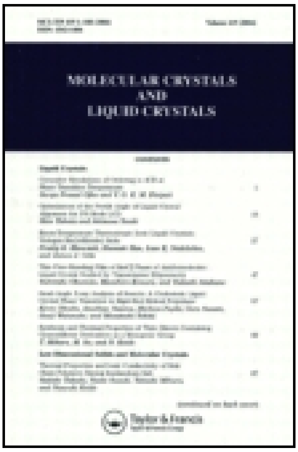

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Micellar Nematic Phase in a Binary Mixture of Two Nonmesogenic Compounds

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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 nonmesogenic compounds, namely, tetradecyl trimethyl ammonium bromide (TTAB) and glacial acetic acid (GAA). The mixture exhibits very interesting schilieren texture of micellar nematic lyophase, smectic A (SmA), and SmG phases for all concentrations of TTAB 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 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. The temperature variation of electrical conductivity is also discussed. The formation of above phases has been confirmed by optical X-ray and differential scanning calorimetry studies.

Keywords Binary mixture; lyotropic phase; nonmesogenic

Introduction

It is very interesting to study the binary and ternary mixture of some nonmesogenic compounds, which exhibit lyotropic and thermotropic mesophases [1,2]. The lyotropic micellar nematic phase was observed by Lawson and Flautt [3,4] in the mixture of higher concentrations of some surfactant solutions of isometric micelles, which possess long-range orientational order [5]. 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 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 isotropic, micellar nematic, and

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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 SmG phases in the binary mixture of tetradecyl trimethyl ammonium bromide (TTAB) and glacial acetic acid (GAA). We have discussed results of X-ray diffraction (XRD) studies of SmG phase at a temperature of 56°C, and birefringence and optical texture studies 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 TTAB 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 25 different concentrations of TTAB 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 [8]. The density and refractive indices in the optical region are determined at different temperatures by employing the techniques described by the earlier investigators [9,10].

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 45% TTAB is shown in Fig. 1. The sequence of occurrence of different phases is as follows:

$$\mathrm{I} - 146^\circ\mathrm{C},\ \mathrm{N_D} - 112^\circ\mathrm{C},\ \mathrm{SmA} - 82^\circ\mathrm{C},\ \mathrm{SmG} - 54^\circ\mathrm{C}$$

The X-ray diffractometer traces were obtained at a temperature of 56°C using JEOL diffractometer. The electrical conductivity measurements of the mixture at different temperatures were carried out using digital *LCR* meter and a proportional temperature control unit.

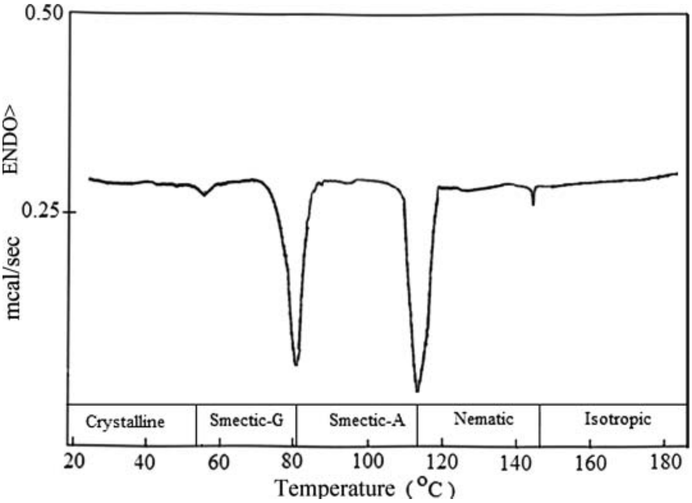

Figure 1. DSC thermogram for the sample of 45% of TTAB in GAA.

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 TTAB exhibit a Schlieren texture, which is the characteristic of micellar nematic lyophase (N_D). Raja et al. [11] have also carried out 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, 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 second order, looking into following considerations.

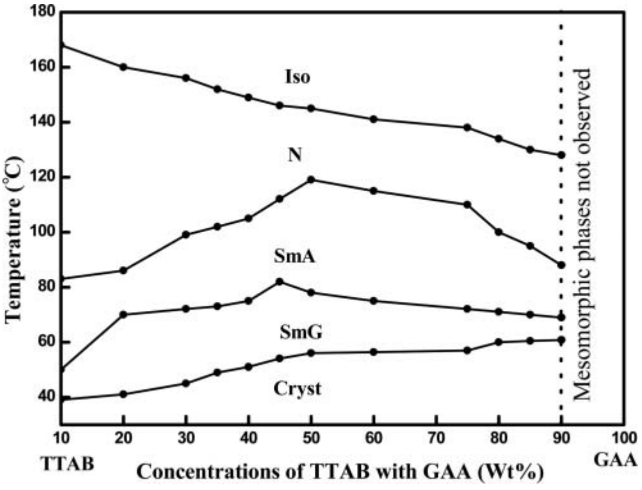

Figure 2. Partial phase diagram for the mixture of TTAB and GAA.

During the phase transition in DSC thermograms, we observe that the enthalpy change at SmA–N transition is higher than at N–SmA transition, which is usually observed for this type of phase transition [12].

It is well known that the transition between isotropic liquid and the 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 wide nematic phase is more likely to exhibit a second-order nematic to SmA transition [13].

Since the width of the nematic phase in the present case is wide, the nematic to SmA transition observed in the present case appears to be of second order.

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 TTAB and GAA have been considered for the experimental studies. When the specimen of 45% TTAB is cooled from isotropic liquid phase, it exhibits I–N_D–SmA–SmG–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, which is characterized by the focal conic fan texture of SmA phase and is shown in Fig. 3(c). Before crystallizing the specimen, SmA phase changes over to a broken banded focal conic fan texture of chiral SmG phase, as shown in Fig. 3(d). If the constituent molecules of the materials, which exhibits a SmG phase, are of a chiral nature, then the phase itself may also be weakly optically active; it is then termed as a chiral SmG phase [14]. 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, SmI, and SmF phases. In this case, the molecules would be hexagonally closely packed in layers within each of which tilts must be in the same direction. In 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 anticlockwise or a clockwise direction, depending upon the sign of the optical asymmetry of the system, and this would give a helical change in the tilt direction [15] and the same texture is retained up to room temperature. Whereas the concentrations from 10% to 90% of TTAB exhibit a micellar nematic phase and this phase appears to be stable, and finally changes over from SmA to SmG phase. The micellar nematic phase has a long-range orientation order and the micelles are arranged in columns. The phase behavior is also discussed with the help of a phase diagram given in Fig. 2. XRD recordings lend support to the above phases observed. Similar micellar nematic phase has been reported by our group in the mixture of N-Cetyl-N, N, N, trimethyl ammonium bromide, and GAA [16].

XRD Studies

The X-ray recording has been obtained for the mixture of 45% TTAB in GAA at the temperature of 56°C, as shown in Fig. 4, and the recordings at this temperature, respectively,

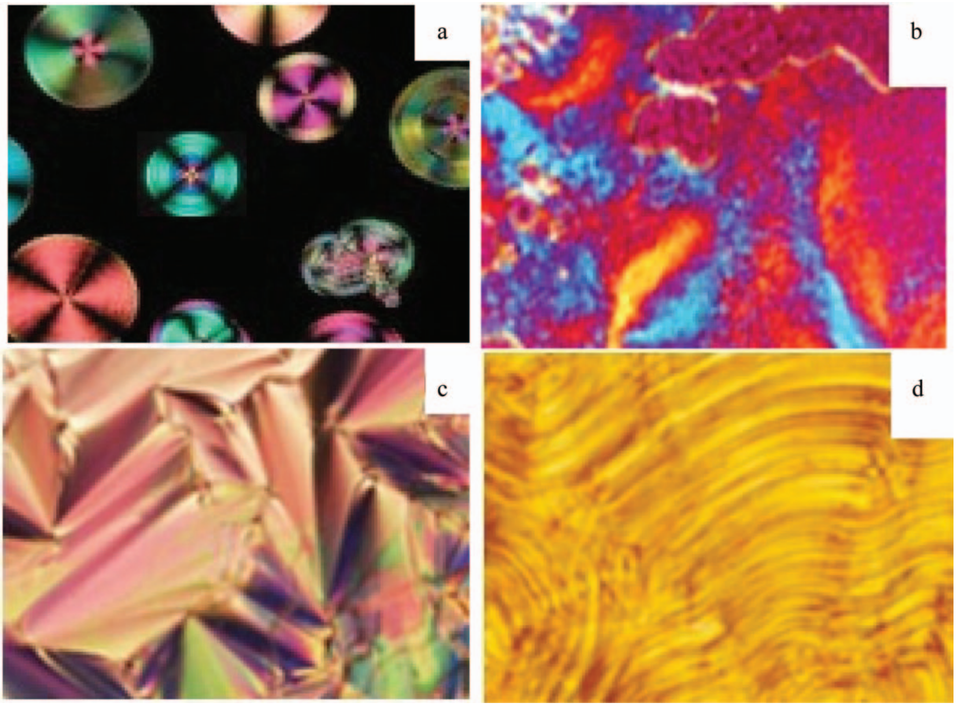

Figure 3. Microphotographs showing: (a) nematic drops (180×), (b) Schlieren texture of nematic phase (180×), (c) focal conic-fan-shaped texture of SmA phase (180×), and (d) chiral SmG phase (180×).

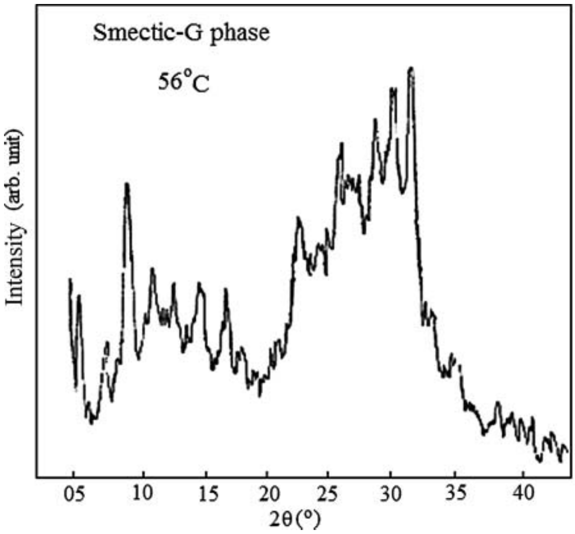

Figure 4. XRD traces obtained for the mixture of 45% of TTAB in GAA at 56°C in SmG phase.

Table 1. X-ray data of 45% TTAB in GAA at 56°C

h	k	l	2θ (obs)	2θ (cal)	Cell parameters
1	0	1	8.235	8.236	$a = 20.2180$ Å
2	1	0	12.370	12.360	$b = 16.9870$ Å
2	1	1	15.110	15.120	$c = 5.33920$ Å
2	1	3	20.370	20.371	$\alpha = 90°$
3	2	1	24.101	24.100	$\beta = 90°$
2	4	1	27.673	27.674	$\gamma = 90°$
5	4	0	34.486	34.487	
			Unit cell volume = 1873.76 A^3		

correspond to the SmG phase. Peaks obtained in XRD traces reveal that the reflections are corresponding to the SmG phase. The cell parameters are obtained by trial and error method. Here, the program starts with an initial set of parameters ($a, b, c, \alpha, \beta, \Upsilon$) and refines this set of parameters until all the observed X-ray reflections (h, k, l) are identified. The parameters obtained are given in Table 1 and it gives the volume of unit cell as 1873.76 A^3, which is the approximated volume of the micelles.

Birefringence Studies

The micellar nematic phase in lyotropic system is generally formed by amphiphilic aggregation with bilayer structure [17]. 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 anisotropic properties of the samples. The orientational order parameter of the nematic phase is essential to understand the degree of orientations of the micelles [18].

In the present investigation, we have measured the temperature variation of refractive indices (n_1 and n_2) and densities for the mixture with different concentrations by using Abbe refractometer and precision Goniometer spectrometer using the wavelength 5893 Å in the nematic and smectic phases. Refractive indices n_1 due to extraordinary ray and n_2 due to ordinary ray have been determined. Saupe et al. [19] have used the modified Lorentz–Lorentz [20] formula for the calculation of orientational order parameters of the lyotropic mixture. The refractive indices n_1 and n_2 are given by:

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

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

where N is the number of molecules per unit volume of the mixtures, W_{GAA} and W_{TTAB} are the mole fractions of GAA and TTAB, respectively, and 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 TTAB molecules [17]. The polarizability tensor of TTAB can be approximated with principle polarizability α_1 parallel to the long axis of the molecule and α_2 perpendicular to it. The optical anisotropy ($\Delta\alpha$) contribution from acetic acid is neglected. Therefore, only $\Delta\alpha$of TTAB 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 TTAB 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 Equations (1) and (2) and using $\Delta n = (n_e - n_o) \ll 1$, we obtain

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

In order to estimate the value of optical anisotropy ($\Delta\alpha$) of TTAB molecule, the value of $(\alpha_{||})_{\mathrm{eff}}$, i.e., the polarizability along the axis of the molecules, and $(\alpha_{\perp})_{\mathrm{eff}}$, i.e., the polarizability perpendicular to the long axis of the molecule, the value of $(\alpha_{||})_{\mathrm{eff}}$ of each methylene group is calculated from the optical anisotropy of bond polarizability data for the wavelength 5893 Å [20,21], assuming that the molecules have all trans configuration, and hence $(\alpha_{\perp})_{\mathrm{eff}}$ may also be calculated. By using the values of $(\alpha_{||})_{\mathrm{eff}}$, $(\alpha_{\perp})_{\mathrm{eff}}$, and α the mean polarizability, the value of $\Delta\alpha$ is estimated [22]. The value of ($\Delta\alpha$) for TTAB 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 is 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 orientational order. However, we also note that the order parameter varies with the mole percentage of TTAB in micellar nematic phase and it is observed that order parameter (S) decreases with decreasing the concentrations of TTAB. The temperature variations of order parameter (S) of the micellar nematic phase are shown in Fig. 5, and the experimental values of order parameters are compared with the Maier–Saupe theoretical curve. It is observed that 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 [23].

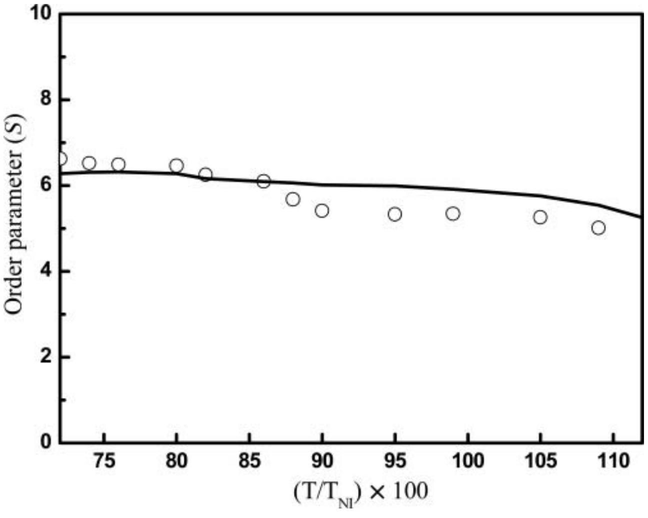

Figure 5. Temperature variation of order parameter of micellar nematic phase. The solid curve represents the Maier–Saupe theoretical curve.

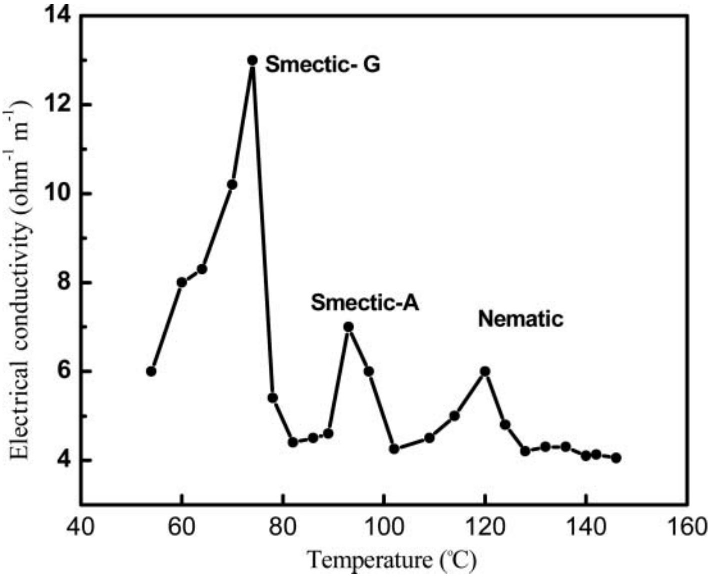

Figure 6. Temperature variation of electrical conductivity σ (Ω^{-1} m^{-1}) for the sample of 45% of TTAB in GAA.

Conductivity Measurements

To obtain reliable data on the phase behavior with temperature, electrical conductivity measurements are necessary. An abrupt increase or decrease of electrical conductivity with temperature relates to the phase behavior of lyotropic systems [24]. The temperature variation of electrical conductivity is shown in Fig. 6. Changes have been observed in the value of electrical conductivity near phase transitions. They have also been identified by DSC and optical texture studies. It was observed that there are abrupt changes in electrical conductivity at temperatures 82°C, 109°C, and 126°C, which correspond to phase transition from SmA to SmG, nematic to SmA, and isotropic to nematic, respectively. This type of behavior is observed in hexagonal phase of lyotropic system [25]. These abrupt changes cannot be thought of only due to change in the orientation of molecules. They can be attributed to changes in the dimension of disks along with changes in orientation.

Conclusion

Microscopic investigation of the binary mixture of TTAB and GAA shows the existence of Schilieren texture of micellar nematic phase, SmA, and SmG phases for all concentrations of TTAB. 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 TTAB. The drastic changes in the value of electrical conductivity with the variation of temperature unambiguously correspond to smectic and micellar nematic phases. Drastic changes in electrical conductivity are expected to be due to changes in the dimension of disks along with changes in the orientation order of the arrangement. X-ray and DSC studies also lend support to these observations. It is observed that the variation in order parameter values is in good agreement with the Maier–Saupe theoretical curve.

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