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Nano Molecular Self Assembly in the Formation of Induced Mesomorphism in Mixture of ChCl, DTAC, and EG

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ABSTRACT

The multi-component system of cholesteryl chloride (ChCl), dodecyl trimethylammonium chloride (DTAC), and ethylene glycol (EG) exhibits very interesting liquid crystalline mesophases like cholesteric and SmA, SmC, and SmB phases sequentially when the specimen is cooled from its isotropic phase. These phases have been characterized by employing optical and X-ray studies. Pitch of the cholesteric phase has been calculated and discussed. Variation of pitch from the cholesteric phase to smectic phase is smooth and continuous. The temperature variation of optical anisotropy and electrical-conductivity has also been discussed. It has been found that wherever there is a phase transition, the value of electrical susceptibility changes appreciably.

KEYWORDS

Molecular orientation; nano molecular aggregation; optical anisotropy; pitch; temperature dependence

Introduction

Liquid crystals, named as mesophases, which are pure organic substances, in aqueous solutions, are capable to reach a special state of aggregation, intermediary between liquid state and solid state. They preserve both the flow proprieties of a liquid and the ordering of crystal and exhibit multiple anisotropies. The existent domain is named as mesomorphic and it is defined by two distinct temperatures situated at its limits; the lower one is the melting point at the solid-state border and the higher one is the clearing point upon which the isotropic liquid state begins.

Pure organic substances providing liquid crystals properties and reach the mesomorphic domain by varying temperature have been named as thermotropic liquid crystals. Other organic substances, in aqueous solutions, reach the mesomorphic domain by varying temperature and concentration and have been named as lyotropic liquid crystals. Depending on the molecular orientation, these two types of liquid crystals may show number of specific structures [1–3]. Hence the transition from the solid state to the liquid isotropic state is not a single one, but a succession of transitions passing by several thermodynamically stable phases. The microscopic investigation may be considered as one of the most important tool for the identification and the ulterior classification of different liquid crystalline phases.

The molecules of thermotropic liquid crystals are able to orient themselves with the long axis parallel to a certain direction. By consequence, they can exist in a series of different structures such as nematic, smectic, or cholesteric phases [4]. Each of them is defined by some

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ordering particularities: the nematic phase has a molecular parallel ordering but the structure is not stratified; the smectic phase has a planar stratified structure and the cholesteric phase has a helicoidal structure. Thermotropic liquid crystals are of great interest as a research topic in physics and chemistry and have found applications in many other domains such as optical devices, nondestructive testing of materials and medicine.

Molecular species able to form lyotropic liquid crystals, also called amphiphilic or surfactants, have two distinct parts very much unlike as solubility. One part is hydrophilic, with a high solubility in polar solvents, while the other one is hydrophobic, with a high solubility in hydrocarbon. This part of the molecule consists of long linear or ramified hydrocarbon chains with or without benzene cycles. This is a good reason to imagine such a molecule as a little sphere representing the hydrophilic "head" continued with a long zigzag "tale" representing the hydrophobic chain. Conforming to the nature of the hydrophilic part, the amphiphilic molecule may belong to one of the following types: ionic, nonionic or zwitterionic. In solution, at certain concentrations, the amphiphilic molecules form aggregates with different shapes, which become structural units and by ordering lead to specific structures, such as lamellar, cubic, hexagonal, nematic or cholesteric. Parameters describing the lyotropic mesomorphism are investigated by multiple experimental techniques such as optical microscopy in polarized light, neutron scattering or fluorescence quenching. Complementary investigations about molecular organization and motion in lyotropic liquid crystals can be obtained from X-ray structural analysis and from magnetic resonance studies of deuterated compounds.

It has been found some organic materials pass through intermediate states between solid and liquid; these states are called mesophases. Attention has to be paid towards the study of these mesophases because they enable display devices and have become commercially important through the so-called liquid-crystal technology. Phase diagrams are used to describe the occurrence of mesophases [2].

In the present investigation, our aim is to study the multi-component system of mesogenic and nonmesogenic compounds, namely, cholesteryl chloride (ChCl), dodecyl trimethylammonium chloride (DTAC) and ethylene glycol (EG), which exhibits liquid crystalline cholesteric and smectic phases, like SmA, SmC, and SmB phases, respectively at different temperatures. They were observed using microscopic technique and also have been verified from the results of X-ray and optical anisotropic technique.

Experimental studies

In the present study, mixtures of twenty different concentrations of ChCl in (DTAC+ EG) were prepared by taking the compounds by weight percent - ranging from 5wt% to 55 wt% of ChCl in (DTAC+EG), and they were mixed thoroughly. DTAC used in this investigation was obtained from the Basic Pharma Life Science, P. Ltd., India. It was further purified twice by recrystallization in benzene. Other two compounds were supplied by M/s SISCO Research Laboratory, Mumbai, India. Purity of the samples is 98%. These mixtures of different concentrations were kept in desiccators for 6 hrs. Samples were subjected to several cycles of heating, stirring, and centrifuging to ensure homogeneity. Phase transition temperatures of these mixtures were measured with the help of a Leitz-polarizing microscope and conventional hot stage. The samples were sandwiched between the slide and cover slip and were sealed for microscopic observations. The density and refractive indices of the mixtures were measured at different temperatures employing the technique described in our earlier paper [5]. Electrical conductivity measurements at different temperatures were carried out using digital LCR

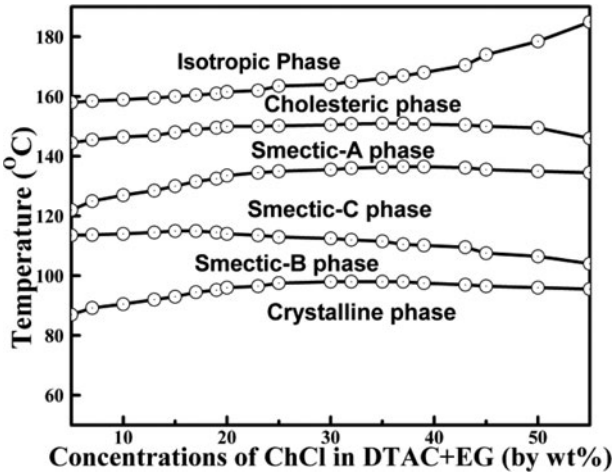


Figure 1. Phase diagram for the different mixtures of ChCl in (DTAC+EG).

meter and a proportional temperature control unit. The X-ray diffraction studies were undertaken by using JEOL-X-ray diffractometer (with the settings: TC4, CPS400, channel width 100 for $\lambda = 1.934$ Å - Fe Kα).

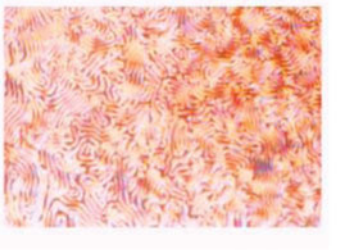
Results and discussion

Phase diagram

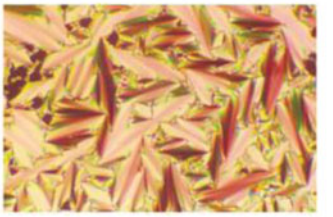
The multi-component system of ChCl in DTAC+ EG exhibits a different liquid crystalline phases, the phase transition temperatures was measured by using Leitz-polarizing microscopic. The partial phase diagram shown in Figure 1 and it is obtained by plotting the concentrations against the phase transition temperatures of the multi-component system, clearly illustrates that, the mixtures with concentrations ranging from 5% to 55% of ChCl in DTAC+ EG exhibit cholesteric and smectic phases, such as SmA, SmC and SmB phases sequentially when the specimen is cooled from isotropic liquid phase.

Optical texture studies

For the purpose of optical texture studies, the sample was sandwiched between slide and cover glass and then optical textures were observed using Leitz-polarizing microscope in conjunction with specially constructed hot stage. The mixtures were slowly cooled from the isotropic melt. The genesis of nucleation starts in the form of small bubbles and slowly grows radially, which forms a fingerprint pattern of cholesteric phase with large values of pitch as shown in Fig. 2(a) [6, 7]. On further cooling, the cholesteric phase slowly changes over to focal conic fan-shaped texture, which is the characteristics of SmA phase and is shown in Fig. 2(b). Sequentially on further cooling, SmA phase changes over to SmC phase and then it changes over to SmB phase, then it becomes a crystalline phase at room temperature.



a) Fingerprint pattern of cholesteric phase (250X).



b) Focal conic fan shaped texture of SmA phase (250X).

Figure 2. Microphotographs obtained in between the crossed polars, (a) Fingerprint pattern of cholesteric phase (250X). (b) Focal conic fan shaped texture of SmA phase (250×).

Optical anisotropy

Results of this investigation are further supported by the optical studies. The refractive indices for extraordinary ray (n_e) and ordinary ray (n_o) of the given mixture were measured at different temperatures for the different mixtures using Abbe Refractometer and Precession Goniometer Spectrometer. The temperature variations of refractive indices for 30% of ChCl in DTAC+ EG are shown in Fig. 3. The values of electrical susceptibility for 30% of ChCl in DTAC+ EG have been calculated using Neugebauer relation [8] at different temperatures.

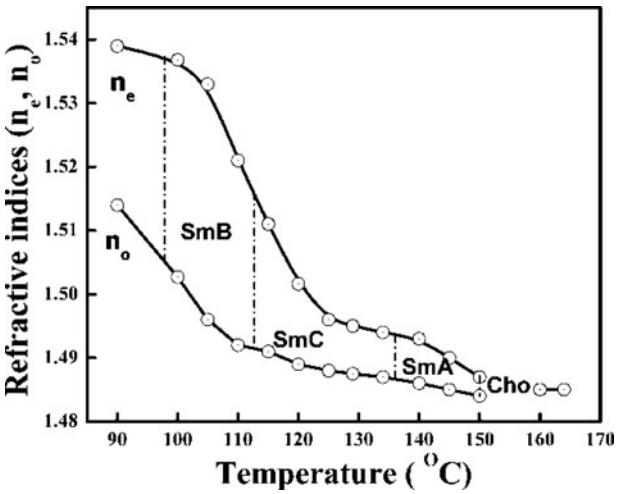


Figure 3. Temperature variations of refractive indices for the mixture of 30% ChCl in (DTAC+EG).

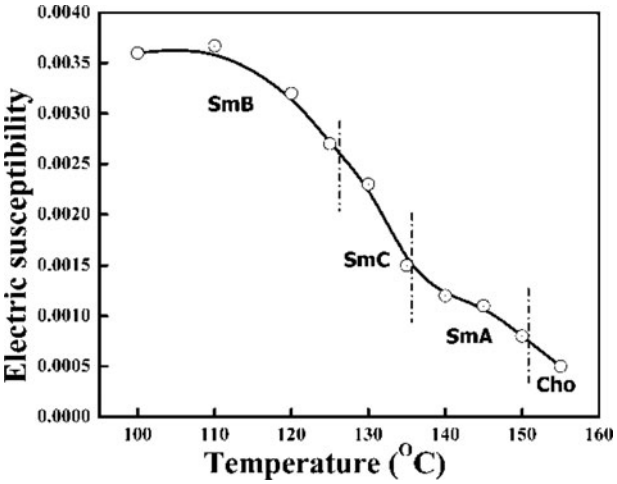


Figure 4. Temperature variation of electric susceptibility for the mixture of 30% ChCl in (DTAC+EG).

The temperature variations of electrical susceptibility for the mixtures are as shown in Fig. 4. From the figure, it can be observed that wherever there is a phase transition, the value of electrical susceptibility changes appreciably. Further, with increase in the concentration of ChCl in mixture of DTAC+ EG, the value of electrical susceptibility decreases with temperature. This is because; the effective optical anisotropy associated with the molecules of ChCl also decreases.

Helical pitch measurement

The helical pitch measurements were performed in the cholesteric phase using the well known Grandjean–Cano wedge method [9, 10]. The ternary mixture was taken in a wedge-shaped cell treated for homogeneous alignment. The two glass plates form a small angle at the wedge. The mixture was cooled slowly (0.2°C min^{-1}) from isotropic cholesteric phase to smectic phase, which induces an array of equidistant Grandjean–Cano lines. The pitch of the cholesteric phase was determined by measuring the distance between the Grandjean–Cano lines as a function of temperature. As the temperature was lowered from the cholesteric phase to smectic phase, spacing between the lines are increased, indicating that the pitch in the cholesteric phase are also increasing. The temperature variation of pitch for the mixture of 15% ChCl in DTAC + EG is shown in Fig. 5. From this figure, it is evident that, the variation of pitch from the cholesteric phase to smectic phase is smooth and continuous. But the value of pitch gradually increases from 0.17 mm to 0.19 mm was observed upon cooling the sample from cholesteric phase to smectic phase. The value of pitch increased steeply and reached a maximum of 0.52 mm at the cholesteric to smectic phase transition. But, in the study, we have been notice that the sequence is Iso-Cho-SmA-SmC- SmB-Cryst on cooling. Most of the data about the helical pitch have been previously given in reference [11]. The pitch is continuous at cholesteric to SmA transition in spite of a rather energetic transition. It increases on cooling to smectic phase and diverges on approaching the SmA, SmC, and SmB phases. This divergence is related to the second order nature of the transition. It exhibits a steep decrease, close to cholesteric phase, which is usually a characteristic of second-order SmA–SmC transition.

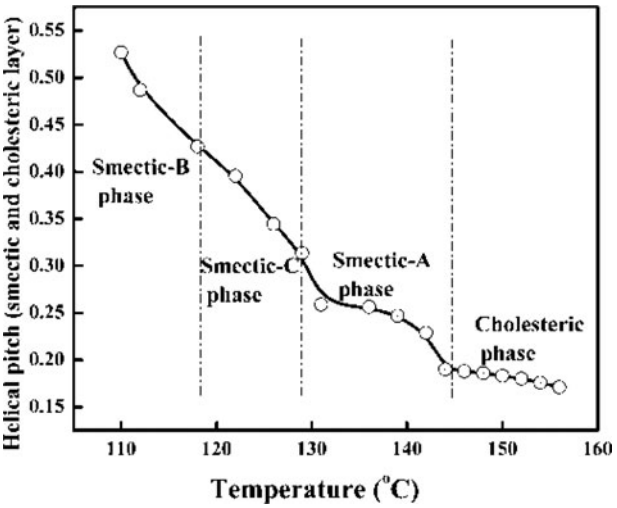


Figure 5. Temperature variations of pitch for the mixture of 15% ChCl in (DTAC+EG).

Conductivity measurement

Electrical-conductivity measurements are helpful in the study of phase behavior with temperature. An abrupt increase or decrease of electrical-conductivity with temperature relates to the phase behavior of lyotropic, thermotropic and also chromonic systems [12]. The temperature variations of electrical-conductivity in the present study are as shown in Fig. 6. The figure clearly illustrates that there is increase in the value of electrical conductivity up to 112°C, while cooling from isotropic phase for the mixture of 30% ChCl. With further decrease in temperature, the electrical conductivity starts decreasing as we move towards the room temperature. The decrease in the value of electrical conductivity is observed only after further cooling the specimen below 112°C. This suggests that, the size of aggregates starts growing towards decreasing temperature and the system moves toward more orderliness. Finally, below 112°C

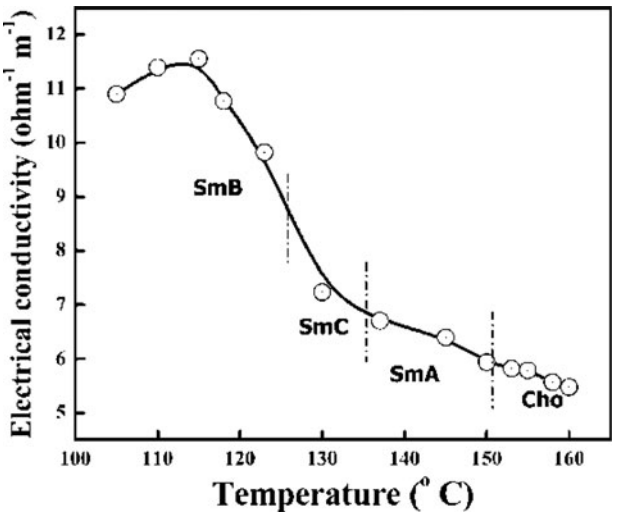


Figure 6. Temperature variation of electrical-conductivity σ (Ω^{-1} m^{-1}) for the sample with 30% of ChCl in (DTAC+EG).

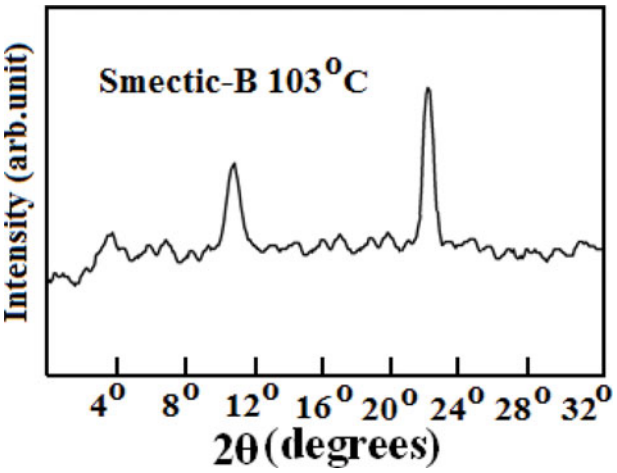


Figure 7. XRD traces obtained for the mixture of 30 % ChCl in (DTAC+EG).

size of aggregates becomes so large that the specimen starts moving towards crystalline nature [13, 14].

Characterization of nano aggregated grains

The X-ray diffractometer traces obtained for the mixture of 30% ChCl at temperature 103°C is shown in Fig. 7. The diffraction peaks at this temperature correspond to smectic-B phase (by using JEOL diffractometer with the settings: TC4, CPS400, channel width 100 for $\lambda =$ 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 [15, 16]. The X-ray traces obtained for the perfect liquid crystals would extend in all directions to infinity, so we can say that no crystal is perfect due to its finite size. The deviation from perfect liquid crystallinity leads to a 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 (1.934 Å), K is usually taken as 0.89, β is the line width at half maximum and θ is the diffraction angle. With decrease of temperature [17, 18], the nano aggregated grain size of the molecules increases. From Fig. 7, we have observed that, the structure of molecular orientation for broken banded focal conic fan texture of smectic-B phase is energetically more stable and molecular ordering of this phase shows two peaks. The nano aggregated grain size of liquid crystalline material for smectic-B phase comes out to be 45.9nm. From this study, we have observed that, the phase transition behavior of molecular ordering of the liquid crystalline materials is increasing as we move towards lower temperature. This clearly illustrates that, nano aggregated grain size of liquid crystalline materials of different phases are big enough to indicate that the molecular ordering [19] of layer structure increases with decrease in the temperature.

Conclusions

In light of the above results, we have drawn the following conclusions. The mixtures with 5% to 55% concentrations of ChCl in (DTAC+ EG) exhibit cholesteric phase and also induced smectic phases SmA, SmC, and SmB phases, sequentially when the specimen is cooled from its isotropic liquid phase. The phase behavior is discussed with the help of phase diagram. The changes in value of electrical conductivity with temperature unambiguously correspond to smectic and cholesteric phases. With increase in the concentration of ChCl in mixture of (DTAC+ EG), the value of electrical susceptibility decreases with temperature since the effective optical anisotropy associated with the molecules of ChCl also decreases. Electrical conductivity measurements reveal that below 100°C size of aggregates becomes so large that the specimen starts moving toward crystalline nature. X-ray studies help us to found the nano aggregated grain size are 45.9 nm.

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