the specimen, the lyotropic micellar nematic (N_D) phase changes over to lamellar smectic phase, which is characterized by the focal conic fan-shaped texture of SmA phase and is shown in Figure 2(b). Before crystallizing the specimen the SmA phase changes over SmG phase. The molecules in the SmG phase are packed within the layers, having their long axes tilted with respect to normal to the layer planes [17]. A mixture with all concentrations of DTAC and GAA exhibits a broken banded focal conic fan-shaped texture of the chiral SmG phase, as shown in Figure 2(c). If the constituent molecules of the material, which exhibits a SmG phase, are of a chiral nature, then the phase itself may also be weakly optically active; it is then termed a chiral smectic-G phase. The structural studies have been carried out at that time on chiral SmG phases and it was originally simply presumed that the structure of the phase is similar to that of chiral SmC, SmG, and SmG phases. In this case, the molecules would be hexagonally closely packed in layers, within each of which the tilts must be in the same direction. The layer above and below the tilt direction will, however, be turned through a small angle. Thus, on passing from layer to layer, the tilt direction will turn slowly either in an anti-clockwise or in a clockwise direction, depending upon the sign of the optical asymmetry of the system; this would lead to a helical change in the tilt direction, as described earlier for the SmC and SmF phases. Finally the chiral SmG phase changes over to crystalline phase at room temperature.

The mixtures with concentrations of DTAC ranging from 55% to 80% exhibit lyotropic nematic and SmG phases, whereas mixtures with concentrations from 5% to 55% exhibit a lyotropic micellar nematic (N_D) phase, and this phase appears to be unstable and hence it change over SmA and finally change over to SmG phase. The lyotropic micellar nematic (N_D) phase has a long-range orientation order and the micelles are arranged in columns. The phase behavior has also been discussed with the help of phase diagram given in Figure 1.

The sequence of phase transition observed in the present investigation is given below;

$$\text{Iso} \rightarrow 153.5^\circ\text{C, N} \rightarrow 136^\circ\text{C, SmA} \rightarrow 112^\circ\text{C, SmG} \rightarrow 64.5^\circ\text{C, Cryst} \rightarrow \text{below } 64.5^\circ\text{C,}$$

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/lyotropic system,

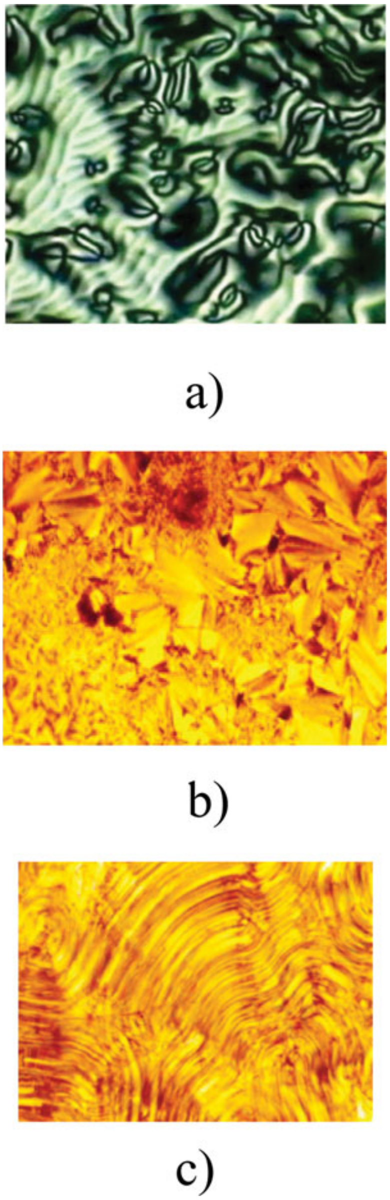

Figure 2. Microphotographs showing, (a) Schlieren texture of lyotropic micellar nematic phase (180×) (b) Focal conic fan-shaped texture of SmA phase (180×) (c) Chiral SmG phase (180×).

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 anisotropic properties of the samples. The orientational order parameter of the lyotropic micellar nematic (N_D) 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 of different concentrations of DTAC in GAA by using Abbe Refractometer and Precision Goniometer spectrometer using the wavelength 589.3 nm in the lyotropic nematic and lamellar smectic phases. The refractive index n_1 due to extraordinary ray and n_2 due to ordinary ray 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

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

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

where, N is the number of molecules per unit volume of the mixtures and W_{GAA} and W_{DTAC} are the mole fractions of GAA and DTAC, respectively, α is the mean polarizability of the respective compounds. For the estimation of orientational order parameter of the lyotropic micellar nematic (N_D) phase, we assume only the birefringence Δn of the DTAC molecules [16]. Because the polarizability tensor of DTAC 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 DTAC 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 DTAC molecules, where θ is the angle between the long molecular axis and optic axis of the molecular disc in the lyotropic micellar nematic (N_D) phase 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

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

In order to estimate the value of optical anisotropy ($\Delta\alpha$) of DTAC molecule, the value of $(\alpha_{çç})_{eff}$ i.e., the polarizability along the axis of the molecules and $(\alpha_\perp)_{eff}$ the polarizability perpendicular to the long axis of the molecule, the value of $(\alpha_{çç})_{eff}$ of each group is calculated from the optical anisotropy of bond polarizability data for the wavelength 5893 Å [22] assuming that the molecules have all trans-configuration and hence $(\alpha_\perp)_{eff}$ may also be calculated. Using the values of $(\alpha_{çç})_{eff}$, $(\alpha_\perp)_{eff}$ and α the mean polarizability, the value of $\Delta\alpha$ is estimated [23]. The value of ($\Delta\alpha$) for DTAC molecules turns out to be 34.562×10^{-24} cm^3. The order parameter (S) of the lyotropic 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. [7] 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 DTAC in the lyotropic micellar nematic (N_D) phase. It is observed that the order parameter (S) decreases with decreasing the concentrations of DTAC. The temperature variations of order parameter of the lyotropic micellar nematic (N_D) phase are as shown in Figure 3, 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].

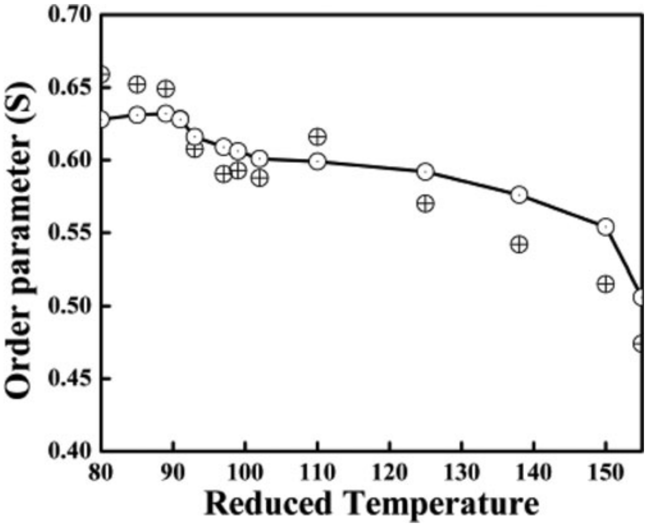

Figure 3. Temperature variations of order parameter of lyotropic micellar nematic phase.

Conductivity Measurements

To obtain reliable data on the phase behavior with temperature, electrical-conductivity measurements are necessary. A small change in electrical-conductivity with temperature relates to the phase behavior of the lyotropic and thermotropic systems [25]. The temperature variations of electrical-conductivity are as shown in Figure 4. The changes were observed in electrical-conductivity, the values correspond to different liquid crystalline phase transitions of the thremotropic and lyotropic system at various temperatures and they

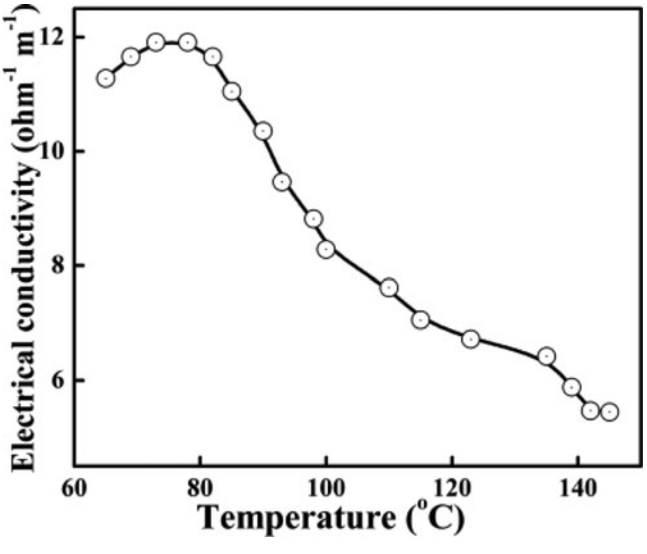

Figure 4. Temperature variation of electrical-conductivity σ (Ω^{-1} m^{-1}) for the sample of 45% of DTAC and GAA.

were also identified by DSC and optical texture studies. It was observed that, a change in electrical-conductivity at different temperatures respectively which corresponds to the phase transition from crystalline to SmG, SmG to SmA and SmA to lyotropic nematic phases, respectively. This type of behavior is generally observed in hexagonal, cubic, and lamellar phase of lyotropic and thermotropic systems [26, 27].

Conclusions

Microscopic investigation of the binary mixture of DTAC and GAA shows the existence schlieren texture of lyotropic micellar nematic (N_D) phase, SmA and SmG phases for different concentrations and at different temperatures. The phase behavior is discussed with the help of phase diagram. Birefringence study shows the contribution of birefringence of the given mixture is mainly due to DTAC. Changes in the value of electrical-conductivity with the variation of temperature suggest that as the mixture is cooled from the isotropic phase, the size of aggregates goes on increasing and the electrical conductivity also goes on increasing. But below a particular temperature, the size of aggregates becomes so large that the specimen moves towards crystalline nature. It is observed that the variation of order parameter values is in good agreement with the Maier–Saupe theoretical curve.

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