Research Article

OPTICAL AND ELECTRICAL CONDUCTIVITY MEASUREMENTS OF INDUCED REENTRANT SMECTIC PHASES OF IN TERNARY MIXTURE OF LIQUID CRYSTALLINE MATERIALS

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ABSTRACT

The multi-component system of *p-n*-Decyloxybenzoic acid (10OBAC), 4, 4'-di-n-heptyl-azobenzene (7AB7) and cholesteryl nanonate (CN), exhibits liquid crystalline mesophases, like cholesteric and induced smectic phases, such as SmA, SmC, ReSmA, SmC* and SmE phases sequentially when the specimen is cooled from its isotropic phase. These phases have been observed by using microscopic and optical anisotropic technique. The experimentally measured optical transmittance and electrical conductivity has been discussed based on the phase transition behavior of different temperature.

INTRODUCTION

For many applications of liquid crystal, some requirements and characteristics need to be satisfied, such as stability and mesophase range and existence if the mesophase at desired temperature of operation. Although there are many liquid crystalline materials some difficulties is often experienced in achieving technologically useful temperature range for the existence of mesophase and response to external filed as well as stability of the substance. To overcome this difficulty, different mixtures of different liquid crystalline materials can be used. In generally the binary mixture has transitions at temperature in between the transition temperature of the pure compounds. It is also known that: when the small concentrations of an optically active material are mixed with a nematic compound, the pitch of the cholesteric increases. Cholesteric to nematic mixtures can show the so called the injected smectic phase, although none of the compounds used is smectic. This smectic can be stabilized and its transition temperature increased. This results in an enhanced smectic-phase [1-4].

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In the present study, we have considered the multi-component system namely, *p-n*-Decyloxybenzoic acid (10OBAC), 4, 4'-di-n-heptyl-azobenzene (7AB7) and cholesteryl nanonate (CN). Different liquid crystalline phases such as cholesteric, SmA, SmC, ReSmA, SmC* and SmE phases were observed by using optical microscopic technique and hence they have been verified from the results of optical anisotropic techniques.

Experimental Studies

In the present investigation, we have considered multi-component system of liquid crystalline materials namely: *p-n*-Decyloxybenzoic acid (10OBAC), 4, 4'-di-n-heptyl-azobenzene (7AB7) and cholesteryl nanonate (CN), which are obtained from M/s Eastman Organic Chemicals, USA. They were further purified twice by re-crystallization in benzene. The ternary mixtures of different concentrations of 10OBAC in 7AB7+CN were kept in desiccators for a long time. The samples were subjected to several cycles of heating, stirring and centrifuging to ensure homogeneity. The melting points of purified samples are in good agreement with the reported value.

Polarizing Microscopic Studies

Polarizing microscopic technique is the most widely used method in identifying different phases. Liquid crystalline

substance is placed between two glass cover slips. Depending on the boundary condition and the type of phase, various textures which are characteristics of a phase are observed. Usually the texture changes while going from one phase to another. Polarizing microscopy is a powerful tool when used in combination with miscibility of binary mixtures. Liquid crystalline phases possess characteristic textures when viewed under polarized light. These textures, which can often be used to identify phases, result from defects in the liquid crystals. Polarizing Microscopy is used for various phases like Nematic, Cho, TGB and induced smectic phases such as SmA, SmB, SmC*, SmC, ReSmA, and SmE etc. As the liquid crystalline material goes from solid to liquid crystalline phase, the degree of order decreases. This is expressed by decrease in the value of order parameter. In case of orientational disorder it is possible to see changes between different liquid crystal phases during the heating and cooling cycles of liquid crystals.

Refractive index measurement

Refractive index has been measured using Abbe's Refractometer. A polarizer has been introduced in Abbe's refractometer to block the extraordinary ray, which clears the contrast of the boundary line at view of Refractometer. To calculate birefringence Δn following relation has been used $\Delta n = n_e - n_o$ The temperature of Abbe's Refractometer is controlled by circulating heated oil using JULABO F-25, refrigerated circulator. The temperature was measured by placing a thermocouple in close vicinity of the sample with an accuracy of +0.1°C.

Optical Transmittance Measurement

For the Optical Transmittance Measurement, the sample was in to the standard sample holder pretreated for planar alignment having 5 μm spacer by heating it 10 °C above the clearing point of the sample and then introducing the sample at one end of the holder it was filled in the sample holder by the capillary action and sample holder was slowly cooled up to the room temperature. Now sample holder is placed between two crossed polarizer of polarizing microscope model CENSICO (7626) fitted with a hot stage and light intensity coming through the eyepiece has been measured by light-dependent resistance (LDR). The resistance value of LDR corresponding to varying light intensity due to temperature variation of the sample is proportional to the inverse of optical transmittance and has been directly measured by attached digital multi-meter.

Electrical Conductivity Measurements

The electrical conductivity measurements were carried out at different temperatures in the heating/cooling cycles, with the constant rate of scanning 2°C/min. The temperature was stabilized using a homemade thermoelectric cooler, based on Peltje elements and it was recorded by a Teflon-coated K-type thermocouple (±0.1°C) and it was connected to the data logger thermometer centre 309 (JDC Electronic SA, Switzerland). The un-oriented samples were used and the conductometric cell included two horizontal platinum electrodes of 14 mm in diameter, with 0.5 mm inter-electrode space. Before the measurements, the cell parts were washed in hexane and dried at 117 °C. The electrical conductivity of the samples was measured by the inductance, capacitance, and resistance (LCR) meter 819 (Instek, 12Hz–100 kHz). The measurements were done under the applied external voltage of 1 V and frequency of 500 Hz. This frequency was selected for avoidance of significant polarization effects on the electrodes.

Theoretical analysis

Geneural theory on polarizability

The electric displacement $\vec{D}$, field intensity $\vec{E}$ and electric polarization $\vec{P}$ are related by

$$\vec{D} = \epsilon_0 \vec{E} + \vec{P}$$

Since $\vec{D} = \dfrac{q}{A} = \dfrac{\epsilon_0 \epsilon_r q}{A \epsilon_0 \epsilon_r} = \epsilon_0 \epsilon_r \vec{E} = \epsilon \vec{E}$

Where $\epsilon = \epsilon_0 \epsilon_r$

Therefore $\epsilon \vec{E} = \epsilon_0 \vec{E} + \vec{P}$

$$\vec{P} = \epsilon_0 \epsilon_r \vec{E} - \epsilon_0 \vec{E} = \epsilon_0 \vec{E}(\epsilon_r - 1)$$

$$(\epsilon_r - 1) = \frac{\vec{P}}{\epsilon_0 \vec{E}}$$

Where ϵ_r is the electrical susceptibility of the liquid crystalline medium.

When electric field is applied, the dipole length increases and the dipole moment is given by

$$\overrightarrow{\mu_e} \vec{E}$$
$$\overrightarrow{\mu_e} = \alpha_e \vec{E}$$

Where α_e is called electronic Polarizability.

The dipole moment for unit volume called electronic polarization is given by

$$\vec{P}_e = N \overrightarrow{\mu_e} = N \alpha_e \vec{E}$$

Where N is the number density of molecules of liquid crystal.

But $\vec{P}_e = \epsilon_0 \vec{E}(\epsilon_r - 1)$

Therefore $\epsilon_0 \vec{E}(\epsilon_r - 1) = N \alpha_e \vec{E}$

or $(\epsilon_r - 1) = \dfrac{N \alpha_e}{\epsilon_0}$

RESULT AND DISCUSSION

Optical Texture Studies

For the purpose of optical texture studies, the given mixtures of the samples was sandwiched between a slide and a cover glass and then the optical textures were observed using a Leitz polarizing microscope in conjunction with a hot stage. When ternary system of given mixtures shows the existence of different liquid crystalline induced phases such as cholesteric, SmA, SmC, ReSmA, SmC* and SmE phases: that have been obtained at different concentrations of given multi-component systems are at different temperatures sequentially when they cooled from their isotropic melt. The mixture with different concentrations ranging from 5% to 50% of 10OBAC in 7AB7+CN has been considered for the experimental studies. When the specimen of 35 % of 10OBAC in 7AB7+CN is cooled from their isotropic liquid phase, it exhibits I–Cho–

SmA–SmC-ReSmA-SmC*–SmE–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 form a fingerprint pattern of cholesteric phase with large values of pitch [5-7] is shown in Figure 1(a). On further cooling the specimen, the cholesteric phases are slowly changed over to a well-defined focal conic fan-shaped texture, which is the characteristic of SmA phase and is shown in Figure 1(b). The SmA phase is unstable and then changes over to the schlieren texture of SmC phase as shown in Figure 1(c), and then this phase is also not energetically stable, which changes over to ReSmA [8] phase. On further cooling the specimen, this phase changes over to SmC∗ phase, which exhibits radial fringes on the fans of focal conic textures, they are the characteristic of chiral SmC∗ phase, sequentially this phase changes over to SmE phase and then this phase remains stable till at room temperature.
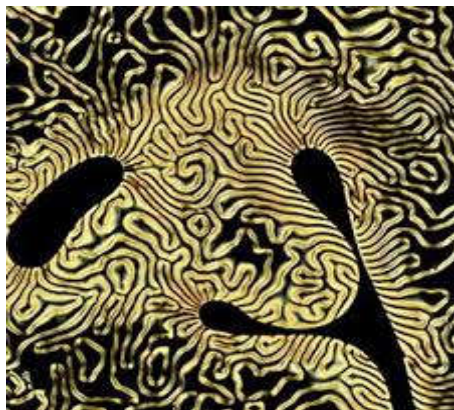
A Fingerprint pattern of cholesteric phase at temperature 112 ^{O}C (250X).
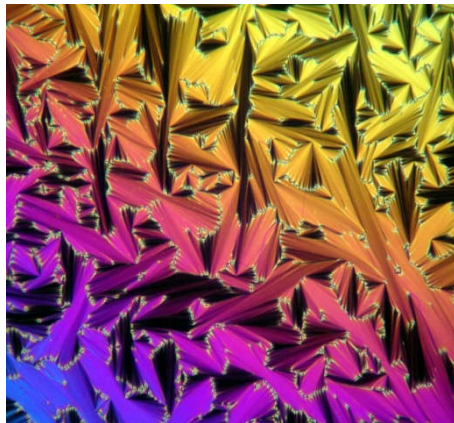
B Focal conic fan shaped texture of SmA phase at temperature 93 ^{O}C (250X).
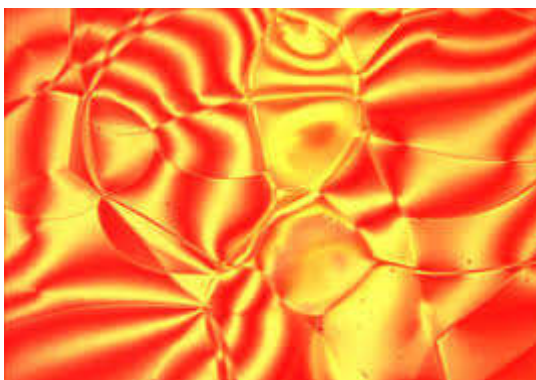
C Schlieren texture of SmC phase at temperature 75 ^{O}C (250X).
Figure1 Microphotographs showing,

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 mixtures were measured for the different concentrations and at different temperatures using Abbe Refractometer. The variation of refractive indices as a function of temperature for the samples of 35 % of 10OBAC in 7AB7+CN is shown in Figure 2.
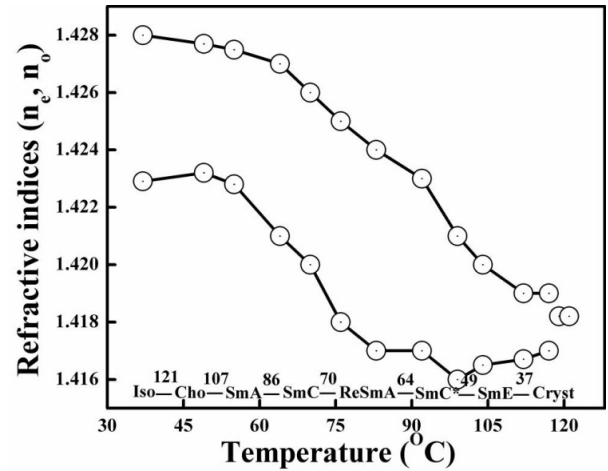

Figure 2 Temperature variations of refractive indices for the mixture of 35 % of 10OBAC in 7AB7+CN.

The value of n_e is greater than n_o, indicating that the material is uniaxial positive. The values of electrical susceptibility for the sample of 35 % of 10OBAC in 7AB7+CN have been calculated using Neugebauer relation [9-10,] at different temperatures. The variation of electrical susceptibility as a function of temperature of the given ternary mixture is shown in Figure 3. From the figure, it can be observed that: wherever there is transition between isotropic and liquid crystalline phase, the value of electrical susceptibility changes appreciably, which indicates that the changes correspond to cholesteric and induced reentrant smectic modifications. Further, with increase in the concentrations of 10OBAC, the value of electrical susceptibility decreases with temperature because the effective optical anisotropy associated with the molecules of 10OBAC also decreases.
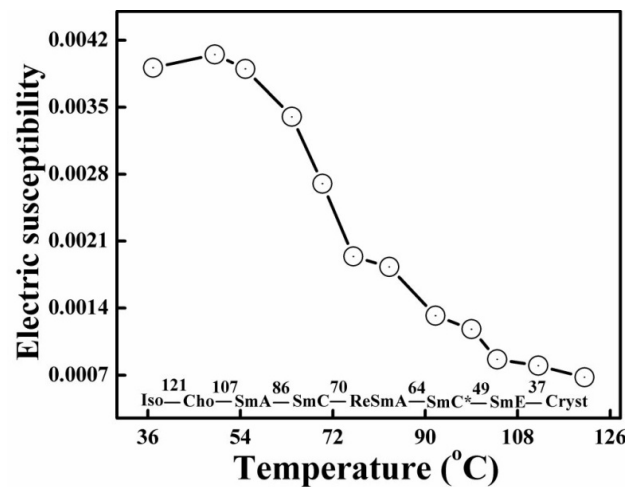

Figure 3 Temperature variation of electrical susceptibility for the mixture of 35 % of 10OBAC in 7AB7+CN.

Optical Transmittance Studies

Temperature variation of optical transmittance for the samples of 35 % of 10OBAC in 7AB7+CN is shown in Figure 4. This

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clearly illustrates that, the value of optical transmittance increases slowly with increase in temperature from 37^0C to $104\ ^0C$, while the sequence of phase appear from crystalline region to near isotropic region and there region suddenly some changes have been observed in the value of optical transmittance from $104\ ^0C$ to $121\ ^0C$ [11-12]. The optical transmittance is continuous at the SmE-SmC*, SmC*-ReSmA, ReSmA-SmC, SmC-SmA and SmA-Cho transition. Here it can be noted that, the molecular orientations of different liquid crystalline phase transition is not (stable) energetic. The optical transmittance decreases while increasing the temperature and it diverges on approaching SmA and Cho phases. The divergence of optical transmittance can be related to the first-order or second order transition. Here in the region of SmA and Cho phases, the optical transmittance shows a steep decrease and it is very nearer to isotropic region: it is also one key role to observe the phase transition by detecting the enthalpy change associated with. Also by measuring the level of enthalpy change, we can learn the type of the phase transition [13], which is the characteristic of first-order transitions of Cho and SmA phases respectively at different temperatures.
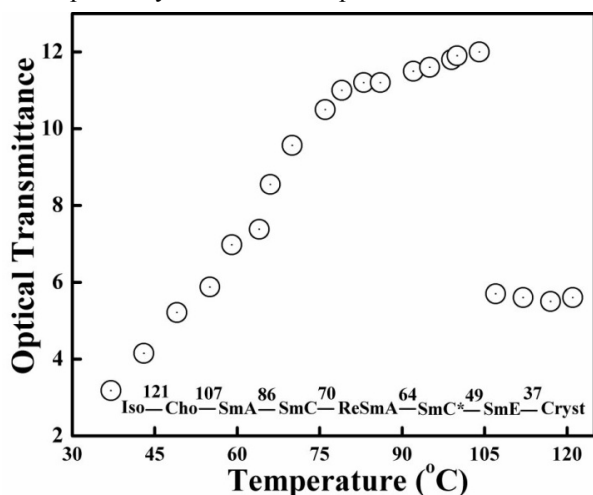

Figure 4 The temperature variation of optical transmittance for the mixture of 35 % of 10OBAC in 7AB7+CN.

Conductivity Measurements

Electrical-conductivity measurements help in getting better idea on the phase behavior with temperature. An abrupt increase or decrease of electrical-conductivity with temperature relates to the phase transition behavior of lyotropic, thermotropic and chromonic systems [14].
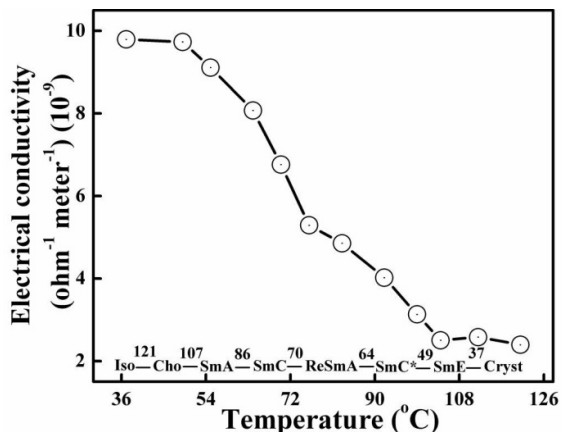

Figure5 Temperature variation of electrical-conductivity σ (x 10^{-9} Ω^{-1} m^{-1}) for the mixture of 35 % of 10OBAC in 7AB7+CN.

The temperature variations of electrical conductivity are as shown in Figure 5. From this figure some changes are observed in the value of electrical conductivity temperature ranging from 45°C to 127°C, while the specimen cooling from its isotropic phase for the mixture of 50% of 7AB7 and CN. From the microscopic observation: the sequence of liquid crystalline phase changes from Cho–SmA–SmC-ReSmA-SmC*–SmE phases respectively at different temperatures. Here it has been found that the electrical conductivity goes on increasing as the temperature decreases. This suggests that aggregated molecular size starts growing towards lower temperatures and then the system becomes more ordered [15–20].

CONCLUSION

Microscopic investigation of the binary/ternary mixture of 10OBAC in 7AB7+CN shows the existence of Iso→Cho→SmA→SmC→ReSmA→SmC*→SmE→Cryst phases for all concentrations of given mixture. The phase behavior is discussed with the help of phase diagram. The drastic changes in the optical anisotropic measurements with variation of temperature unambiguously correspond to cholestric and induced reentrant smectic, respectively at different concentrations. Optical transmittance and electrical conductivity measurements have also done to understand the molecular orientations and stability of the liquid crystalline phases.

References

1. de Gennes, P.G. and Prost, J. (1993). *The Physics of Liquid Crystals*, Clarendon Press, ISBN 0-19-852024-7, Oxford, England
2. Gray, G.W. (Ed.). (1987). *Thermotropic Liquid Crystals*. John Wiley & Sons, Ltd., ISBN 0- 471-91504-1, Chichester, United Kingdom
3. Govindaiah, T. N. and Sreepad, H. R. (2015). Phase transition and thermal characterization of induced smectic phases in a ternary mixture. *Molecular Liquids*, 202:75-78.
4. Friedel, G. (1922). The Mesomorphic States of Matter Annales de Physique 18, 273-474.
5. Demus, D. and Richter, C. (*1978*). Textures of Liquid Crystals. Verlag Chemie, Weinheim, New York.
6. Govindaiah, T. N. (2016). Nano segregation and thermal stability of TGB and re-entrant smectic-A phases in a ternary mixture of liquid crystalline materials. Mol. Cryst. Liq. Cryst. 625, 93–98.
7. Nagappa, Revanasiddaiah, D. Krishnamurti, D. Optical Behaviour of Mixtures of Nematic and Cholesteric Compounds. *Mol. Cryst. Liq. Cryst*. 1983, 101(1-2); 103-127.
8. Govindaiah, T. N., Sreepad, H. R., Kempegowda, B. K. and Nagappa. (2013). Induced Reentrant Smectic-A Phase in Binary Mixtures of Liquid Crystals. *Mol. Cryst. Liq.Cryst.* 587, 54–59.
9. Neugebauer HEJ. Clausius_Mosotti equation for certain types of anisotropic crystals. *Can. J. Phys.* 1954; 32(1):1-8.
10. Mahadeva, J. Govindaiah, T. N., Rajashekara Prasad, K. and Nagappa. (2009). Mesomorphic Behaviour of Lamellar Smectic Phases in the Binary Mixture of

Non-Mesogenic Compounds. *Mol. Cryst. Liq. Cryst.* 511, 218/1688–230/1700.

11. Vaz NA and Montgomery GP (1987) Refractive indices of polymer-dispersed liquid- crystal film materials: Epoxy based systems. *J. Appl. Phys.* 62, 3161-3172.

12. Govindaiah, T. N. (2016). Optical Studies on Smectic-Isotropic Phase Transition Behavior of Two Thermotropic Liquid Crystals. *Mol. Cryst. Liq. Cryst.* 626, 108–114.

13. Collings, P.J. and Hird, M. (1997). Introduction to Liquid Crystals: Physics and Chemistry, Taylor and Francis, London.

14. Marthandappa, M., Nagappa and Lokhanatha Rai, K. M. (1991). Thermotropic liquid- crystalline phases in binary mixtures of nonmesogenic compounds *J. Phys. Chem.* 95(16), 6369-6372.

15. Methemitis, C., Morcellet, M., Sabbadin, J., & Francois, J. (1986). Interactions between partially hydrolyzed polyacrylamide and ionic surfactants. *Euro. Poly. J.,* 22(8), 619-627.

16. Govindaiah, T. N., Sreepad, & Nagappa. (2015). Formation of lyotropic micellar nematic phase in binary mixture of liquid crystals. Mol. Cryst. Liq. Cryst., 608(1), 166-173.

17. Pandey, M. B., Dhar, R., Achalkumar, A. S., & Yelamaggad, C. V. (2007). Characteristic dielectric behaviour of the wide temperature range twist grain boundary phases of unsymmetrical liquid crystal dimmers. *J. Phys. Condens.Matter*.19, 436219.

18. Goncharuk, A. I., Lebovka, N. I., Lisetski, L. N., & Minenko, S. S. (2009). Aggregation, percolation and phase transitions in nematic liquid crystal EBBA doped with carbon nanotubes. *Journal of Physics D:Applied Physics*, 42, 165411.

19. Lisunova,M. O.,Mamunya, Y. P., Lebovka, N. I., &Melezhyk, A. V. (2007). Percolation behaviour of ultrahigh molecular weight polyethylene/multi-walled carbon nanotubes composites. *Eur. Polym. J.* 43, 949-958.

20. Ponevchinsky,V.V.,Goncharuk, A. I., Denisenko, V.G., Lebovka, N. I.,N. Lisetski, L., Nesterenko, M. I., Panikarskaya, V. D., & M. Soskin, S. (2013). LC nanocomposites: induced optical singularities, managed nano/micro structure, and electrical conductivity. Proc. SPIE, 8637. doi:10.1117/ 12.2000064.

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