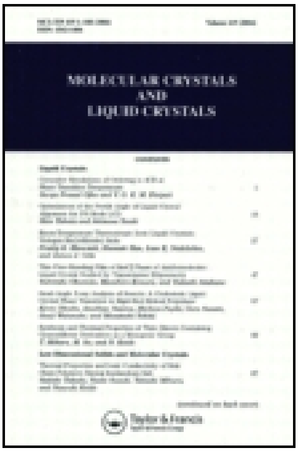

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Magnetic Susceptibility Studies on a Ternary Lyotropic Liquid Crystal System

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We have carried out mass diamagnetic susceptibility studies on (SdS)/decanol/water system for two different concentrations of the constituents namely 41.6/6.6/51.8 wt% and 35.47/7/57.5 wt%. This system exhibits calamitic nematic (N_c), isotropic (I) and hexagonal phases (H) on heating from room temperature. We find the isotropic phase susceptibility is temperature dependent at low temperatures and temperature independent at high temperatures. The susceptibility in the nematic phase of sample 1 is temperature independent while that of sample 2 is temperature dependent. We find marked differences in the diamagnetic anisotropy of these two samples. We infer that this may be related to the difference in the shape of the micelles in these samples. We also report the changes in the nematic phase susceptibility in the sample 1 on dispersing a small amount of carbon nanotubes.

Keywords Diamagnetic anisotropy; magnetic susceptibility; micelles; ternary lyotropic liquid crystal

1. Introduction

Lyotropic liquid crystals are mixtures of amphiphilic molecules and water, which exhibit liquid crystalline phases under proper temperature-concentration conditions [1]. The basic units of these systems are anisotropic micelles [2]. Unlike the thermotropic liquid crystals, magnetic susceptibility studies on these lyotropic liquid crystal systems are rarely found in the literature. Stefanov and Saupe first reported the magnetic susceptibility measurements on the nematic and isotropic phases of a ternary lyotropic liquid crystal system consisting of decylammonium chloride, ammonium chloride and water for two different concentrations of the constituents [3]. In this system, the micelles were disk shaped and in the nematic phase (N_d) it exhibited negative diamagnetic anisotropy. They measured the principle susceptibility perpendicular to the optical axis. The temperature and concentration dependence of susceptibility is very weak and they attributed the isotropic phase susceptibility to that of bulk water. We recently reported magnetic susceptibility studies on the nematic and isotropic phases of a binary lyotropic liquid crystal system consisting of cesium perfluorooctanoate (CsPFO) and water for various concentrations of CsPFO [4]. The micelles in this system were disk shaped and in the nematic phase (N_d) it

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exhibited positive diamagnetic anisotropy. In this binary system, we found a strong concentration and temperature dependence of the mass diamagnetic susceptibility and attributed this to the changes in the micellar sizes and shapes, order and water bound to the micelles [4,5]. In the present paper, we report the mass diamagnetic susceptibility studies on sodium decyl sulfate (SdS)/water/decanol liquid crystal system which exhibits isotropic (I), calamitic nematic (N_c) and hexagonal (H) phases on heating from room temperature [6,7]. The micelles in this system are rod shaped (prolate micelles) and exhibit positive diamagnetic anisotropy in the calamitic nematic phase. In general, we find slope changes in the magnetic susceptibility in the vicinity of the phase transition temperatures. We have evaluated the diamagnetic anisotropy in the nematic phase (N_c) from the susceptibility data.

2. Experimental

We used the lyotropic liquid crystal system consisting of sodium decyl sulfate (SdS), decanol and water. The chemicals SdS and decanol were procured from sigma Aldrich and used as it is without any further purification. The susceptibility measurements were carried out on two different concentrations of the constituents namely, SdS/decanol/water = 41.6/6.6/51.8 wt% (sample 1) and SdS/decanol/water = 35.4/7/57.5 wt% (sample 2). The calamitic nematic-isotropic transition temperatures (T_{NI}) were 40 and 44.6°C for the samples 1 and 2 respectively and the corresponding isotropic–hexagonal transition temperatures (T_{IH}) were 48 and 56°C. Octadecylamine (ODA) functionalized high purity SWCNTs (P5-SWNT) were procured from Carbon Solutions Inc. (USA) and used as it is.

Oxygen was removed from the millipore water by bubbling dry nitrogen gas through it for several hours. This water was added to the required amount of SdS and mixed thoroughly and then decanol was added slowly. This three component mixture was gently sonicated in an ultrasonic bath for few minutes for homogeneous mixing. For doped sample, 0.056 wt% of SWCNTs were dispersed in the ternary lyotropic liquid crystal by means of ultrasonication. Differential scanning calorimetry (DSC) studies were carried out using a Perkin-Elmer DSC-7 instrument under N_2 gas flow. The data was collected while heating the samples at the rate of 5°C/min. Typically about 5.2 mg of the sample was taken in a Perkin Elmer DSC sample cup and sealed to prevent evaporation of water using standard procedure. This sealed sample was used for susceptibility measurements.

The diamagnetic susceptibility χ relates the induced magnetic moment **M** (per unit mass), and the applied field **H** [8]

$$M_\alpha = \chi_{\alpha\beta} H_\beta; \alpha, \beta = \mathrm{x, y, z}, \tag{1}$$

where $\chi_{\alpha\beta}$ denotes an element of the susceptibility tensor χ. Choosing the z-axis along the director, the tensor corresponding to the nematic phase is give by

$$\chi = \begin{pmatrix} \chi_\perp & 0 & 0 \\ 0 & \chi_\perp & 0 \\ 0 & 0 & \chi_{||} \end{pmatrix}, \tag{2}$$

where the subscripts || and ⊥ refer to the directions parallel and perpendicular to the director, respectively. The average mass susceptibility is given by

$$\chi = \frac{1}{3}\sum_{\gamma} \chi_{\gamma\gamma} = \frac{1}{3}(\chi_{||} + 2\chi_{\perp}). \tag{3}$$

The average mass susceptibility is equal to the isotropic phase susceptibility and hence the magnetic anisotropy can be defined as

$$\Delta\chi = \chi_{||} - \chi_{\perp} = 3/2(\chi_{||} - \bar{\chi}). \tag{4}$$

We measured the magnetic susceptibility by the classical Faraday-Curie method. The energy U of the sample of mass m and magnetic susceptibility χ when kept in horizontal magnetic field H_x is given by

$$U = -(m\chi\ H_x^2)/2. \tag{5}$$

The vertical force F_z exerted on this sample is given

$$F_z = \chi m H_x \left(\frac{dH_x}{dH_z}\right). \tag{6}$$

$F_z = \Delta Mg$, where ΔM can be considered as the extra mass measured by the balance due to the force exerted by the field gradient, and g is the acceleration due to gravity. For $\Delta\chi > 0$, the field causes a uniform alignment of the director along the direction of the field, and χ can be measured. A measurement of χ in the isotropic phases gives the value of $\bar{\chi}$.

We used a Faraday balance (Oxford Instruments) to measure the susceptibility as a function of temperature. The details of our experimental set up and the measurement of the sample susceptibility is given else where [4]. The susceptibility measurements were carried out while heating the sample from room temperature.

3. Results and Discussion

Figure 1 shows the DSC thermogram for samples 1 (SdS/decanol/water = 41.6/6.6/51.8 wt%) and for sample 2 (35.4/7/57.5 wt%) on heating. The thermogram for samples 1 showed peaks at 40 and 48°C and for sample 2 showed peaks at 44.6 and 56°C. From the phase diagram reported for these ternary systems by Yu and Saupe [6], we identified the peaks seen in sample 2 to the calamitic nematic to isotropic and isotropic to hexagonal phase transitions respectively. Kroin etal [9] reported the calamitic nematic to isotropic transition temperature for sample 1 to be 41°C that agrees well with the peak seen for sample 1.

The mass diamagnetic susceptibility as a function of temperature for sample 1 and sampler 2 are shown in Figure 2. We find slope changes in the susceptibility-temperature plot at 40°C and 50°C for sample 1 which corresponds to the nematic-isotropic and isotropic-hexagonal phase transition temperatures respectively. For sample 2, a slope change is seen at 55°C which corresponds to its

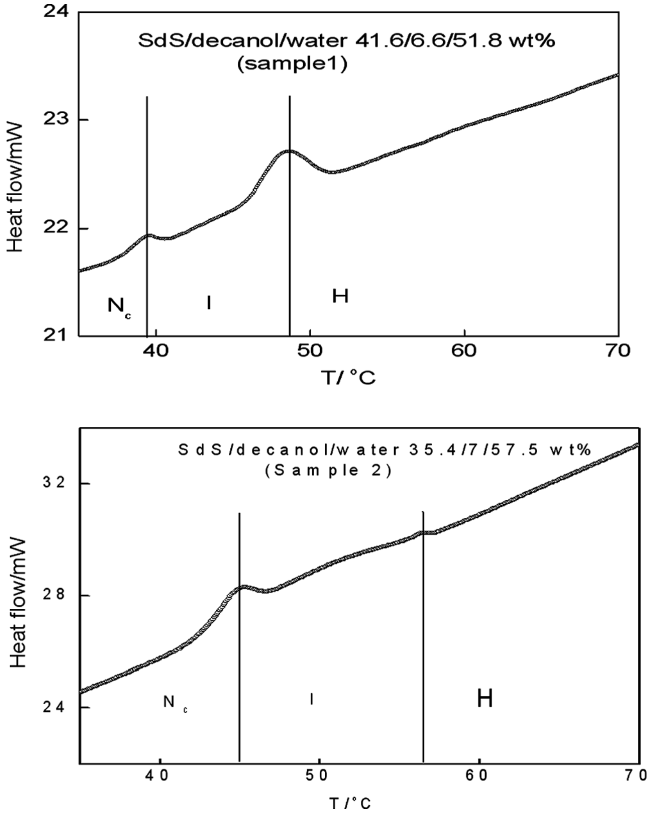

Figure 1. DSC thermograms for sample 1 and sample 2 on heating the samples.

isotropic-hexagonal phase transition temperature and the susceptibility exhibits a continuous behavior in the N-I transition temperature region.

The susceptibility in the isotropic phase of sample 1 exhibits temperature dependent behavior at low temperature and temperature independent behavior at higher temperatures. Similar temperature dependence of susceptibility is seen in the isotropic phase of sample 2 as shown in the inset of Figure 2. Yu and Saupe [6] for Sds/decanol/water (35.4/7/57.5 wt%) sample observed that the phase immediately after the nematic-isotropic phase transition temperature is an admixture of isotropic and lamellar phases which on further heating results in a pure isotropic phase. Based on this observation, we attribute the temperature dependent susceptibility to the two phase co-existence (isotropic and lamellar) and the constant or temperature independent susceptibility to the pure isotropic phase respectively.

Usually, in lyotropic nematic liquid crystals, the susceptibility exhibits a distinct but small discontinuous change near the nematic-isotropic transition temperature [3,4]. In our ternary samples, the isotropic phase consists of two regions: in the low temperature region the susceptibility is temperature dependent and at high temperature region the susceptibility is temperature independent. These two regions correspond to the admixture and pure isotropic phases respectively. In our samples, the nematic to isotropic transition involves a phase transition from nematic to the

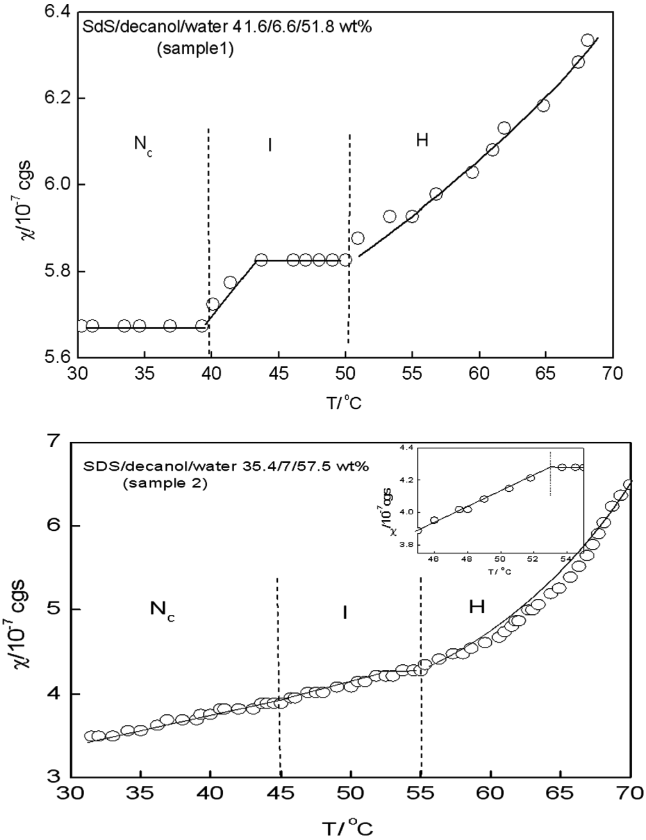

Figure 2. Mass diamagnetic susceptibility (χ) as a function of temperature on heating for sample 1 and sample 2. The solid lines are guide to the eyes. Slope changes are seen in the vicinity of N$_c$-I transition temperature of sample 1 and I-H transition temperatures of both the samples. The isotropic region of sample 2 is shown separately in the inset.

admixture isotropic phase unlike the usual samples where the phase transition is from nematic to a pure isotropic phase. We believe that the susceptibility is not very sensitive to the nematic - admixture isotropic phase transition. In the vicinity of such a transition, the susceptibility exhibits a slope change as seen in sample 1 or exhibits a continuous change as seen in sample 2 depending on the dominance of this admixture phase over the pure isotropic phase in the isotropic region. For example, in sample 1, the admixture phase exists only for a small temperature range and susceptibility at the N-I transition temperature exhibits a slope change. For sample 2, the admixture phase exists for a larger temperature range (as seen from the inset of Fig. 2) and the N-I transition is continuous.

For both the samples, a slope change is seen at the isotropic to hexagonal phase transition temperature (T_{IH}). In the H-phase, the susceptibility increases markedly with increasing temperature. This temperature dependent susceptibility may be due to increase in the hexagonal ordering of the micelles and/or due to the changes in the aggregation number (sizes) of the micelles. Our earlier susceptibility studies on (ionic) CsPFO micelles revealed that the susceptibility in general, is inversely related to the sizes of the micelles [4]. Assuming that such correlation exists for the (ionic) SdS micelles also, we infer that the susceptibility increase with increasing temperature in the hexagonal phases of our samples may be mainly related to the decrease in the sizes of the micelles. Interestingly, reported fluorescence studies on a binary system consisting of sodium dodecyl sulfate(SDS)/water showed that the aggregation number of the SDS micelles decreases with increasing temperature [10].

Figure 3 shows the temperature dependence of susceptibility for sample 1 doped with a small amount of (0.056 wt%) SWCNTs. The susceptibility in the nematic phase of the doped sample increases with increasing temperature unlike the temperature independent behavior seen in the pure sample. In the isotropic phase, the susceptibility increases with increasing temperature through out the isotropic region. This indicates that the pure isotropic phase may be absent in the doped sample. We are unable to calculate the diamagnetic anisotropy for this sample as we infer that the pure isotropic phase is absent in this sample. The inset of Figure 3 shows exclusively the temperature dependence of susceptibility in the nematic and isotropic phases of this sample. A very small discontinuous change in susceptibility is discernible at the nematic-isotropic transition temperature.

Diamagnetic anisotropy ($\Delta\chi$) in the nematic (N_c) phase of samples 1 and 2 is evaluated from the susceptibility data by using Eq. (4). For the value $\bar{\chi}$, we have substituted the temperature independent pure isotropic phase susceptibility value in Eq. (4). Figure 4 shows the temperature dependence of diamagnetic anisotropy in the N_c region for sample 1 and sample 2. The anisotropy of sample 1 is nearly temperature independent and its value (0.2×10^{-7} cgs) agrees well with that reported through an indirect measurement of diamagnetic anisotropy in the same sample concentration [9].

For sample 2, the anisotropy decreases with increasing temperature. Its value at room temperature is about six times higher with respect to that of the sample 1. The

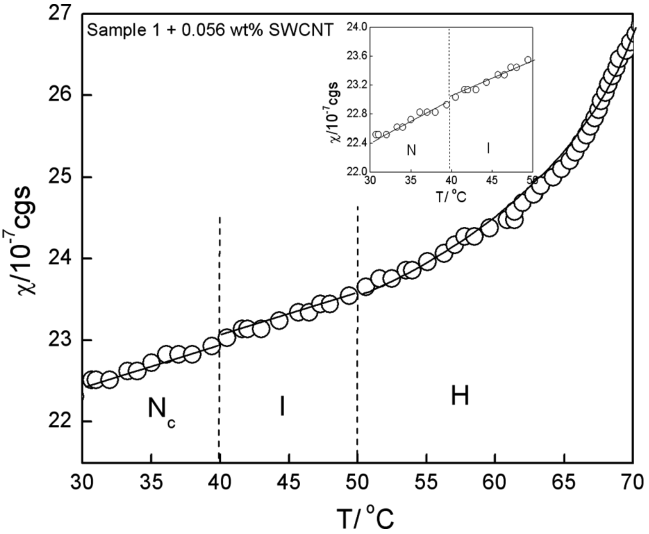

Figure 3. Mass diamagnetic susceptibility (χ) as a function of temperature on heating the sample 1 doped with 0.056 wt% SWCNTs. Nematic and isotropic regions of the doped sample is shown separately in the inset. A very small discontinuous change of susceptibility at the N-I transition temperature is discernible.

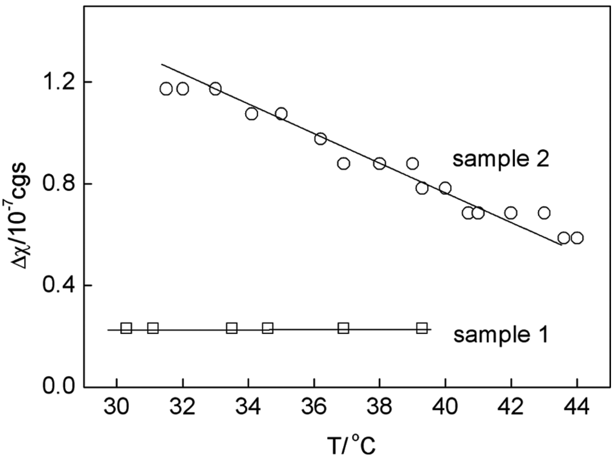

Figure 4. Diamagnetic anisotropy ($\Delta\chi$) in the calamitic nematic phase (N_c) as a function of temperature for sample 1 and sample 2. A marked enhancement in $\Delta\chi$ is seen for the sample 2 with respect to that of sample 1. The solid lines are guide to the eyes.

increase in the shape anisotropy of the micelles in sample 2 due to higher concentration of decanol and lower concentration of SdS may be responsible for this observation. For example, neutron scattering studies on a ternary lyotropic liquid crystal system namely, pottasium laurate/decanol/water showed that the alcohol and the soap (potassium laurate) molecules are not uniformly distributed in the micelle and are located mainly in the flat and curved parts of the micelles respectively [11]. We infer that, increasing the concentration of alcohol increases the flat portion of the micelles and decrease in the concentration of SdS decreases the curved portion of the micelles. The resulting changes in the micellar shape lead to an increase in the shape anisotropy (length to diameter ratio) of these prolate micelles.

4. Conclusions and Perspectives

We have carried out mass diamagnetic susceptibility studies on a ternary lyotropic liquid crystal system SdS/decanol/water for two different concentrations of the constituents. We infer that the temperature dependence of susceptibility is related to that of the sizes and ordering of the micelles. We find slope changes in the susceptibility – temperature plot at the liquid crystalline phase transition temperatures. We have evaluated the diamagnetic anisotropy in the calamitic nematic phase from the susceptibility data. We find the diamagnetic anisotropy and its temperature dependence markedly depend on the concentrations of the constituents. We infer that this can be related to the changes in the shape anisotropy of the micelles. We dispersed a small amount of SWCNTs on one of these samples. We find changes in the temperature dependence of susceptibility in the nematic and isotropic phases of the doped sample with respect to that of the pure sample. In general, these magnetic studies will help to understand the micellar systems better. Further, the knowledge of diamagnetic anisotropy in these systems is interesting not only from fundamental point of view but also for technological reasons.

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