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ORIGINAL RESEARCH PAPER

Physics

OPTICAL ANISOTROPY OF GEOMETRICAL AND ORDER PARAMETER OF LYOTROPIC NEMATIC PHASE IN MIXTURE OF CETYL TIMETHYL AMMONIUM BROMIDE MOLECULES

KEY WORDS: Binary mixture: Birefringence: lyotropic nematic phase: Order parameter: Geometrical parameter

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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 anisotropic technique, By using experimentally measured data; calculations have been made to study the optical anisotropy of effective geometrical parameter, which helps to understand the order of molecules are occupied and optimized molecular designing of particular phase of oriented molecules.

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). 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 sandwiched between the slide and cover slip and are sealed for microscopic observation Refractive indices in the optical region were determined at different temperatures using multi-wavelength Abbe-refractometer (Atago:DR-M4) including constantly circulating constant bath and six interference color filters. [5].

Properties of Liquid Crystalline Phases

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.

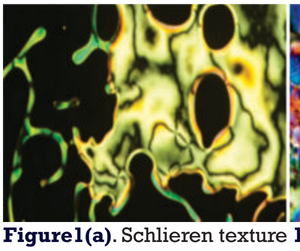

Figure 1(a). Schlieren texture of lyotropic nematic phase.

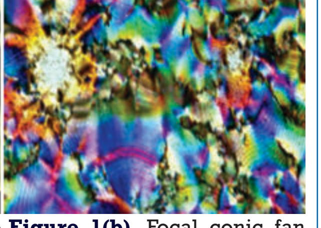

Figure 1(b). Focal conic fan shaped texture of SmE phase.

Optical Anisotropy of 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

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

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

Where N is the number of molecules per unit volume of mixtures, WGAA and WCTAB 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 αΔof CTAB molecules is considered, =)(21αα–and S=½ [3cos²-1] 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 cos² is the average over the molecular motion.

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

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

ln order to estimate the value of optical anisotropy of CTAB molecules. The value of mean polarizability of α‖ and α⊥ of the CTAB molecules is estimated using Haller Plot method.

The value of () 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].

Studies On Optical Anisotropy Of Effective Geometrical Parameter

The effective geometrical parameter represents the spreading of light on the surface of liquid crystalline material. The temperature dependent refractive indices of given non mesogenic molecules occupied an order to optimize the cell designing of particular phase of oriented molecules. As usually the operating temperature changes the molecular orientations of morphology of different phase of liquid crystals: which can be obtained by the following equation

$$\alpha_{eg} = \frac{n_o}{n_e}$$

It is well known that ordinary (n_e) and extraordinary (n_o) rays are varying with temperature. Hence, the effective geometrical parameter should also be temperature dependent. Consequently, transition behavior of effective geometrical parameter of liquid crystalline compounds determined based on the experimentally measured data of refractive index. Temperature dependence of effective geometrical parameter (α_{eg}) for the given binary mixture is shown in figure 3. From the figure: it is very clear that: the values of effective geometrical parameter increases with increasing the phase transition temperature [8-10]. Remarkably it understood: the liquid crystalline properties of rod or disc shaped long chain organic molecules molecules shows the existence of intermolecular irregularities increases with increasing the temperature and hence it move towards the nematic phase of liquid crystal. At the isotropic region, the effective geometrical parameter (α_{eg}) eaches a unity, this is because: the lower molecular orientation of the material. Due to the higher sensitivity of $n_e(T)$ to the temperature variation than that of $n_o(T)$, effective geometrical parameter (α_{eg}) slightly increases usually as the temperature increases and that reaches unity as the operating temperature approaches an isotropic phase transition temperature.

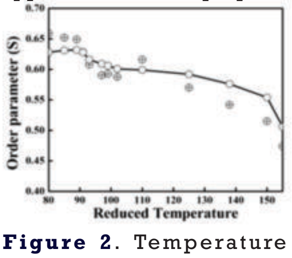

Figure 2. Temperature variations of order parameter of micellar nematic phase.

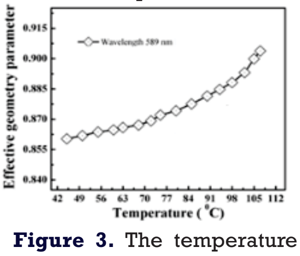

Figure 3. The temperature dependence of effective geometrical parameter (α_{eg}) for the binary mixture of CTAB in GAA

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 (14CH2) 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 [11-14].

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. The effective geometrical parameter of liquid crystalline phase has also been discussed with the help of refractive index data. The optical anisotropy of effective geometrical parameter helps to understand the order of molecules are occupied and optimized molecular designing of particular phase of oriented molecules.

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