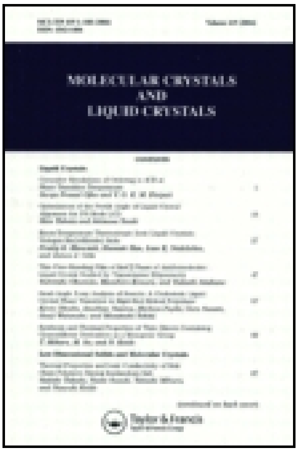

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Observation of Hysteresis in the Properties of a Ternary Lyotropic Liquid Crystal System

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Observation of Hysteresis in the Properties of a Ternary Lyotropic Liquid Crystal System

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We have carried out differential scanning calorimetry (DSC), electrical conductivity and mass diamagnetic susceptibility studies on sodium decylsulfate(SdS)/ decanol/water system for two different concentrations of the constituents. In these concentrations, this system exhibits calamitic nematic (N_c), isotropic (I) and hexagonal (H) phases on heating from the room temperature. On heating the samples, the DSC thermograms exhibit two peaks which can be related to the reported N_c-I and I-H phase transition temperatures. However, on cooling from a high temperature they do not exhibit any peak. The temperature dependence of electrical conductivities and magnetic susceptibilities of these samples are also different while heating and on cooling. Based on our reported correlation between the susceptibility and micellar sizes in an ionic micellar system, we infer that the observed hysteresis behavior in the susceptibility in this system is related to the difference in the temperature dependence of the micellar sizes on heating and on cooling. The electrical conductivity in these ternary systems is related to the mobility of the counter ions which in turn depends on the viscosity of water. Hysteresis seen in the conductivity may be related to the changes in the viscosity of water due to the difference in the temperature dependence of the micellar sizes on heating and cooling. Incidentally, in water based nanofluids, the sizes of the suspended nanoparticles have profound influence on the viscosity of water.

Keywords Electrical conductivity; hysteresis; magnetic susceptibility; micelles; viscosity of water

1. Introduction

Lyotropic liquid crystalline phases are mostly exhibited by surfactant molecules dissolved in water under proper temperature-concentration conditions [1]. The basic units of these systems are anisotropic micelles [2]. Lyotropic liquid crystals find diverse applications from ordinary soaps to biophysics and in oil recovery. Their applications mainly depend on the concentration of the constituents and temperature. Therefore, it is imperative to understand their phase behavior as a function of concentration and temperature. We have carried out differential scanning calorimetry (DSC), mass diamagnetic susceptibility and electrical conductivity of a ternary lyotropic liquid crystal system consisting of SdS/decanol/water as a function

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of temperature for two different concentrations of the constituents. In these concentrations, this system exhibits calamitic nematic (N_c), isotropic (I) and hexagonal (H) liquid crystalline phases on heating from room temperature. Yu and Saupe reported a detailed phase diagram for this system on heating for various concentrations of the constituents [3]. DSC is often used to study the phase transition temperatures of lyotropic liquid crystal systems. Electrical conductivity of lyotropic liquid crystal systems are widely used as it is a readily accessible transport property [4–7]. It is determined by the diffusion of the current carrying ions through the mesophase structure and is therefore, potentially useful in the investigations of mesophase structures and phase transitions. Magnetic susceptibility studies on 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 [8]. They find the temperature and concentration dependence of susceptibility is very weak and they attributed the isotropic phase susceptibility to that of bulk water. We reported magnetic susceptibility studies on the nematic and isotropic phases of a binary liquid crystal system consisting of cesium perfuorooctanoate (CsPFO) and water for various concentrations of CsPFO [9,10]. In this binary system, we found a strong temperature and concentration dependence of mass diamagnetic susceptibility and attributed this to micellar aggregation number, ordering and water bound to the micelles. In this paper we report the temperature dependent hysteresis in the thermal, electrical and magnetic properties of this ternary lyotropic liquid crystal system (SdS/decanol/water). We infer that the hysteresis is mainly due to the changes in the viscosity of water brought about by the changes in the sizes of the micelles on heating and cooling cycles.

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. DSC, magnetic susceptibility and electrical conductivity 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. 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. Differential scanning calorimetry (DSC) studies were carried out using a Perkin-Elmer DSC-7 instrument under N_2 gas flow. The data was collected by varying the sample temperature at the rate of 5°C/min. A Faraday balance (Oxford Instruments) was used to measure the magnetic susceptibility of the sample. The details of our susceptibility measurements were described else where [9]. 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. Electrical conductivity measurements were carried out on unaligned samples with heating/cooling rate of 2°C/min using a conductivity meter PC TESTr35 (Eutech Instruments, Singapore).

3. Results and Discussion

Figure 1a shows the DSC thermogram for sample 1 for both heating and cooling. On heating from room temperature, the DSC thermogram exhibits two peaks at 40 and 48°C which can be related to the N_c-I and I-H phase transition temperatures. Nc-I transition temperature agrees well with that reported by Kroin *et al.* [11]. However, on cooling from high temperature, it does not exhibit any peak indicating the absence of the liquid crystalline phases. Figure 1b shows the mass diamagnetic susceptibility as a function of temperature for sample 1. On heating, the susceptibility of the sample increases with increasing temperature. It exhibits slope changes near N_c-I and I-H phase transition temperatures. On cooling, the susceptibility increases with decrease in temperature. On further decrease in temperature, the susceptibility exhibits a constant value and decreases rapidly near room temperature. Figure 1c shows the electrical conductivity as a function of temperature for sample 1. On heating, in the nematic phase, the conductivity of the sample increases and exhibits a maximum in the vicinity of N_c-I transition temperature. In the isotropic and hexagonal phases, it increases slowly. On cooling, conductivity decreases rapidly and exhibits a nearly constant value with small increase near room temperature.

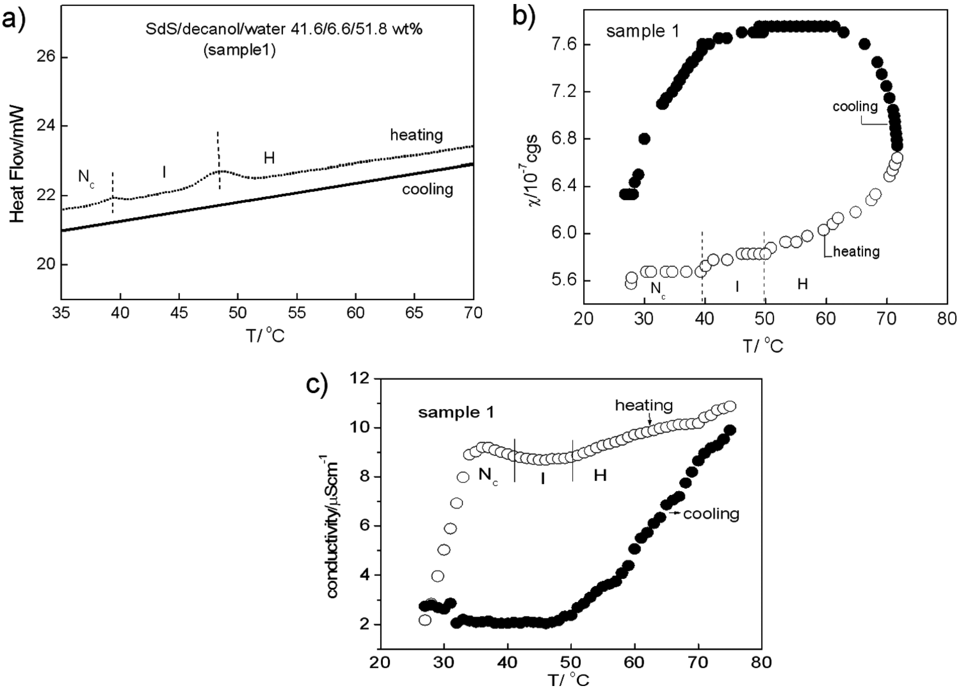

Figure 1. DSC thermogram for sample 1 (a), mass diamagnetic susceptibility (χ) as a function of temperature for sample1 (b), electrical conductivity as a function of temperature for sample 1 (c).

Figure 2a shows the DSC thermogram for sample 2. For this sample also, on heating, two peaks at 45 and 56°C are seen in the DSC thermogram corresponding to N_c-I and I-H transition temperatures. These transition temperatures agree well with those reported by Yu and Saupe in their phase diagram [3]. (They observed that on heating the sample, the isotropic phase immediately after the nematic phase (N_c) is an admixture phase consisting of nematic and lamellar phases which on further heating leads to a pure isotropic phase followed by an hexagonal phase). However, on cooling, we find the DSC peaks are absent. Figure 2b shows the mass diamagnetic susceptibility as function of temperature for sample 2. The temperature dependence of magnetic susceptibility of sample 2 is similar to that of sample 1. Figure 2c shows the electrical conductivity for sample 2. On heating, in the nematic and hexagonal phases, it decreases and in the isotropic phase it increases slowly. In the vicinity of the I-H transition temperature it exhibits a discontinuous change. On cooling, the conductivity decreases initially, exhibits a constant value and increases again.

Malliaris *et al.* reported the temperature dependence of the micellar aggregation number for various kinds of ionic, nonionic and zwitter ionic surfactants using fluorescence studies [12]. They found that in the case of ionic micelles, the aggregation number decreases with increasing temperature. Our magnetic susceptibility studies on ionic CsPFO micelles revealed an inverse correlation between the aggregation number and the diamagnetic susceptibility [9]. Combining these two results on ionic

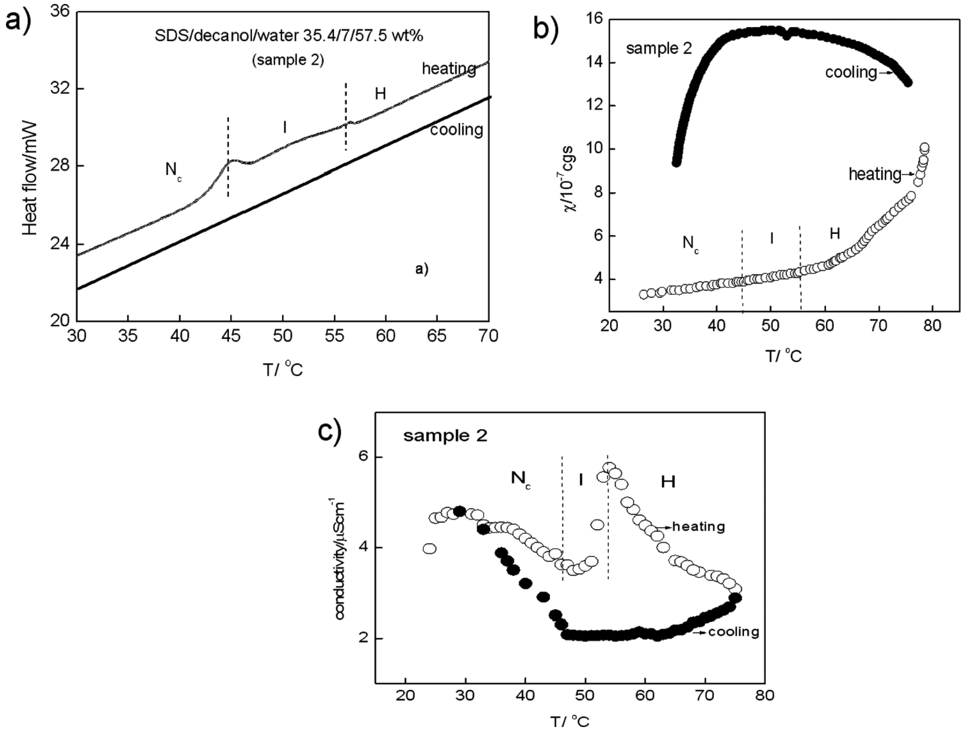

Figure 2. DSC thermogram for sample 2 (a), mass diamagnetic susceptibility (χ) as a function of temperature for sample 2 (b), electrical conductivity as a function of temperature for sample 2(c).

micelles, we infer that the increase in the susceptibility on heating the samples 1 and 2 may be related to the decrease in the aggregation number of the ionic SdS micelles. Consequently, the temperature dependent hysteresis seen in the susceptibility may be related to the hysteresis in the aggregation number or the sizes of the micelles.

In general, a major component to the temperature variation of the conductivity in lyotropic liquid crystal systems is due to the variation of viscosity of water with temperature [4–7]. This affects the motion of the counter ions, which are the effective charge carriers in these systems. For sample 1, on heating, the conductivity increases with increasing temperature and exhibits a peak in the vicinity of N-I transition temperature. This observed temperature dependence of conductivity in sample 1 on heating is similar to that seen in many lyotropic liquid crystal systems before correcting for the viscosity of water [4,7]. This shows that the temperature dependence of conductivity is mainly related to that of the viscosity of water in sample 1. We believe that the hysteresis seen in the conductivity may be related to the hysteresis in the viscosity of water.

For sample 2, the temperature dependence of conductivity on heating is different with respect to that of sample 1. The conductivity decreases with increasing temperature in the nematic and hexagonal liquid crystalline phases. This indicates that the conductivity in this sample is related to the ordering of the micelles. Interestingly, similar temperature dependence of the electrical conductivity after applying correction for the temperature dependence of viscosity of water is reported for the nematic phases of a ternary liquid crystal system (potassium laurate/ decanol/water) aligned in a magnetic field [7]. Sample 2 has higher concentration of decanol and lower concentration of SdS with respect to that of sample 1. This can lead an enhancement in the shape anisotropy of the micelles in sample 2. 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 [13]. 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 can lead to an increase in the shape anisotropy (length to diameter ratio) of these prolate micelles. This increase in the shape anisotropy may lead to an increase in the ordering of the micelles in the liquid crystalline phases. Therefore, the difference in the conductivity behavior seen in sample 1 and sample 2 on heating may be related to the difference in the ordering of the micelles in the liquid crystalline phases of these samples. In sample 1, the ordering is weak and the temperature dependence of conductivity is mainly due to the viscosity of water. As the ordering is strong in sample 2, the temperature dependence of conductivity is mainly related to the ordering of the micelles. However, on cooling, for both the samples, the temperature dependence of conductivity is related to that of viscosity of water as the liquid crystalline phases are absent on cooling in both the samples as seen from our DSC thermograms (Figs. 1a and 2a).

We believe that the observed hysteresis in the conductivity is related to the temperature dependent hysteresis in the viscosity of water. We also infer that the temperature dependent hysteresis in the magnetic susceptibility is related to the hysteresis in the aggregation number or the sizes of the micelles. Therefore, on the one hand, we find the susceptibility hysteresis is related to the hysteresis in the aggregation number of the micelles. On the other hand, we find the conductivity hysteresis is related to the hysteresis in the viscosity of water. This indicates that the changes in the micellar sizes may be responsible for the changes in the viscosity of water. Interestingly, in water based nanofluids, the sizes of the suspended nanoparticles have profound influence on the viscosity of water [14]. In these systems it is reported that smaller the sizes of the nanoparticles, higher is the viscosity of water. Interestingly, we have also used similar micellar size dependent viscosity of water to understand our experimental observations.

4. Conclusions

We have carried out DSC, mass diamagnetic susceptibility and electrical conductivity studies on a ternary lyotropic liquid crystal system of SdS/decanol/water for two different concentrations of the constituents. We find a temperature dependent hysteresis in their thermal, magnetic and electrical properties. DSC peaks corresponding to the liquid crystalline phase transition temperatures are seen while heating. However, on cooling no peaks are seen indicating the absence of liquid crystalline phases. We attribute the hysteresis in the magnetic susceptibility to the hysteresis in the sizes of the micelles and the hysteresis in the electrical conductivity to the hysteresis in the viscosity of water. We infer that the changes in the aggregation number or the sizes of the micelles on heating and cooling cycle influences the viscosity of water and this can lead to the hysteresis in the electrical conductivity of this system. It is reported that in the water based nanofluids, the sizes of the suspended nanoparticles have profound influence on the viscosity of water.

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