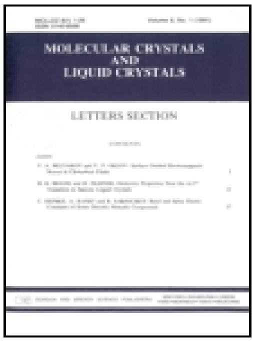

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Induced Reentrant Nematic and Smectic—A Phase in Mixture of Mesogenic and Nonmesogenic Compounds

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We report the results of our studies on the optical and thermal properties of the mixture of 4-cyano-4′-octyloxybiphenyl (80CB) and N-Cetyl-N, N, N, trimethyl ammonium bromide (CTAB) + Glacial acetic acid (GAA), which exhibits a very interesting lower temperature reentrant nematic and smectic-A phases, sequentially when the specimen is cooled from its isotropic liquid phase. The different phases of these mixtures are identified using optical and microscopic techniques. The temperature variations of optical anisotropy, Ultrasonic velocity, molar compressibility, and adiabatic compressibility have been also discussed.

Keywords Molecular orientation; optical texture and optical anisotropy; reentrant nematic; ultrasonic velocity

Introduction

Liquid crystalline material research is fascinating for both basic and technological reasons. No single mesogen has all the physical parameters in the desired range for a particular device application. This is usually achieved only by preparing a mixture of liquid crystalline compounds that have collectively the desired properties [1]. It is a common experience to obtain a uniform nematic liquid crystal by mixing two thermotropic (enantiotropic or monotropic) nematic liquid crystalline materials [2,3]. However, sometimes by mixing two nematogenic compounds, unusual phenomenon like induced smectic phase, reentrant nematic phase, etc., are also obtained [4,5]. Occasionally, the re-appearance of thermodynamic phase as the temperature is lowered and it is termed as "reentrance." Reentrant phases are common to many substances, but the reentrant nematic phase was first observed by Cladis [6] in a mixture of two liquid crystal molecules with benzene rings and a strongly polar cyano group. Specifically, a nematic phase was found at temperature above the smectic

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phase (which is the usual) and also below the smectic phases at lower temperature, which is unusual, the lower temperature nematic phase was called reentrant nematic. The higher and lower temperature of nematic phase was identified on the basis of microscopic textures. These phases are unstable and occur over a wide range of temperatures and compositions in the mixed system [7].

In the present investigation, our aim is to study the mixture of mesogenic and non-mesogenic compounds, namely, 4-cyano-4′-octyloxybiphenyl (80CB) and N-Cetyl-N, N, N, trimethyl ammonium bromide (CTAB) + Glacial acetic acid (GAA), which exhibits a very interesting reentrant nematic/smectic-A phases, respectively, at different temperature for different concentrations. They were observed using microscopic and optical anisotropic techniques. From the experimentally measured data of ultrasonic velocity, density, and refractive indices, thermodynamic and other related parameters are calculated.

Experimental Studies

In the present study, we use the materials, namely, 4-cyano-4′-octyloxybiphenyl (80CB) and N-Cetyl-N, N, N, trimethyl ammonium bromide (CTAB) + Glacial acetic acid (GAA). Mixtures of 20 different concentrations of 80CB in CTAB + GAA were prepared and they were mixed thoroughly. These mixtures of concentrations were kept in desiccators for 6 hr. 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 polarizing microscope in conjunction with a hot stage. The samples were sandwiched between the slide and cover slip and were sealed for microscopic observations. Ultrasonic velocity was measured using a single crystal interferometer working at 2 MHz with an accuracy of ±0.05%.

Phase Diagram

Mixture of 80CB in CTAB + GAA exhibits very interesting different liquid crystalline phases and the phase transition temperatures are measured by using Leitz polarizing microscope. The partial phase diagram is shown in Fig. 1, and it is obtained by plotting the concentrations against the phase transition temperatures of the given mixture, which clearly illustrates that the mixture of some concentrations of 80CB in CTAB + GAA exhibits nematic and smectic phases, such as SmA, SmG phases with lower temperature reentrant nematic and lower temperature reentrant SmA phases, respectively, at different temperatures, when the specimen is cooled from its isotropic liquid phase. The concentrations of the mixture from 5% to 24% of 80CB show a very interesting unusual behavior of lower temperature reentrant nematic and lower temperature reentrant SmA phases, respectively, at different temperatures, but in the range from 17% to 24% of 80CB, reentrant nematic phase decreases at temperature 115°C and hence the concentrations from 24% to 40% of 80CB, we observe conventional liquid crystalline phases, such as nematic, SmA, and SmG phases. The smectic-G phase remains up to room temperature.

Optical Texture Studies

The optical textures exhibited by the samples were observed and recorded using the Leitz polarizing microscope and specially constructed hot stage. The specimen was taken in the form of thin film and sandwiched between the slide and cover glass. The concentrations from 5% to 40% of ternary mixture of 80CB in CTAB + GAA have been considered

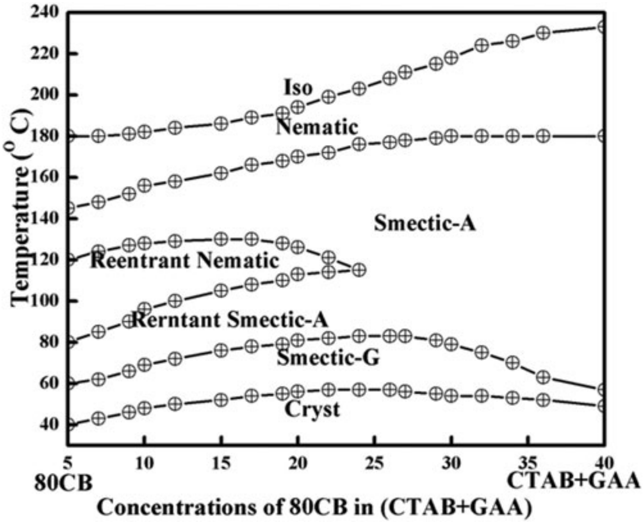

Figure 1. Partial phase diagram for the mixtures of 80CB in CTAB + GAA.

for the experimental studies. When the specimen of 20% 80CB is cooled from isotropic liquid phase, it exhibits I–N–SmA–RN–RSmA–SmG–K phases sequentially. While the sample is cooled from isotropic liquid phase, the genesis of nucleation starts in the form of small bubbles growing radially, which are identified as schlieren texture of nematic phase as shown in Fig. 2(a). On further cooling the specimen, the schlieren texture of nematic (N) phase changes over to lamellar (L) phase, which is characterized by the focal conic fan texture of SmA phase and this phase appears to be metastable and undergoes slow transformations to give a thread-like texture of nematic phase, which has been termed as the lower temperature reentrant nematic phase and this phase is shown in Fig. 2(b). On further cooling the specimen, the reentrant nematic phase was slowly changed over to bubbles in the form of battonnets, which are the characteristic of SmA phase and this phase has been termed as the reentrant SmA (RSmA) phase. Before crystallizing the specimen, the RSmA phase changes over to a broken banded focal conic fan texture of chiral SmG phase. If the constituent molecules of the materials, which exhibit an SmG phase, are of a chiral nature, then the phase itself may also be weakly optically active; it is then termed as a chiral SmG phase [8]. The structural studies have been carried out at that time on chiral SmG phases and it was originally simply presumed that the structure of the phase is similar to that

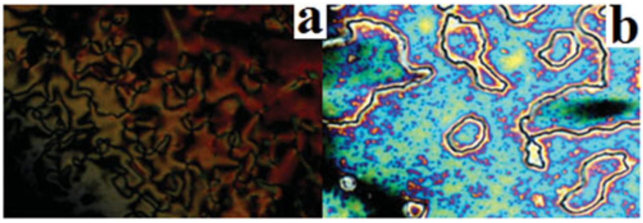

Figure 2. Microphotographs showing (a) schlieren texture of nematic phase (180X) and (b) thread-like texture of nematic phase (180X).

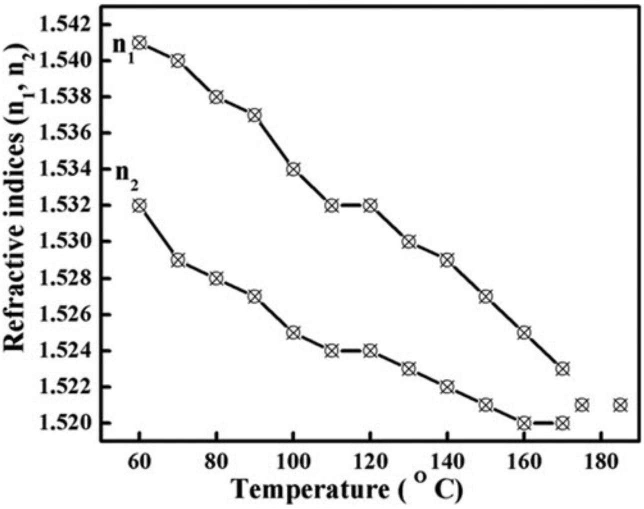

Figure 3. Temperature variation of refractive indices for the mixture of 20% 80CB in CTAB + GAA.

of chiral SmC, SmI, and SmF phases. In this case, the molecules would be hexagonally closely packed in layers within each of which tilts must be in the same direction. In the layer above and below, the tilt direction will, however, be turned through a small angle. Thus, on passing from layer to layer, the tilt direction will turn slowly either in an anticlockwise or a clockwise direction, depending upon the sign of the optical asymmetry of the system, and this would give a helical change in the tilt direction [9], and the same texture is retained up to room temperature. Whereas the concentrations from 24% to 40% of 80CB exhibit a nematic phase and this phase appears to be unstable, and finally changes over from SmA to SmG phase. The phase transition between a liquid crystal nematic phase (which has orientational order) and its smectic phase (which has both orientational and positional order) has long been studied for subtle effects that arise from the intrinsic coupling of their order parameters [10].

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 mixture were measured at different temperatures for different concentrations using Abbe Refractometer and precession Goniometer Spectrometer. The temperature variations of refractive indices for 20% of 80CB in CTAB + GAA are as shown in Fig. 3. The value of n_e is greater than n_o, indicating that the material is uniaxial positive. The values of electrical susceptibility for 20% of 80CB in CTAB + GAA have been calculated using Neugebauer relation [11] at different temperatures. The temperature variations of electrical susceptibility for the mixture are as shown in Fig. 4. 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 each change corresponds to the occurrence of different liquid crystalline phases. Further, with increase in the concentration of 80CB, the value of electrical susceptibility decreases with temperature, because the effective optical anisotropy associated with the molecules of 80CB also decreases.

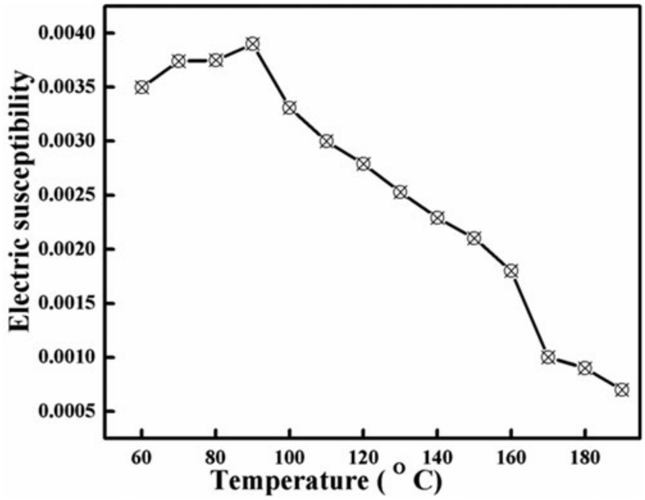

Figure 4. Temperature variation of electric susceptibility for the mixture of 20% 80CB in CTAB + GAA.

The Temperature Variations of Ultrasonic Velocity, Adiabatic, and Molar Compressibility

The mixtures of liquid crystalline materials due to their unusual behaviors have very attracted considerable attention. In order to obtain reliable data on the phase behavior with temperature, ultrasonic velocity measurements are necessary [12]. The molecular orientation in liquid crystalline materials changes with increasing the concentration of one more addictive substance and hence the attractive force between the components of the molecules is the measure of ultrasonic velocity, absorption should give the nature of attractive forces existing between the mixtures of the given molecules. Data on some of the properties associated with the like refractive index, ultrasonic velocities, and surface tension find extensive application in chemical engineering process simulation, solution theory, and molecular dynamics [13]. The temperature variation of ultrasonic velocity, adiabatic compressibility, and molar compressibility is shown in Figs. 5(a)–(c). The velocity exhibits an anomalous behavior at the isotropic mesophase transition, while it varies linearly in the isotropic and mesomorphic phase away from transition. The velocity shows a dip at the transition. The ultrasonic velocity and related parameter show anomalous behavior of isotropic mesophase transition of the liquid crystals. The ultrasonic velocity linearly increases in isotropic phase up to the transition with decreasing temperature [14,15]. The increase in velocity is explained as the decrease in mean distance between the molecules, thereby increasing the potential energy of the interaction between the molecules. The velocity reaches a minimum at the transition temperature and increases sharply below the transition, then it shows a linear increase in mesophase. The change in velocity and other parameters [16] at the transition results from disordered molecular arrangement in isotropic phase to an ordered arrangement of molecules in the liquid crystalline phase with long-range orientational order [17]. The variation of adiabatic compressibility [18] is remarkably linear in the isotropic and mesomorphic phases, but it shows a step jump at the isotropic–mesomorphic phase transition. The result of molar compressibility varies linearly with temperature at the isotropic phase transition. In this study, the higher values

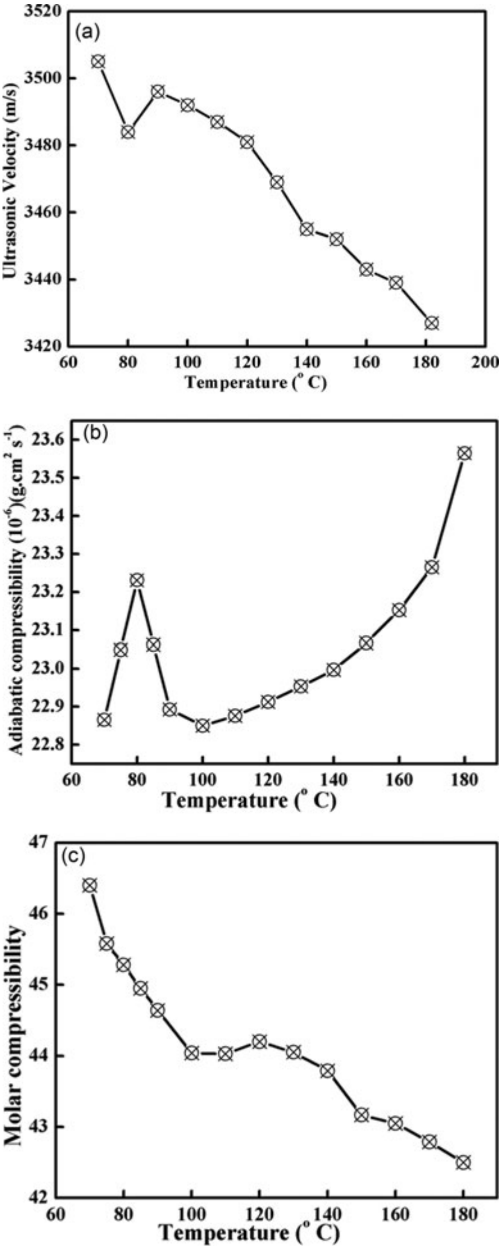

Figure 5. (a) The temperature variation of ultrasonic velocity for the sample of 20% of 80CB in CTAB + GAA. (b) The temperature variation of adiabatic compressibility for the sample of 20% of 80CB in CTAB + GAA. (c) The temperature variation of molar compressibility for the sample of 20% of 80CB in CTAB + GAA.

of thermal expansion co-efficient in mesophase than in the isotropic phase confirm the tendency of increasing order of molecule with decrease in temperature. Hence, it is firmly established that the ultrasonic velocity and related parameters [19] are structure dependent. Besides depending on the structure, they are related to intermolecular interactions and degree of molecular order in liquid crystalline mixture. It is well known that in liquid crystalline phases, the molecules are arranged in order and the orderliness increases from nematic to smectic phase. The hexagonal, lamellar, and cubic phases are known to exhibit polymorphism at higher and lower temperature compare to other phases, such as cholesteric, nematic, and twisted grain boundary (TGB) phases [20,21].

Conclusions

In light of the above results, we have drawn the following conclusions. The multi-component system of mesogenic and nonmesogenic compounds exhibits an unusual sequence of phases, showing the formation of lower temperature reentrant nematic and smectic-A phases in the concentration range of 5% to 24% of 80CB in CTAB + GAA. The phase behavior is discussed with the help of phase diagram. The changes in value of electrical susceptibility with the variation of temperature unambiguously correspond to liquid crystalline phases. The anomalous behavior of liquid crystalline physical properties, such as ultrasonic velocity, adiabatic compressibility, and molar compressibility, is discussed at the isotropic mesosphere transition.

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