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Thermodynamical response of optical anisotropy on polymorphic smectic-phases in a binary mixture of liquid crystalline materials

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ABSTRACT

The binary mixture of two non-mesogenic compounds, namely: dodecyl trimethylammonium chloride (DTAC) and ortho-phosphoric acid (H_3PO_4) exhibits very interesting liquid crystalline smectic phases at large range of concentrations and temperature. The mixture with lower and higher concentrations of DTAC exhibits SmA, SmD, SmB and SmE phases, sequentially when the specimen is cooled from its isotropic phase. Different liquid crystalline phases observed in the mixture were studied using optical microscopic techniques. The temperature variation of optical-anisotropy has been discussed. Thermodynamical response of electrical susceptibility has also been discussed to understand: the phase stability, chemical structure and molecular dynamics of the binary mixture of liquid crystalline materials.

KEYWORDS

Polymorphic smectic phases;
Optical studies;
Susceptibility;
Thermodynamical studies;
Molecular segregation;
Temperature dependence.

INTRODUCTION

A material designated as a liquid crystal has a liquid crystal phase. This is a phase between solid and liquid which only appears in certain materials, also called mesogenic materials. The liquid crystalline phases can be subdivided by the amount of order they possess. This is possible because the molecules show a certain orientational order, while they show no or limited positional order in various degrees. Apart from the liquid crystal phase, there is a mesophase called plastic crystal phase or disorder crystal phase[1]. In such a phase, the molecules do have positional order but lack of orientational order. The liquid crystal phases are usually divided in nematic and smectic. The former term is used when only orientational order is present in the material. The latter is used when next to orientational order also positional order is a characteristic of the material. The smectic liquid crystals themselves then are further subdivided according to their degree of order[2, 3].

In this study, we have considered the mixture of non-mesogenic compounds, namely, dodecyl trimethylammonium chloride (DTAC) and orthophosphoric acid (H_3PO_4). These mixtures show different liquid crystalline phases over a wide range of temperature. The polymorphic smectic modifications of the liquid crystalline phases were observed using microscopic technique and they have been verified from the results of optical anisotropic techniques.

EXPERIMENTAL STUDIES

The mixture of different concentrations of DTAC in H_3PO_4 was prepared and kept in desiccators for a long time. Phase transition temperatures of the mixtures with different concentrations were measured using Leitz-polarizing microscope and conventional hot stage. The sample was sandwiched between the slide and cover slip, which was sealed for microscopic observation. The sample whose refractive indices have to be determined is introduced between two prisms of the Abbe refractometer. The combination of prisms containing liquid crystalline material is illuminated by a monochromatic light (λ=5893Å). The refractometer is in conjunction with a temperature bath from which hot water can be circulated to maintain the sample at different temperatures. In the field of view, two lines of demarcation of slightly different polarization are observed. The horizontal polarization corresponds to the ordinary ray and vertical polarization is due to the extraordinary ray. By matching the cross-wire, the refractive indices of the ordinary ray and extraordinary ray are read directly. Measured refractive indices of mixtures using Abbe refractometer are compared with the results obtained by measurement using goniometer spectrometer developed by Chatelain[4]. The density and refractive indices in the optical region are determined at different temperatures by employing the techniques described by the earlier investigators[5, 6].

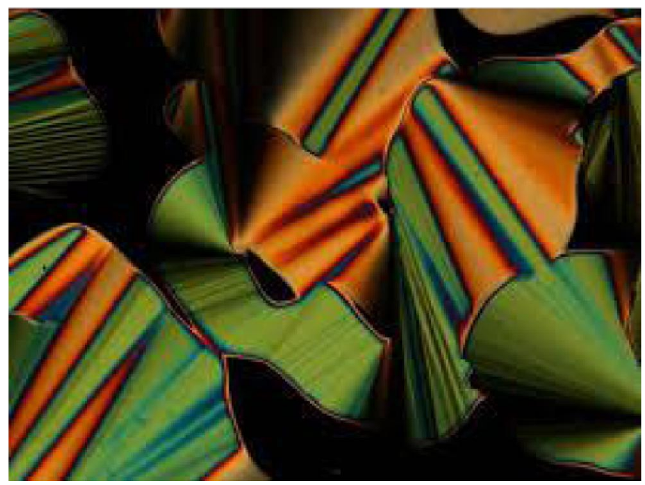
RESULTS AND DISCUSSIONS

Optical studies

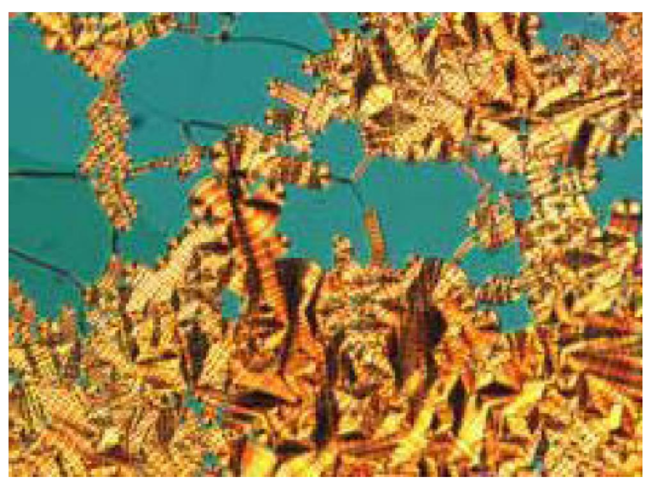
The polymorphic smectic modifications and the corresponding isotropic to liquid crystalline phase transition temperatures for the mixture with 50 % of DTAC in H_3PO_4 are given below.

I-159 ^{0}C, SmA-138 ^{0}C, SmD-127 ^{0}C, SmB-112 ^{0}C, SmE-97 ^{0}C.

On cooling, the specimen from its isotropic melt, the setting point is marked by the genesis of nucleation at several points which appear as minute bubbles initially, but which progressively grow radially and form a focal conic fan texture of SmA phase in which the molecules are arranged in layers and the texture is shown in Figure 1(a) at temperature 145 ^{0}C. This phase appears to be metastable and undergoes slow transformations to give a viscous SmD phase[7]. When the optically extinct SmD phase is submitted to the external pressure or stress by touching the cover slip over the sample, no flash or change in the birefringence was observed. This is one of the basic tests to identify the SmD phase. The isotropic lamellar viscous SmD phase is also metastable and transforms to focal conic fan-shaped texture on cooling the specimen. This texture corre-



(a) Focal conic fan-shaped texture of SmA (Lamellar) phase at temperature 145 ^{0}C



(b) Focal conic fans with radial striation of SmE phase at temperature 100 ^{0}C

Figure 1 : Microphotographs obtained in between the crossed polars

sponds to the paramorphotic[8] focal conic fan-shaped texture of highly ordered SmB phase in which the molecules are arranged in a hexagonal close-packed structure. On further cooling, focal conic fan texture with radial striation on the fans, which is the characteristics of SmE phase, is observed and it is shown in Figure 1(b) at temperature 100 ^{0}C. At this phase transition, i.e., from SmB phase to SmE phase, it is observed that there is a drastic change in the values of density and refractive index of the sample. This anomalous behavior is presumably associated with high degree of order of the molecular arrangement in SmE phase.

Optical anisotropy

Results of this investigation are further supported by the optical studies. We have measured the temperature variation of the refractive indices (n_e and n_o) for the mixture of different concentrations of DTAC and H_3PO_4 by using Abbe refractometer and precision goniometer spectrometer using the wavelength 589.3 nm in the lyotropic nematic and lamellar smectic phases. The refractive index n_e due to extraordinary ray and n_o due to ordinary ray have been determined. The temperature variations of refractive indices for 50 % of DTAC in H_3PO_4 are shown in Figure 2. The value of n_e is greater than n_o, indicating that the material is uniaxial positive. The values of electrical susceptibility for 50 % of DTAC in H_3PO_4 have been calculated using Neugebauer relation[9] at different temperatures. The variation of electrical susceptibility as a function of temperature for the mixture is shown in Figure 3. From the figure, it can be observed that wherever there is an isotropic–liquid crystalline phase transition, the value of electrical susceptibility changes appreciably, which indicates that the changes correspond to various smectic modifications. Further, with increase in the concentration of DTAC, the value of electrical susceptibility decreases with temperature because the effective optical anisotropy associated with the molecules of DTAC also decreases[10, 11].

Themodynamical response of electrical susceptibility

Studies on different mixtures of liquid crystalline materials are more important not only from the viewpoint of their technological applications but also from that of fundamental studies in the field of molecular interactions[12]. Thermodynamic studies are very important role to understand the phase stability, chemical structure and dynamics of liquid crystals[13, 14]. Temperature dependent molecular orientations of liquid crystalline phases have been considered in many technological applications. The applied applications of these technologies are based on the properties of molecular structure and intermolecular interactions. The intermolecular forces such as van der Waals interaction, hydrogen bonds, electron donor interactions and steric repulsive in-

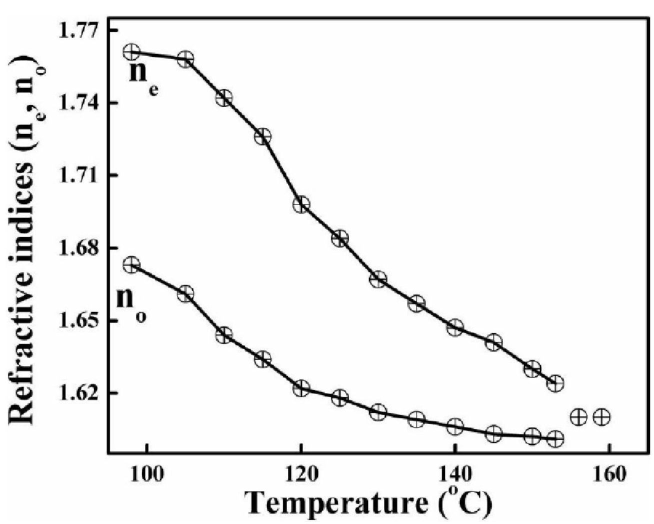


Figure 2 : Temperature variations of refractive indices for the sample of 50 % of DTAC in H_3PO_4

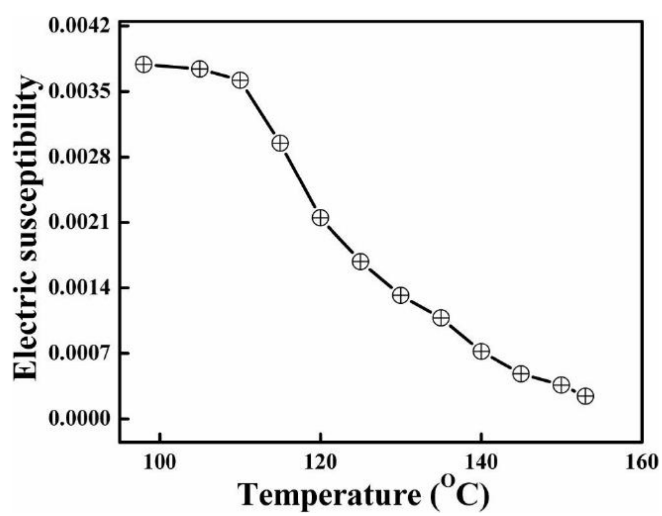


Figure 3 : Temperature variations of electrical susceptibility for the sample of 50 % of DTAC in H_3PO_4

teractions are they individually or together may be responsible for increasing or decreasing the thermal stability of liquid crystalline phase[15]. Thermodynamical studies on liquid crystalline phase at different concentrations of binary mixtures of liquid crystalline materials are estimated using Boltzmann distribution laws. Draw a graph of variations of thermodynamical response of electrical susceptibility as a function of mole fraction for the sample of DTAC in H_3PO_4 at constant temperature 88 ^{0}C is presented in Figure 4, which clearly shows, the degree of microphase separations are one of the parameters to controlling a physical properties of liquid crystalline materials[16]. In this context the existence parameter can be varied either through chemical modification or through physical modification and hence they are depends on nature of additives molecules. From the figure clearly we observed that, statistically how the electrical susceptibility is thermodynamically changes at different concentrations in order to show the thermal stability of liquid crystalline phase. Here if at constant temperature: the given molecules are fractionally varies as increasing the concentrations of the additive molecules. In this study: it is very interesting to observe a spin temperature. Due to this gradient temperature: on the surface area of liquid crystalline smectic phase, the degrees of freedom of molecules are thermodynamically varies with one mole fraction to the other. If an increasing the mole fractions for the sample of DTAC

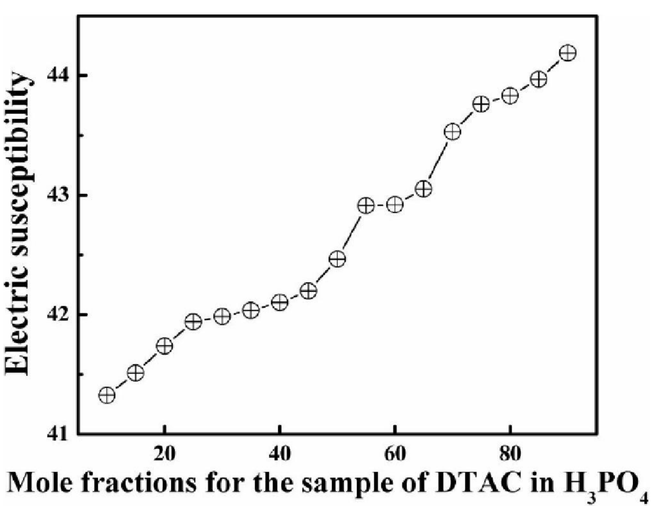


Figure 4 : Variations of thermodynamical response of electrical susceptibility as function of mole fractions for the sample of DTAC in H_3PO_4

in GAA; the value of thermodynamical response of electrical susceptibility increases with spin temperature, because the effective intermolecular interactions of anisotropic energy associated with the molecules of DTAC increases with the additive ones. The molecular ordering or the phase stability of liquid crystalline phase at given constant temperature: the intermolecular interactions of anisotropic energy are responsible for the charges of carbon and the adjacent hydrogen molecules and which shows the correct electrostatic potentials are reproduced by different partial charge distributions. If increasing / decreasing the mole fractions for the sample DTAC in GAA and hence it shows small variation of electrostatic potentials: which they around the molecule. In spite of these uncertainties, the full set of partial charges is very useful, as it can provide a detailed insight into the molecular arrangement in mesophases and they reproduce the electrostatic potential.

CONCLUSIONS

In light of the above results, we have drawn the following conclusions. The mixtures with all concentrations of DTAC in H_3PO_4 exhibit polymorphic smectic phases, such as SmA, SmD, SmB and SmE phases, sequentially when the specimen is cooled from its isotropic liquid phase. The drastic changes in the value of refractive indices/ electrical susceptibility with the variation of temperature unambiguously correspond to polymorphic smectic phases. Thermodynamical response of electrical susceptibility have also been discussed to understand: statistically how the electrical susceptibility is thermodynamically changes at different concentrations in order to show the thermal stability, phase stability, chemical structure and molecular dynamics of the binary mixture of liquid crystalline phase.

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