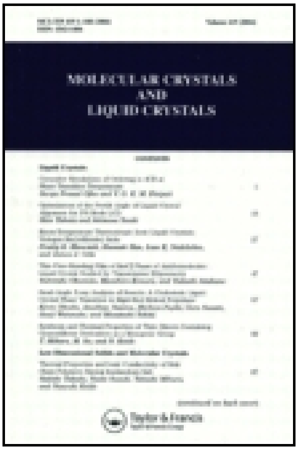

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Lyotropic Liquid Crystalline Phases in the Mixtures of Non-Mesogenic Compounds

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Lyotropic Liquid Crystalline Phases in the Mixtures of Non-Mesogenic Compounds

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We report the results of our studies on the optical and thermal properties of two non-mesogenic compounds N-Cetyl-N, N, N, trimethyl ammonium bromide (CTAB) and Glacial acetic acid (GAA). The mixture exhibits schlieren texture, which is the characteristic of micellar nematic lyophase at higher concentrations of CTAB. The Sm A and Sm E phases are occurs at lower concentration of CTAB at higher temperatures when the specimen is cooled from its isotropic phase. The order parameter of micellar nematic phase of the mixture is estimated. The temperature variation of order parameter of the experimental curve is well fitted with the Mayer-Saupe theoretical curve.

Keywords: lyotropic; mixture; non-mesogenic

INTRODUCTION

In recent years there has been an increasing interest in the study of optical, thermal and electrical properties of the mixtures of two non-mesogenic compounds [1]. The binary mixtures of the amphiphilic compounds and the organic solvents exhibit a lyotropic and thermotropic liquid crystalline phases depending on the composition of the mixtures and the temperatures. The micellar nematic phase was observed by Lawson and Flautt [2,3] in the mixture of higher concentrations of some surfactant solutions of isotropic micelles, which possess a long-range orientation order [4]. The micellar nematic phase was identified on the basis of microscopic textures. This phase is stable

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and occurs over a wide range of temperatures and compositions in the mixed system [5–7].

In the present investigation our aim is to illustrate the phase behaviour of the binary mixtures of N-Cetyl-N, N, N, trimethly ammonium bromide (CTAB) and Glacial acetic acid (GAA) which are exhibiting micellar nematic phase, smectic A (Sm A) and smectic E (Sm E) phases. We discuss the results of X-ray diffraction studies in the Sm E and Sm A phases. The birefringence and texture studies of the micellar nematic (N_D) phase are also discussed. In light of the above investigations we are able to understand the coupling between aggregate structure and mesophase order.

EXPERIMENTAL STUDIES

The compounds N-Cetyl-N, N, N, trimethyl ammonium bromide (CTAB) used in this investigation is obtained from M/s Chemie, Bombay, India and it is further purified twice by re-crystallization method using benzene as a solvent. Glacial acetic acid (GAA) supplied from Kodak Ltd., Kodak house, Mumbai, India. The mixtures of twenty-five different concentrations of mixture of lyotropic liquid crystals were prepared and are mixed thoroughly. These mixtures were kept in desiccators for 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 are sealed for a microscopic observation.

The DSC thermograms were taken for all the concentrations using the Perkin-Elmer DSC II Instrument facility available at Raman Research Institute, Bangalore, India. The DSC thermogram for the sample of 50% CTAB is shown in Figure 1. The sequential representation of phases is as follows.

$$\text{Iso } 115.2^\circ\text{C} \rightarrow N_D \; 96.9^\circ\text{C} \rightarrow \text{Sm A } 79.90^\circ\text{C} \rightarrow \text{Sm E } 54.9^\circ\text{C} \rightarrow \text{Cry}$$

The partial phase diagram is drawn, considering the transition temperatures against the concentrations of mixture of lyotropic liquid crystals as shown in Figure 2 and which illustrates the phase behavior of the concentration ranging from 32% to 73% of CTAB. The phase transition from Iso- N_D is very well accounted with the help of McMillan's Mean Field Theory [8] in the case of thermotropic liquid crystals. Chandrasekhar *et al.* [10] have also carried out the experimental studies on nematic to smectic-A transition in the nematic

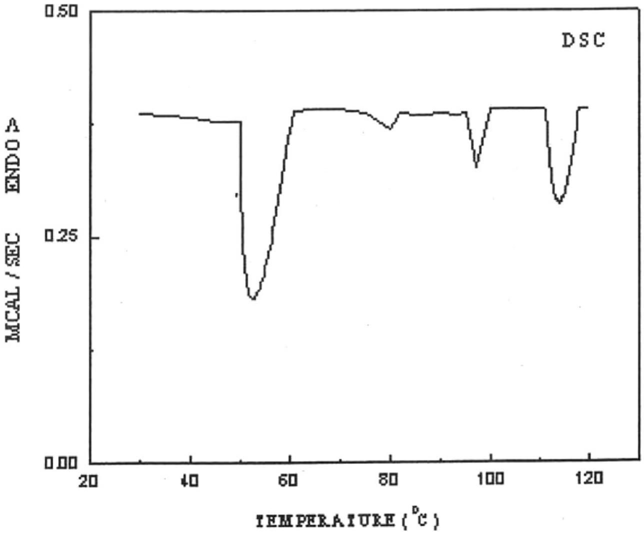

FIGURE 1 DSC thermogram for the mixture of 50% of CTAB in GAA.

mixtures and located the tricritical point, where the change of phases occurs from first order to second order. Which clearly illustrates the Iso- N_D transition is first order and micellar nematic to lamellar (L)

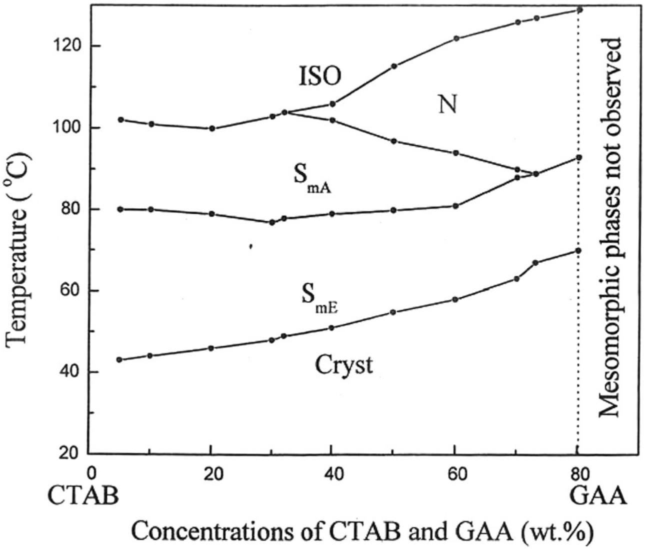

FIGURE 2 Partial phase diagram for the mixture of CTAB in GAA.

transition is second order, because of the coexistence of the phases near Iso- N_D transitions. The second order transition of N_D–L phase indicates that there is continuity in the structure of the amphiphile aggregate, therefore it infers that at N_D–L transition, the nematogenic disc shaped micelles condense on the lamellar planes instead of aggregate into infinitely extending molecular lamellae [9,11].

The X-ray diffractometer traces were obtained at room temperature using JEOL diffractometer with in the following settings: TC4, CPS400, channel width 100 for $\lambda = 1.934$ Å. The density and refractive indices in the optical region were determined at different temperatures by employing the techniques [12,13] described in the earlier investigators.

RESULTS AND DISCUSSIONS

Optical Texture Studies

The optical textures exhibited by the samples were studied 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 slip. The concentrations from 10% to 80% of mixture of lyotropic liquid crystals have been considered for the experimental studies. When the specimen of 50% CTAB is cooled from isotropic liquid phase, it exhibits and Iso - N – Sm A – Sm E – Cry phases. While the sample is cooled from isotropic liquid phase, the genesis of nucleation starts in the form of small bubbles grow radially which were identified as nematic drops as shown in the Figure 3(a). The nematic drops change over to Schlieren texture as shown in the Figure 3(b) [13–15], which is the characteristic of micellar nematic phase. On further cooling the specimen micellar nematic (N_D) phase change over to lamellar (L) phase, which is characterized by the focal conic fan texture of smectic-A phase as shown in the Figure 3(c). Before crystallizing the specimen the smectic-A phase change over to smectic E phase as shown in the Figure 3(d), where in the arcs are developed on the focal conic fans and the same texture remains up to room temperature. The micellar nematic phase has a long-range orientation order and the micelles are arranged in columns.

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

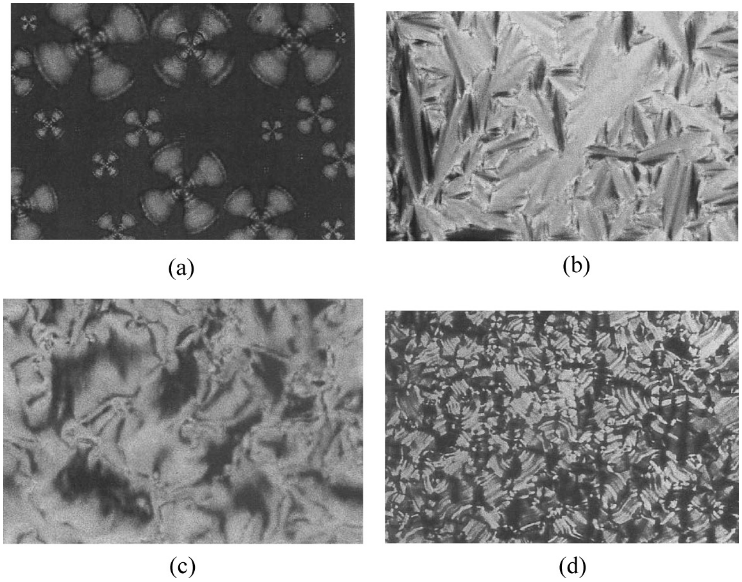

FIGURE 3 Microphotographs of (a) Nematic drops (300X); (b) Schlieren texture of micellar nematic phase (300X); (c) Focal conic fan shaped texture of Sm A phase (220X); and (d) Herring bone pattern of Sm E phase (300X).

of parallel orientation, which is responsible for the macroscopic anisotropy of the phase [18]. The birefringence study helps us to understand the optical anisotropic properties of the samples. The orientation order parameter of the nematic phase is essential to understand the degree of orientations of the micelles [11,18].

In the present investigation we have measured the temperature variation of the refractive indices n_1 and n_2 of the mixture of different concentrations of CTAB with 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. Saupe [15] used the modified Lorentz-Lorentz [19] formula for the calculation of orientation order parameters of the lytropic mixture. The refractive indices n_1 and n_2 are given by

$$(n_1^2 - 1)/(n_2^2 + 2) = 4\pi/3N\,[(W_{GAA}\,\alpha_{GAA} + W_{CTAB}\,\alpha_{CTAB}) \\ - 2/3\,(W_{CTAB}\,\Delta\,\alpha_{CTAB}\,S)]$$

$$(n_1^2 - 1)/(n_2^2 + 2) = 4\pi/3N\,[(W_{GAA}\,\alpha_{GAA} + W_{CTAB}\,\alpha_{CTAB}) \\ - 1/3\,(W_{CTAB}\,\Delta\,\alpha_{CTAB}\,S)]$$

Where, N is the number of molecules per unit volume of the mixtures and W_{GAA} and W_{CTAB} are the mole fractions of GAA and CTAB respectively, α is the mean polarizability of the respective compounds. For the estimation of orientation order parameter of the micellar nematic phase, we assume only the birefringence Δn of the CTAB molecules [17]. Because the polarizability tensor of CTAB 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 CTAB molecules is considered, $\Delta\alpha = (\alpha_1 - \alpha_2)$ and $S = ½[3\cos^2\theta - 1]$ is the degree of order of the CTAB molecules where θ is the angle between the long molecular axis and optic axis of the molecular disc in the micellar nematic phases. $\mathrm{Cos}^2\theta$ is the average over the molecular motion.

From the above equations and using $\Delta\alpha = (n_e - n_0) \ll 1$ we obtained

$$\Delta n = [2\pi(n_2^2 + 2)^2 (N\Delta\alpha W_{CTAB}\, S]/9n_2$$

Where N is the number of molecules of CTAB in unit volume.

In order to estimate the value of optical anisotropy ($\Delta\alpha$) of CTAB molecule, the value of $(\alpha_{||})_{eff}$ i.e., the polarizability along the axis of the molecules and $(\alpha_\perp)_{eff}$ the polarizability perpendicular to the long

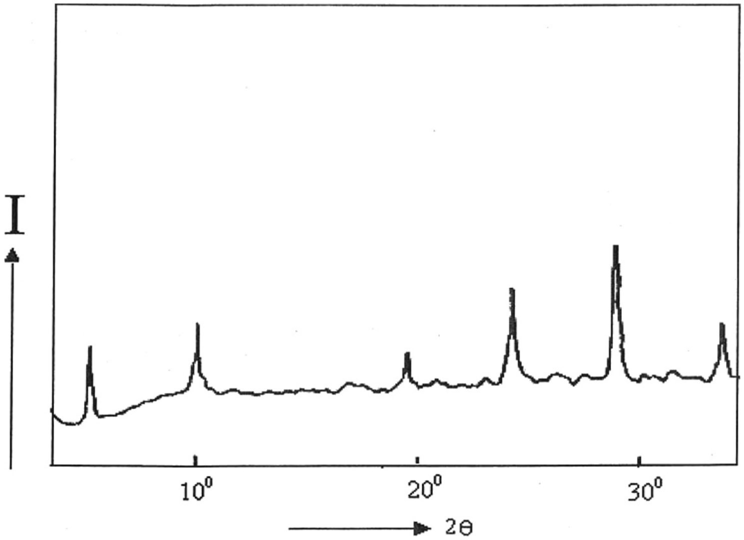

FIGURE 4 X-ray diffraction pattern of Sm E phase for the mixture of 50% of CTAB in GAA at room temperature.

axis of the molecule, the values of $(\alpha_{\|})_{\mathrm{eff}}$ of each methylene group is calculated from the optical anisotropy of bond polarizability data for the wavelength 5893 [20,21] assuming that the molecules have all transconfiguration and hence $(\alpha_{\perp})_{\mathrm{eff}}$ may also calculated. 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 CTAB molecules turns out to be $5.25 \times 10^{-24}\,\mathrm{cm}^3$. 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 on the orientation order. However, we also notice that the order parameter varies with mole percent of CTAB in the micellar nematic phase. It is observed that the order parameter S decreases with decreasing the concentrations of CTAB. The temperature variations of order parameter of the micellar nematic phase are shown in Figure 5, the experimental values of the order parameters are compared with the Maier – Saupe theoretical curve. It is observed that the trend of variation of order parameters S values agrees with the Maier – Saupe

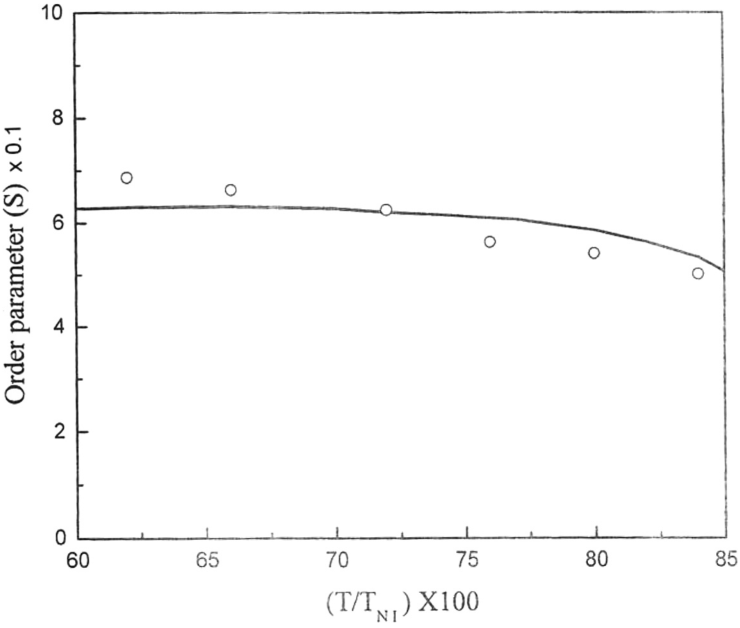

FIGURE 5 Temperature variation of order parameter of miceller nematic phase. The solid curve represents the Maier-Saupe theoretical curve.

TABLE 1 X-Ray Data of 50% of CTAB in GAA at Room Temperature

h	k	l	2θ (obs)	2θ (cal)	Cell parameter
1	0	0	4.000	4.244	a = 20.2080 Å
0	1	0	5.250	5.260	b = 16.7870 Å
2	1	0	10.000	9.996	c = 5.1392 Å
2	0	1	19.250	19.248	$\alpha = 90.000°$
3	2	1	24.000	24.000	$\beta = 90.000°$
2	4	1	28.750	28.751	$\gamma = 90.000°$
6	4	0	33.500	33.499	
			Unit cell volume = 1794.65 Å^3		

theoretical curve. The values of birefringence are in good agreement with the values measured using the interference techniques [16].

X-Ray Diffraction Studies

The X-ray recording has been obtained for the mixture of 50% of lyotropic liquid crystals at the room temperature as shown in the Figure 4, the recordings at these temperatures corresponds to Sm E phase. The X-ray recording is carried out using JEOL (Japan) make with the following settings of voltage 35 kV, current 15 mA, frequency 400 HZ, TC4 and channel width 100 and $\lambda = 1.934$ Å. The cell parameters are obtained by trial and error method. Here the programme starts with an initial set of parameters (a, b, c, α, β, γ) and refines these set of parameter until all the observed X-ray reflections (h, k, l) were identified. Thus the parameters obtained are given in the Table 1 and it gives the volume of unit cell as 1794.65 Å^3, which is the approximated volume of the micelles.

CONCLUSIONS

The micellar nematic lyophases are very useful solute hosts. These general micellar properties are combined with anisotripic orientational effects arising from the shape of the aggregation and magnetic properties. The microscopic investigation allows us to differentiate the three phases Iso - N_D – Sm A – Sm E. The phase behaviour is discussed with the help of the phase diagram, which illustrate that the schlieren texture of micellar nematic (N_D) lyomesophase exhibits at higher concentrations of CTAB and Sm A, Sm Ephases occur at lower and higher concentrations of CTAB at higher temperatures. X-ray and Optical texture studies lend support to the mentioned above facts.

REFERENCES

[1] Saupe, A. (1984). *Navocemento.*, *3*, 16.
[2] Lawson, K. D. & Flautt, T. J. (1967). *J. Amer. Chem. Soci.*, *89*, 5489.
[3] Black, P. J., Lawson, K. D., & Flautt, T. J. (1967). *Mol. Cryst. Liq. Cryst.*, *7*, 201.
[4] Ramesh, V. & Labes, M. (1986). *J. Amer. Chem. Soci.*, *108*, 4643.
[5] Saupe, A. (1977). *J. Collidal Interface Soci.*, *58*, 549.
[6] Chandrashekar, S. (1977). *Liquid Crystals*, Cambridge University Press: London.
[7] Boden, N., Bushby, R. J., Jolley, K. W., Holemes, M. C., & Sex, I. (1987). *Mol. Cryst. Liq. Cryst.*, *152*, 37.
[8] Boden, N., Jackson, P. P., Mc Millan, K., & Holemes, M. C. (1979). *Chem. Phys. Letts.*, *65*, 476.
[9] Boden, N. & Holemes, M. C. (1984). *Chem. Phys. Letts.*, *109*, 1.
[10] Raja, V. N., Krishnamurthy, K. S., Shankar Rao, D. S., & Chandrashekar, S. (1992). *Liq. Cryst.*, *12*, 2239.
[11] Larson, B. D. & Litster, J. D. (1984). *Mol. Cryst. Liq. Cryst.*, *113*, 13.
[12] Nagappa, Nataraju, S. K., & Krishnamurthy, D. (1986). *Mol. Cryst. Liq. Cryst.*, *133*, 31.
[13] Thim, J., Vill, V., & Fischer, F. (1989). *Mol. Cryst. Liq. Cryst.*, *170*, 79.
[14] Yu, L. J. & Saupe, A. (1980). *Phys. Rev. Letts.*, *45*, 1000.
[15] Saupe, A., Boonbrahm, P., & Yu, L. D. (1983). *J. Chem. Phys.*, *80*, 7.
[16] Nagappa, Revannasiddaiah, D., & Krishnamurthy, D. (1983). *Mol. Cryst. Liq. Cryst.*, *103*, 101.
[17] Tom, H., Keith, R., & Saupe, A. (1981). *Mol. Cryst. Liq. Cryst.*, *75*, 87.
[18] Boonbrahm, P. & Saupe, A. (1984). *J. Chem. Phys.*, *81*(4), 2076.
[19] Chavolin, J., Leveveiet, A. M., & Samulski, E. T. (1979). *J. Phys. Letts.* (Paris), *40*(L), 587.
[20] Leferve, G. & Leferve, R. J. W. (1972). *Physical methods of Chemistry*, Weissberger, A. & Rositer, (Eds.), Weisly International Science: New York, Part II P-437.
[21] Bunn, C. W. (1961). *Chem. Crystallography,* 2nd edition, Clarendon Press: Oxford.
[22] Somashekar, R. & Krishnamurthy, D. (1981). *Mol. Cryst. Liq. Cryst.*, *65*, 3.