



ULTRASONIC AND THERMODYNAMIC EFFECTS ON OPTICAL PHASE TRANSITION STUDIES OF TERNARY MIXTURE OF LIQUID CRYSTALS

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ARTICLE INFO

Article History:

Received 15th October, 2018

Received in revised form 7th

October, 2018

Accepted 13th December, 2018

Published online 28th January, 2019

Key words:

Optical studies: Refractive index and ultrasonic

measurements: Adiabatic compressibility:

Thermodynamical studies:

ABSTRACT

We report the results of our studies on optical and thermal properties of ternary mixture of compounds, viz., laurylpyridinium chloride (LPC), cholesteryl oleate (CO) and Glacial acetic acid (GAA). These mixture exhibits a very interesting re-entrant smectic-A and induced chiral smectic phases for different concentrations of CO sequentially when the specimen is cooled from its isotropic phase. The temperature variations of optical-refractive index and ultrasonic measurements have been discussed to understand the phase transition behavior of the given molecules. Thermodynamical response of optical-birefringence has also been discussed to understand: the phase stability, chemical structure and molecular dynamics of the multi-component system of liquid crystalline materials.

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INTRODUCTION

Liquid crystals are a state of matter which is thermodynamically located between the isotropic liquid and the crystalline phase. They exhibit flow properties like a liquid and at the same time partially retain the order of a crystal. For this reason, they possess anisotropic physical properties such as their refractive index, dielectric constant, elastic behavior, or viscosity, just to name a few. But while being partially ordered, liquid crystals also exhibit flow properties like a liquid; they are thus anisotropic fluids [1-3].

In the present investigation, our aim is to study the mixture of multi-component system namely, cholesteryl oleate (CO), laurylpyridinium chloride (LPC) and Glacial acetic acid (GAA). By the microscopic technique, here we have discussed the results of optical textures of cholesteric, re-entrant smectic-A and induced chiral smectic phases, sequentially while the specimen is cooled from its isotropic melt. From the experimentally measured data of ultrasonic velocity, refractive indices, optical-birefringence and thermodynamic related parameters have also been discussed.

Experimental Studies

In the present study, we use the materials, namely, laurylpyridinium chloride (LPC), cholesteryl oleate (CO) and

Glacial acetic acid (GAA). Mixtures of fifteen different concentrations of Co in LPC+GAA were prepared, and they were mixed thoroughly. These mixtures of concentrations were kept in desiccators for 6 hours. 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 Gippon Japan 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 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 ($\lambda=5893\text{\AA}$). 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 [8]. The density and refractive indices in the optical region are determined at different temperatures by employing

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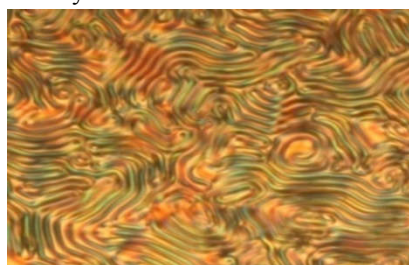
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the techniques described by the earlier investigators [5, 6]. Ultrasonic velocity was measured using a single crystal interferometer [7] working at 2 MHz with an accuracy of $\pm 0.05\%$.

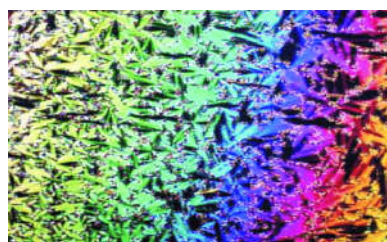
RESULTS AND DISCUSSION

Optical Texture Studies

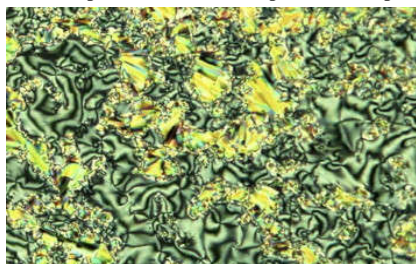
The optical textures exhibited by the samples were observed and recorded using the Gippon Japan polarizing microscope and specially constructed hot stage. The specimen was taken in a form of a thin film sandwiched between slide and cover glass. The concentrations of 5 to 55% of ternary mixture of CO in LPC+GAA were considered for experimental studies. When a specimen of 45% Co in LPC+GAA is cooled from its isotropic melt, it exhibits Iso-Cho-SmA-SmC - ReSmA-SmC*-SmE-SmB-Cryst phases sequentially. While the sample is cooled from its isotropic phase, nucleation starts in the form of minute bubbles, and immediately the bubbles grow radially and form fingerprint pattern as shown in Figure 1(a), which is a characteristic of cholesteric phase with large values of pitch [8]. On further cooling the specimen, the cholesteric phase slowly changes over to focal conic fan-shaped texture of SmA. This is shown in Figure 1(b). Molecular structural confirmations of SmA phase at 83 °C are stable. For thermal variations, the flexibility of molecular layers leads to distortions, which give rise to optical patterns known as focal-conic textures. On further cooling the specimen, SmA phase may transform into the appearance of tilting molecules relative to smectic layers and this is the characteristic of well-defined schlieren textures of SmC as shown in Figure 1(c). If some different smectic phases are observed, these differ from one another in a way of layer formation and existing in an order inside molecular layers.



a) Fingerprint pattern of cholesteric phase (250X)



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



c) Schlieren texture of SmC phase at temperature (250X)

Figure 1 Microphotographs showing,

In this system, the microscopic observation clearly indicates that a given mixture with concentration ranging from 15 to 35% of CO in LPC+GAA exhibits a re-entrant SmA phase [9]. The lowest temperature mesophase of certain compounds exhibits two or more mesophases of the same type over different temperature ranges. Re-entrant mesophases are most commonly observed when the molecules have strong longitudinal dipole moments. The sequences of re-entrant mesophases have also been found in mixtures of non-polar liquid crystalline compounds [10]. In the present system, some of the middle concentrations of CO at lower temperatures did not show molecular aggregates in the preferred direction of alignment toward crystalline phase but it randomly oriented to form a re-entrant SmA phase and then this phase changes over to SmC* phase, which exhibit a radial fringes on the fans of focal conic textures, which are the characteristics of chiral SmC* phase. Sequentially on further cooling the specimen, the unstable SmC* phase slowly changes over to focal conic fan-shaped herring bone pattern of SmE phase and hence this phase changes over to the SmB phase and then it becomes a crystalline phase, which remains stable at room temperature [11].

Optical Anisotropy

Results of this investigation are further supported by the optical studies of different mixtures of liquid crystalline materials. We have measured the temperature variation of the refractive indices (n_e and n_o) for the mixture of different concentrations of CO in LPC+GAA by using Abbe refractometer and precision Goniometer spectrometer using the wavelength 589.3 nm in the cholesteric, re-entrant smectic-A and induced chiral 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 optical-birefringence for 30% of CO in LPC+GAA are shown in Figure 2. From the figure, it can be observed that wherever there is an isotropic-liquid crystalline phase transition, the values of birefringence changes appreciably, which indicates that the changes correspond to various smectic modifications. Further: with increase in the concentration of CO, the value of optical-birefringence decrease with temperature because the effective optical anisotropy associated with the molecules of CO also decreases [12, 13].

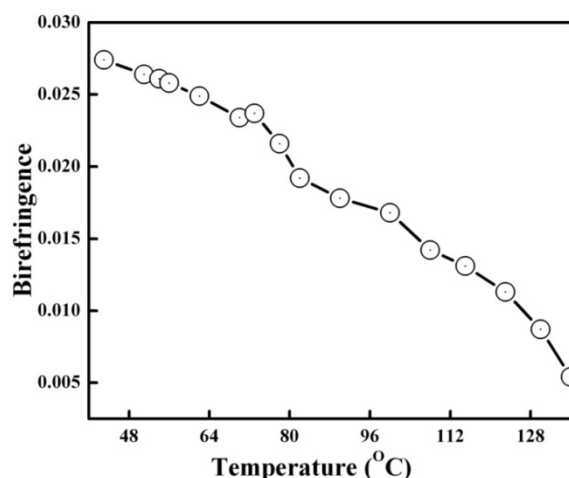


Figure 2 Temperature variations of optical-birefringence for the sample of 30% of CO in LPC+GAA.

Studies on Thermodynamic Response of Optical-Birefringence

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 [14]. Thermodynamical responses are very important role to understand the phase stability, chemical structure and dynamics of liquid crystals [15, 16]. Temperature dependent molecular orientations of liquid crystalline phases have been considered in many technological applications. Applied applications of these technologies are based on the properties of different molecular structure and intermolecular interactions. The intermolecular forces such as van der Waals interaction, hydrogen bonds, electron donor interactions and steric repulsive interactions are they individually or together may be responsible for increasing or decreasing the thermal stability of liquid crystalline phase [17]. Thermodynamical variations of liquid crystalline phase at different concentrations of ternary mixtures of liquid crystalline materials are estimated using Boltzmann distribution laws. Draw a graph of variations of optical-birefringence as a function of mole fraction for the sample of CO in LPC+GAA at constant temperature 80 °C is presented in Figure 3, which clearly shows that: degree of micro-phase separations are the one parameter to controlling a physical properties of liquid crystalline materials [18].

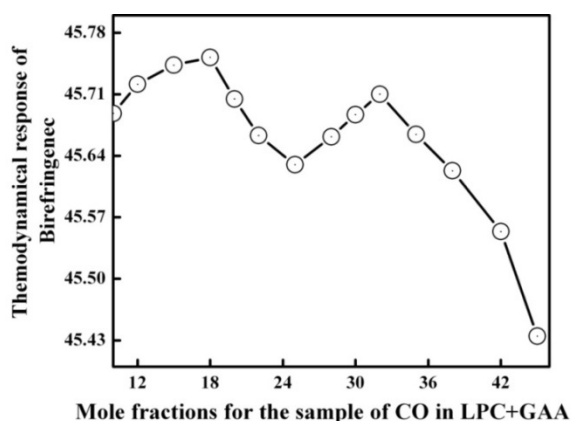


Figure 3 Variations of thermodynamical response of optical-birefringence as function of mole fractions for the sample of CO in LPC+GAA.

In this context the existence parameter can be varied infinitesimally small either through chemical modification or through physical modification and hence they are depends on nature of additives molecules. The figure clearly illustrates that, statistically how the molecular interactions are thermodynamically changes at different concentrations in order to show the thermal stability of liquid crystalline phase. Here we noticed that: 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 the spin temperature. Due to this temperature: on the molecular surface, the internal degrees of freedom of the molecules are thermodynamically equilibrium with one mole fraction to other mole fractions. If either increasing or decreasing the mole fraction; which cause a small variation of electrostatic potentials and which they around the molecule. In spite of these uncertainties, the full sets of partial charges are very useful, as it can provide a detailed insight into the molecular arrangement in mesophases and they reproduce the electrostatic potential very well. The molecular density of mesosphere, charges on molecules

represent an electrostatic molecular interaction, but they do not show the real charge distribution in molecule. The molecular ordering or the phase stability of liquid crystalline phase at given constant temperature: the intermolecular interactions 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.

Temperature Variations of Ultrasonic Velocity, Adiabatic and Molar Compressibility

The mixtures of liquid crystalline materials due to their unusual behaviors have attracted considerable attention. Studies on temperature dependent ultrasonic velocity measurements are also help to study the phase transition behavior of the different molecules [19]. Orientational order of the 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 the molecules, the measure of ultrasonic velocity and absorption should shows nature of attractive forces existing between the mixtures of given molecules. Data on some of the properties are associated with refractive index, ultrasonic velocities and surface tensions are used to find the extensive applications in chemical engineering process, simulation and molecular dynamics [20]. In the present study we have been considered the sample of 30% CO in LPC+GAA. The temperature variation of ultrasonic velocity, adiabatic compressibility and molar compressibility in the present case is shown in Figures 4 (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.

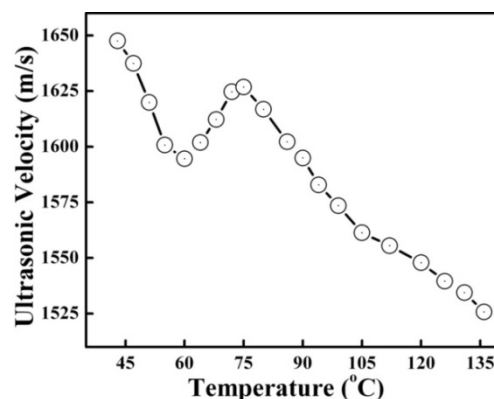


Figure 4(a) The temperature variation of ultrasonic velocity for the sample of 30% of CO in LPC+GAA.

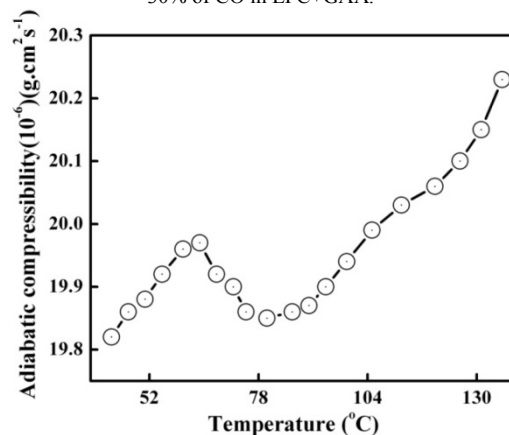


Figure 4(b) The temperature variation of adiabatic compressibility for the sample of 30% of CO in LPC+GAA.

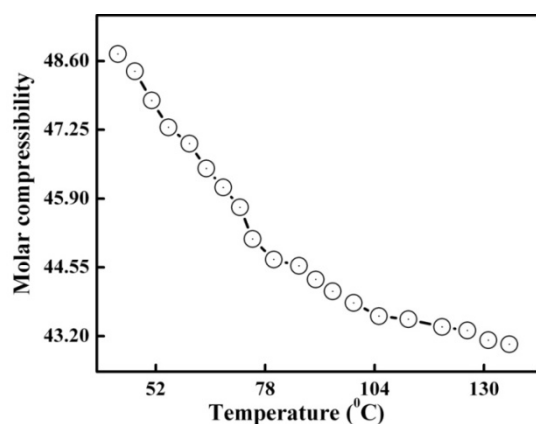


Figure 4(c) The temperature variation of molar compressibility for the sample of 30% of CO in LPC+GAA.

The velocity shows a dip at the transition. The ultrasonic velocity linearly increases in isotropic phases up to the transition with decreasing temperature [21, 22]. 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, and then it shows a linear increase in mesophase. The change in velocity and other parameters [23] 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 [24]. The variation of adiabatic compressibility [25] is remarkably linear in isotropic and mesomorphic phases, but it shows a step jump at the 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 co-efficient in mesophase than in the isotropic phase confirm the tendency of increasing order of molecule with decrease in temperature. It is firmly established that the ultrasonic velocity and the related parameters [26] 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

Iso-Cho-SmA-SmC-ReSmA-SmC*-SmE-SmB-Cryst phases sequentially. The induced reentrant smectic-A phase is known to exhibit at different temperature and at different concentrations of the given molecules compared to cholesteric and induced smectic phases such as SmA, SmC, SmC*, SmE, and SmB phases [27, 28].

CONCLUSIONS

The salient features of this investigation are the following: The existence of re-entrant smectic-A phase and induced chiral smectic phases have been observed by using microscopic technique in multi-component system of CO in LPC+GAA. The drastic changes in the value of optical-birefringence with the variation of temperature unambiguously correspond to re-entrant smectic-A phase and chiral smectic phases. Thermodynamical response of optical-birefringence have also been discussed to understand: statistically how the birefringence is thermodynamically changes at different concentrations in order to show the thermal stability, phase stability, chemical structure and molecular dynamics of multi-

component system of liquid crystalline phase. The anomalous behavior of liquid crystalline physical properties, such as ultrasonic velocity, adiabatic compressibility, and molar compressibility, is discussed at the isotropic mesosphere transition.

References

- Collings, P. J. 1990. *Liquid Crystals: Nature's Delicate Phase of Matter*; Princeton University Press, Princeton, NJ, USA.
- Chandrasekhar, S. 1992. *Liquid Crystals*, 2nd ed.; Cambridge University Press: Cambridge, UK.
- De Gennes, P.G. and Prost, J.1993. *The Physics of Liquid Crystals*, 2nd ed.; Oxford University Press: Oxford, UK;New York, NY, USA.
- Chatelain, P. 1939. *Acad. C.R., Sci. Paris*, 203, 1169.
- Nagappa, Nataraju, S.K. and Krishnamurti, D. 1986. *Mol.Cryst.Liq.Cryst.*133, 31-54.
- Thiem, J., Vill, V. and Fischer, F. 1989. *Mol.Cryst.Liq.Cryst.*170, 43-51.
- Govindaiah, T. N., Sreepad, H.R. and Nagappa. 2013. *Mol.Cryst.Liq.Cryst.*574, 9-18.
- Demus, D. and Richter, C. 1978. *Textures of Liquid Crystals*, Weinheim (NY): Verlag Chemie.
- Govindaiah, T. N., Sreepad, H. R., Nagappa, and Nagendra, P. 2014. *Mol. Cryst. Liq. Cryst.* 605, 82-88.
- Baron, M. (2001). *Pure. Appl. Chem.* 73, 845-895.
- Govindaiah, T. N., Sreepad, H. R., Kempegowda, B. K., and Nagappa. 2013. *Mol. Cryst. Liq. Cryst.*587, 54-59.
- Govindaiah, T. N. and Sreepad, H. R. 2015. *Molecular liquids.* 202, 75-78:
- Govindaiah, T. N., Sreepad, H. R. and Nagappa. 2015. *Mol. Cryst. Liq. Cryst.* 609: 93-99.
- Collings, P, and Hird, M. 1997. *Introduction to liquid crystals*, Taylor & Francis, London.
- Soule, E. R. and Rey, A. D. 2011. *Liq. Cryst.*, 38, 201.
- Amoros, J. G., Szymczyk, A. and Velasco, D. 2009. *Phys. Chem. Chem. Phys.* 11, 4244.
- Lubensky, T. C. 2011. *Mol. Cryst. Liq. Cryst.* 540:3.
- Kercha YuYu. (1979). *Physical chemistry of polyurethanes*. Kyiv: Naukova Dumka.
- Pandey, J. D. and Mishra, R. L. 1978. *Acta Acust United Acust.* 40, 335-339.
- Mchaweh, A., Alsaygh, A. and Moshfeghian, M. A. 2004. *Fluid Phase Equilib.* 224,157-167.
- Kiyohara, O. and Benson, G. C. 1979. *J Chem Thermodyn.* 11, 861-873.
- Ewing, M. B., Levian, B. J. and Marsh, K. N. 1970. *J. Chem. Thermo.* 2, 689-695.
- Govindaiah, T. N., Sreepad, H. R. and Nagappa. 2013. *Mol Cyst Liq Cryst.* 574, 9-18.
- Shastri, N., Vyas, P. R. and Gupta, S. J. 2010. *Indian J Pure Appl Phys.* 48, 556-561.
- Jacobson, B. 1952. *Acta Chem Scand.* 6, 1485-1498.
- Susmita, K., Satyaban, J. and Bipin, B. S. 2005. *J. Chem. Thermo.* 37(8), 820-825.
- Sulek, M. W. In: Biresaw, G. and Mittal K. L. 2008. Editors. *Surfactants in tribology*; New York: CRC Press.325-353.
- Wasilewski, T. In: Biresaw, G. and Mittal, K. L. 2008. Editors. *Surfactants in tribology*: New York: CRC Press. p. 371-406.