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Optical and thermal studies on lyotropic nematic phase in mixture of non-mesogenic compounds

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ABSTRACT

We report the results of our studies on the optical and thermal properties of two non-mesogenic compounds, namely, N-Cetyl-N,N,N, trimethyl ammonium bromide (CTAB) and glacial acetic acid (GAA). The mixture exhibits very interesting schilieren texture of lyotropic nematic phase, smectic A (SmA), and SmE phases for all concentrations of CTAB sequentially when the specimen is cooled from its isotropic phase. The order parameter (S) of the lyotropic 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 formation of above phases has been confirmed by optical, X-ray and differential scanning calorimetry studies.

KEYWORDS

Binary mixture;
Lyotropic phase;
Non-mesogenic;
X-ray studies.

INTRODUCTION

Liquid crystals are liquid substances that exhibit anisotropic physical properties like a solid crystal, because the molecules of liquid crystal are oriented along a preference direction (the director) and additionally may possess one or two dimensional long range positional order. Since their physical properties as well as their existence of phase transition temperature regions are located between the crystalline and liquid state, this state was denoted mesophase: which came from Greek mesos means middle or liquid crystal. Hence, over the existence region of the liquid crystal phase mesomorphic materials are fluid and, at the same time, exhibit anisotropic physical properties, such as the birefringence, as well as anisotropic elasticity, viscosity and conductivity[1-4].

In the present investigation: results of our studies on the optical and thermal properties of different mixtures of compounds viz., N-Cetyl-N,N,N, trimethyl ammonium bromide (CTAB), which is non-mesogcnic in pure state but it exhibits a liquid crystalline phase when it is mixed with Glacial acetic acid (GAA). The different liquid crystalline phases have been observed using microscopic technique and these phases have been characterized with the help of X-ray and optical anisotropic studies, H'NMR and IR studies have also been carried out to understand the chemical nature of the system.

EXPERIMENTAL STUDIES

In the present investigation: we have prepared the twenty different concentrations of binary mixtures of N-Cetyl-N, N, N, trimethyl ammonium bromide (CTAB) in Glacial acetic acid (GAA) and the phase transition temperature of these mixtures were measured using Leitz.-Polarizing microscope in conjunction with hot stage and they have been verified from DSC. The mixtures were sandwitched between the slide and cover slip and are sealed for microscopic observation. XRD traces are obtained for different concentrations of CTAB in GAA by using Jeol X-ray diffractometer. The density and refractive indices of the mixtures were determined at different temperatures employing the technique[5].

OPTICAL TEXTURE STUDIES

The optical textures exhibited by the samples were observed using Leitz-polarizing microscope and in conjunction with hot stage, The lower concentrations of CTAB in the range from 20 % to 66% exhibit a schlieren texture of lyotropic nematic phase: when the specimen cooled from its isotropic phase and the texture as shown in Figure 1(a), On further cooling the specimen: the lyotropic nematic phase slowly transform to a focal conic fan shaped texture, which is the characterstic of srnectic-A phase, The smcctic-A phase is meta-stable and changes over to SmE phase as shown in Figure 1(b), wherein the arcs are developed on focal conic fans and the same texture remains up to room temperature. Whereas the lower concentrations of CTAB from 20% to 26% exhibit a micellar nematic phase and which is appears to be stable. And finally this phase is change over to SmE phase.

Figure 1(a) : Schlieren texture of lyotropic nematic phase (180X)

BIREFRINGENCE STUDIES

It is well known that; the birefringence study helps us to understand the optical anisotropic properties of the given samples. The refractive indices n_1 and n_2 of the mixtures of different concentrations are measured at different temperatures by using Abbe refractometer and precision Goniometer spectrometer. Saupe used the modified Lorenz-Lorenz formula[6] for the calculation of orientational order parameter of lyotropic/thermotropic mixture, which exhibits the micellar nematic phase. The refractive indices n_1 and n_2 are

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

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

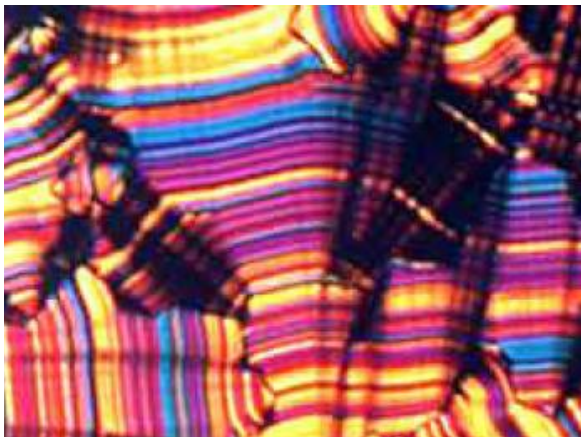

Figure 1(b) : Focal conic fan shaped texture of SmE phase (180X)

Where N is the number of molecules per unit volume of mixtures, W_{GAA} and W_{CTAB} are the mole fractions of GAA and CTAB, α is the polarizability of CTAB molecules. For the estimation of orientational order parameter for micellar nematic phase: if we assume only the birefringence(Δn) of the CTAB molecules. The optical anisotropy contribution from acetic acid is neglected.

Therefore, only $\Delta\alpha$ of CTAB molecules is considered, =and S=½[3cos²θ-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 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

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

ln order to estimate the value of optical anisotropy of CTAB molecules. The value of mean polarizability of $\alpha_{||}$ and $\alpha_{\perp}$ of the CTAB molecules is estimated using Haller Plot method.

The value of (Δα) for CTAB molecules turns out to be $5.251X10^{-24}$ cm^3. The order parameter S values the mixtures are estimated at different temperature for different concentrations. The temperature variations of order parameter of the lyotropic nematic phase as shown in Figure 2, 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[7].

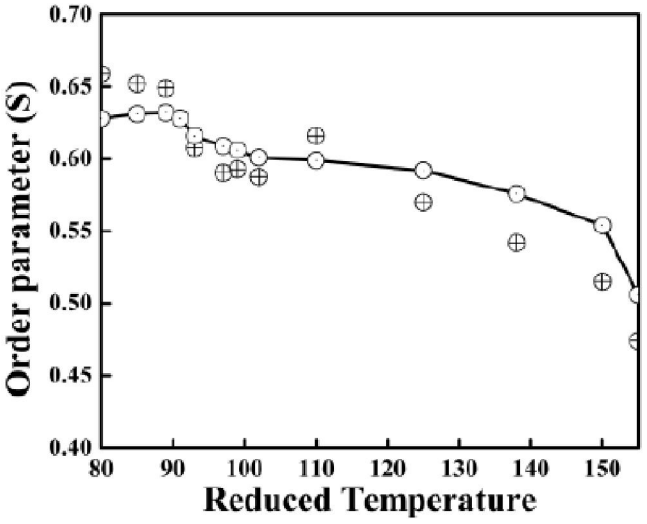

Figure 2 : Temperature variations of order parameter of micellar nematic phase

CHARACTERIZATION OF NANO AGGREGATED GRAINS

The X-ray diffractometer traces obtained for the mixture of 50% of CTAB in GAA at temperature 60 ^{0}C is shown in Figure 3. The diffraction peaks at this temperature correspond to SmE phase respectively by using JEOL diffractometer with the settings: TC4, CPS400, channel width 100 for λ = 1.934 Å). X-ray diffraction study is an important method to determine the nano-aggregated grain size of the molecules for different liquid crystalline phases[8, 9]. The deviation from perfect liquid crystallinity leads to broadening of the diffraction peaks. In order to estimate nano-aggregated grain size of the molecules for different liquid crystalline phases corresponding to broadening of X-ray diffraction peaks we have used the Scherrer's formula

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

where L is the nano-aggregated grain size, λ is the wave length of X-ray radiation (Fe: 1.934 Å), K is usually taken as 0.89, β is the line width at half maxi-

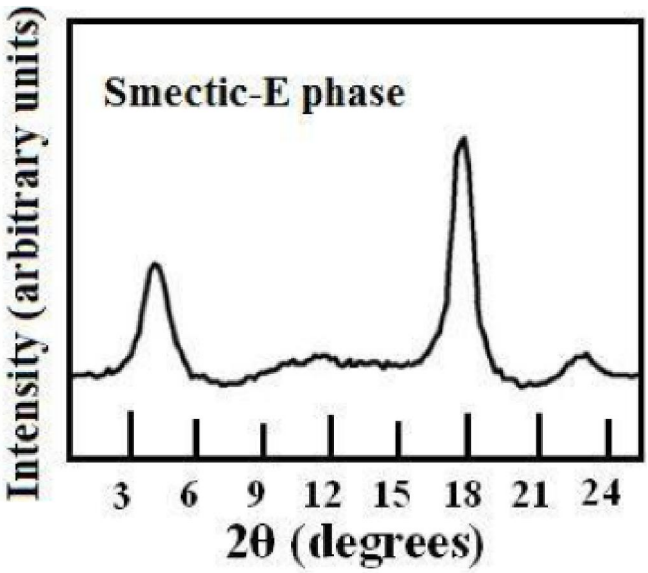

Figure 3 : XRD spectrum for the mixture of 50% of CTAB in GAA at temperature 60 ^{0}C of SmE phase

mum and θ is the diffraction angle. Usually with decrease of temperature[10, 11], the nano aggregated grain size of the molecules increases. Temperature dependent molecular orientations of radial stirrationof SmE phase is more stable and hence the molecular ordering of this phase shows three peaks. The nano- aggregated grain size of liquid crystalline material for SmE phase comes out to be 23.45 nm. From the X-ray studies, we have been observed that, molecular ordering of the liquid crystalline phase increases with decreasing temperature. X-ray studies clearly illustrate that the nano aggregated grain sizes are big enough to indicate that the molecular ordering[12-14] of layer structure increases as well as decrease the temperature.

NMR STUDIES

The H'NMR spectrum for the mixtures of 30 % of CTAB in GAA shows a broad multiplet at δ= 0.8 to 1.4 PPM due to the presence of hydrophobic methylene (l4CH2) and methylene protons (1 CH3), singlet at δ= 2.0 PPM due to Cetyl group of the acetic acid and a broad singlet at δ = 3.35 due to 3N methyl and 1NCH2 group. A peak due to hydroxyl group of acetic acid is missing in the NMR spectrum. This is clearly indicates that when CTAB mixes with acetic acid it removes one molecule of HBr forming a salt like structure.

CONCLUSIONS

The existence of micellar nematic is 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 such as lyotropic nematic phase, Smectic-A phase and Smectic-E phase. The schlieren texture of lyotropic nematic phase exhibits at higher concentrations of CTAB and SmA, SmE phases occur at lower and higher concentrations of CTAB at higher temperatures. X-ray and optical texture studies lend support to the mentioned above facts.

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