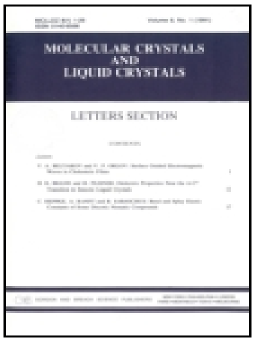

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Optical density and ultrasonic measurements of lyotropic chromonic phase of liquid crystalline materials

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ABSTRACT

We report the results of our studies on optical and thermal properties of binary mixture of compounds, viz. Berberine (BBE) and glacial acetic acid (GAA). The mixture exhibits a very interesting coexistent nematic biphase (N+I) and nematic (N) phase for different concentrations of BBE sequentially when the specimen is cooled from its isotropic phase. Temperature variations in optical density and ultrasonic measurements have been discussed.

KEYWORDS

Binary mixture; optical studies; density and ultrasonic measurements; adiabatic compressibility

Introduction

Progress in optoelectronics is highly dependent on the development of new reliable low cost technologies and materials. New materials for functional integral optical films are in great demand. Recently, a new class of highly perspective optical materials, lyotropic chromonic liquid crystals, has been intensively studied. Lyotropic chromonic liquid crystals are obtained from aqueous solution of dyes: molecules of some dyes aggregate into supramolecular units whose orientation order gives rise to different liquid crystalline phase. Chromonic liquid crystals are still not understood to the same extent as amphiphile-based lyotropic liquid crystals. Lydon et al. summarized the current state of knowledge on chromonics in two excellent reviews [1–5]. Note that chromonic molecules do not show a clear separation of hydrophilic and hydrophobic parts since the hydrophilic (ionic or hydrogen-bonding) groups that impart water solubility are distributed all around the periphery of the hydrophobic aromatic rings. Consequently, chromonic molecules do not form micelles, nor do they show any appreciable surface activity. However, in the presence of Berberine (BBE), the molecules tend to aggregate into stacks due to both weak Van der Waals interactions between the cores and the hydrophobic effect. In all concentrations, there is some degree of aggregation. As the concentration increases, the distribution of aggregate size shifts to higher and higher number of molecules in aggregates. If the concentration is high enough to form large and interacting rod-like aggregates, liquid crystalline phases are formed. The stability of these phases depends on both temperature and concentration.

In the present investigation, we have shown the coexistent nematic biphase (N+I) and nematic (N) phase respectively at different concentrations in the binary mixture of BBE and glacial acetic acid (GAA). Density, ultrasonic velocity, and optical texture studies have been

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carried out to understand the molecular aggregation of the above phases at higher temperatures. In light of the above investigations, an attempt has been made to understand the coupling between aggregate structure and the mesophase order in the light of the observations of lyotropic chromonic liquid crystals [6], wherein it has been observed that the aggregates formed at low concentrations are not large enough to align, and at larger concentrations aggregate size increases into supramolecular assemblies.

Experimental

Mixtures of different concentrations of BBE in GAA were prepared and 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. The permitted temperature control was ±0.1°C. The level of liquid crystal in the capillary was read with a cathetometer to be ±0.01 mm. The absolute error in the density measurements was $\Delta\rho = \pm 0.0001$ g/cc. The ultrasonic velocity was measured at 2 MHz using the ultrasonic interferometer UI 601 NPL India. The cell was essentially the same as that supplied with the interferometer except a few modifications for the heating arrangement. The temperature of the cell was controlled by controlling the current flowing through the heating element surrounding the cell. The permitted temperature control was ±0.2°C. The ultrasonic velocity measurements were accurate to ±0.2%.

Results and discussion

Optical texture studies

The detailed phase diagram of binary system of BBE in GAA has been reported in our earlier publication [7]. The molecular orientations of the optical textures exhibited by the samples were observed and recorded using the Leitz-polarizing microscope and a specially constructed hot stage. The specimen was taken in the form of thin films sandwiched between slide and cover glass. The molecular aggregates are not clear up to 20% concentration of BBE in GAA. The N+I and N phases are clear above 20% of BBE. The concentration of BBE ranging from 20 to 90% has been considered for the discussion. As the concentration of BBE increases, the molecular aggregates are aligned along a particular direction, and hence exhibit a coexistent nematic biphase at higher temperatures. When the specimen of 50% BBE is cooled from its isotropic liquid phase, it exhibits I–(N+I)–N phases sequentially. When the sample is cooled from isotropic liquid phase, the genesis of nucleation starts in the form of molecular orientations, which grow and segregate the molecules that are identified as coexistent nematic biphase (N+I), and the texture is as shown in Figure 1(a). On further cooling, coexistent nematic biphase (N+I) changes over to nematic (N) phase. Nematic (N) phase produces Schlieren textures with disclinations (characterized by two dark brushes of extinction) and point defects-boojums (with four brushes of extinction) as shown in Figure 1(b) and it remains as such toward room temperature. Here it is pertinent to remark that the molecular aggregation increases at low temperature and different concentrations of BBE. In nematic N phase, the molecules stack to form long columnar aggregates, which align parallel to each other. There is no long-range positional order in columns. Here it is very interesting

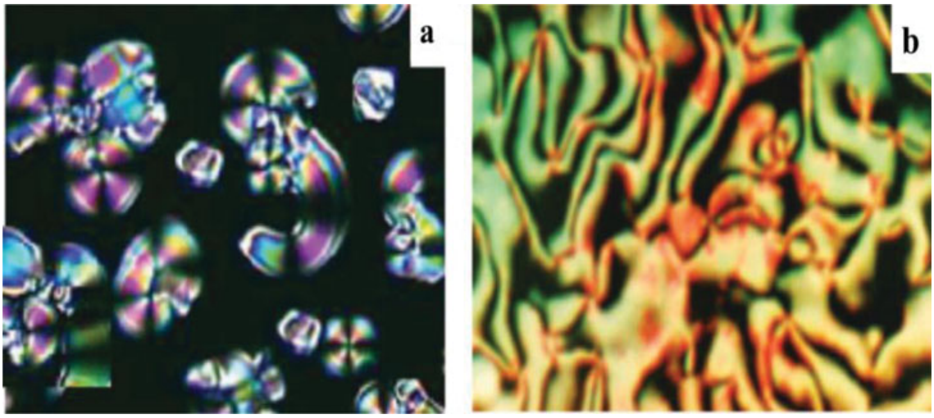


Figure 1. Microphotographs showing (a).Coexistent biphasic region of nematic phase (180×); (b).focal conic fan-shaped texture of SmA phase (180×).

to note that the coexistence of N+I biphases decreases with increasing BBE concentrations, whereas with increase in BBE concentration, N phase increases. Because of the exhibition of this behavior, chromonic liquid crystals hold great promise toward applications as optical materials and devices in high technology. Potential applications reported for chromonic liquid crystals include biosensors [8–10], polarizing films [11–15], optical retardation plates [16,17], and micro-patterned polarizing elements for stereoscopic displays [18,19].

Density measurement

Temperature variations of density for the sample of 40% BBE in GAA is shown in Figure 2, which clearly illustrates that the density increases linearly with decrease in temperature in the optical region between isotropic and crystalline phases of a given mixture. The phase transition is very nearer to isotropic and coexistent nematic biphase (N+I) region. In this transition, at particular region a sudden jump was observed in the values of density. A sudden jump in the value of density shows increase in its value, hence it indicates that the phase transition

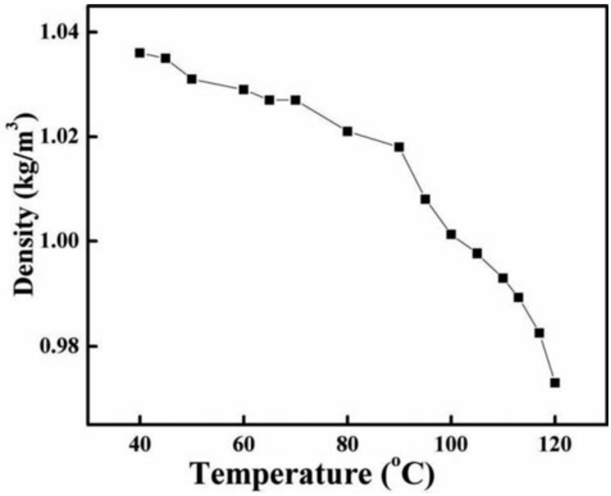
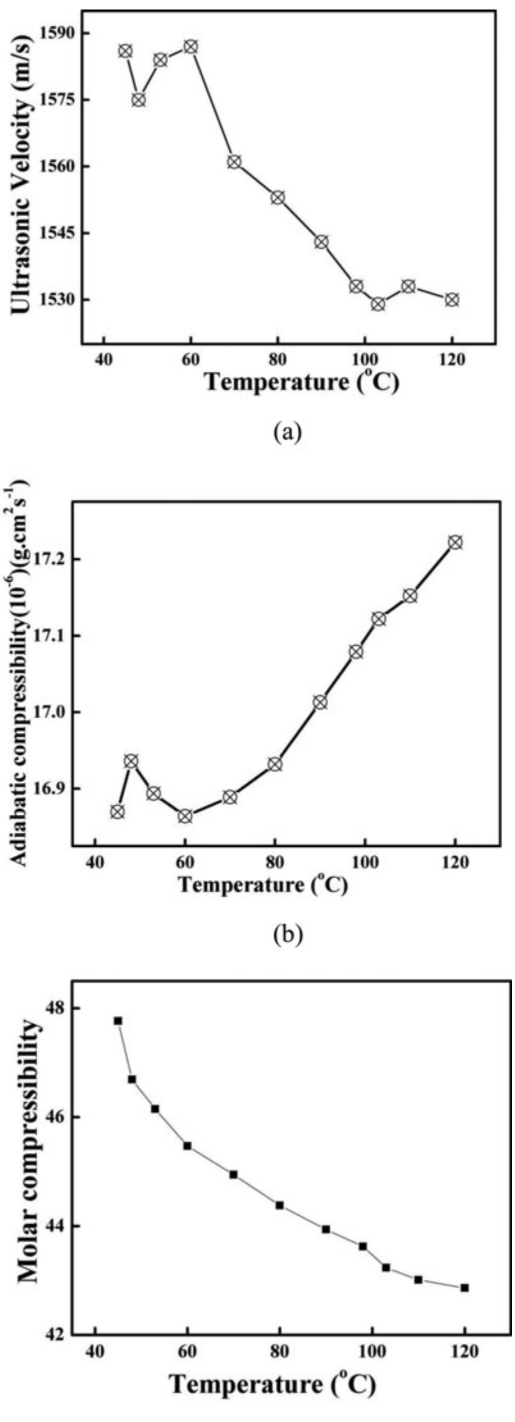


Figure 2. Temperature variations of density for a sample of 40% BBE in GAA.

region in between isotropic and coexistent nematic biphase (N+I) transition is probably of first order. A sudden jump in the value of density at optical region is attributed to a sudden change in molecular structure, and this was confirmed by the optical anisotropic technique. The higher values of density in the coexistent nematic biphase (N+I) region are more than that of in the isotropic region, which clearly indicates that the tendency of increasing molecular order is more with decrease of temperature [20,21]. The pre-transitional effects at optical region between isotropic and coexistent nematic biphase (N+I) phase transitions are observed on the lower side of the transition, which supported the Maier–Saupe theory [22]. After isotropic transition, at coexistent nematic biphase (N+I) region, the density of given mixtures increases linearly with decrease in temperature and then at the optical region between coexistent nematic biphase (N+I) and nematic (N) phase transition the values of density show an increasing trend. The measured higher value of density and thermal expansion coefficient indicate that the phase transition is of first order. Cladis and Torza have suggested a correspondence between a flow anomaly found in certain nematic liquid crystals and a discontinuous change in the thermal expansivity which occurs at the same temperature. Densities of the given mixtures increase gradually with decrease in nematic (N) phase temperature. The increasing values of densities were observed experimentally at different optical regions with decrease in temperature toward the crystalline phase. The measurements of increasing values of densities across different optical regions are more predominant than one to other optical regions.

Temperature variations of ultrasonic velocity, adiabatic, and molar compressibility

The mixtures of liquid crystalline materials due to their unusual behaviors have attracted considerable attention. Ultrasonic velocity measurements also help in the study of phase behavior with temperature [23]. Orientational order of molecules in mesomorphic/non-mesomorphic compound changes with increasing the concentration of one more additive substance, and hence the attractive force between the components of molecules, the measure of ultrasonic velocity, and absorption should show the nature of attractive forces existing between the mixtures of given molecules. Data on some of the properties associated with refractive index, ultrasonic velocities, and surface tension find extensive application in chemical engineering process, simulation, and molecular dynamics [24]. The temperature variation of ultrasonic velocity and adiabatic and molar compressibility in the present case is shown in Figures 3(a)–(c). The velocity exhibits an anomalous behavior at the isotropic mesophase transition, while it varies linearly in the isotropic and mesomorphic phases away from transition. The velocity shows a dip at transition. The ultrasonic velocity linearly increases in isotropic phases up to transition with decreasing temperature [25,26]. An increase in velocity is explained as a decrease in mean distance between the molecules, thereby increasing the potential energy of interaction between molecules. The velocity reaches minimum at transition temperature and increases sharply below the transition, and then it shows a linear increase in mesophase. The change in velocity and other parameters [27] 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 [28]. Variation in adiabatic compressibility [29] is remarkably linear in isotropic and mesomorphic phases, but it shows a step jump at isotropic–mesophase transition. The result of molar compressibility varies linearly with temperature at the isotropic phase transition. In this study, the higher values of thermal expansion coefficient in mesophase than in isotropic phase confirm the tendency of increasing order of molecules with decrease in temperature. It is firmly established that the ultrasonic



(a)

(b)

(c)

Figure 3. (a) Temperature variation of ultrasonic velocity for a sample of 40% BBE in GAA. (b) Temperature variation of adiabatic compressibility for a sample of 40% BBE in GAA. (c) Temperature variation of molar compressibility for a sample of 40% BBE in GAA.

velocity and the related parameters [30] are structure-dependent. Besides, depending on the structure, these 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 isotropic to coexistent nematic biphase (N+I) and nematic (N) phase. The coexistent nematic biphase (N+I) is known to exhibit at different temperatures and at different concentrations of given molecules compared with other conventional liquid crystalline phases such as nematic (N) phase [31,32].

Conclusions

The salient features of this investigation are as follows: The existence of coexistent nematic biphase (N+I) and nematic (N) phase have been observed by using microscopic technique in binary mixture of BBE in GAA. The temperature variation of density across the coexistent nematic biphase (N+I) and nematic (N) phase is more predominant than other transitions. 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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