# Differential Scanning Calorimetric, Polarized Light Microscopic and Impedance Spectroscopic Studies of Bicomponent Mixtures of Liquid Crystals: Cholesteryl Myristate and 4-n-Decyloxy Benzoic Acid

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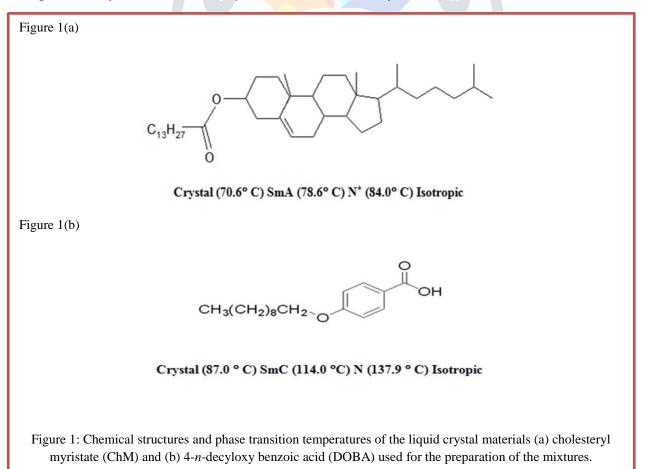
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The binary mixtures of cholesteryl myristate (ChM) and 4-*n*-decyloxybenzoic acid (DOBA) have been chosen for the thermodynamical, optical and dielectric studies. The present article deals with the observed experimental thermodynamical, optical-textures and electrical results on the above studied mixtures. This article presents the determination of transition temperatures and enthalpies by differential scanning calorimeter, the textural characterization by polarized light microscopy and dielectric parameters through Impedance Spectroscopy.

**INTRODUCTION:** Liquid crystals (LCs) have been extensively investigated because they possess properties favourable to many technical applications related to electro-optical (E-O) displays, optical storage devices and non-linear optics [1-3]. Various applications need optimization of physical properties (for example dielectric anisotropic, operating temperature range and stability of the mesophases etc.) by preparing appropriate mixture because none of the LC material discovered till date has all the desired parameters from application point of view. The mixing of liquid crystals allows an adjustment of physical properties and occasionally can lead to induction, expression or suppression of meso phases. Many interactions, which are accountable for the formation of various liquid crystalline phases like Vander Walls forces, hydrogen bonds and electron donor-acceptor interaction in binary mixtures of rod-like LCs have been, reported [4]. Each of these forces, collectively or separately, may be responsible for an increase or decrease of the stability of various liquid crystalline phases or for creating new phases in the mixed systems. Usually such mixtures can be premeditated to have a large thermally stable liquid crystalline (usually nematic or smectic) range, together with optimized values for key material properties. Study of mixtures is important from the point of view of molecular interactions as well. For example a mixture of two cholesteric compounds with opposite optical activities give rise to materials of controllable and temperature sensitive pitch [5]. At a particular composition of cholesteric compounds with opposite optical activities exactly compensated nematic mixture is produced [6]. Mixtures of two non mesogenic compounds may give mesogenic compound [7], mixtures of nematogens may give smectics [8] and mixtures of smectogens may give nematics [9]. Mixtures of smectic C (SmC) and cholesteric (N\*) phases may give chiral smectic C (SmC\*) phase [10]. The phenomenon of re-entrant nematic phases i.e. the reappearance of another nematic (N) phase after a smectic A phase (SmA) by lowering the temperature in rod-like LCs is common in mixtures [11, 12]. Wide varieties of frustrated smectic phases i.e. twist grain boundary (TGB) phases are also observed in mixtures [13-18]. Mixtures of a nematic (N) and a cholesteric (N\*) phase adopts the cholesteric texture [19-20]. These mixtures often show blue phases and that too with increased temperature range [21-22]. Nematics and cholesterics are not thermodynamically distinct and therefore they are supposed to be infinitely miscible [23]. The binary system of cholesterics and nematics are characterized by the induction of extra helical twisting which is presumably due to peculiar features of interaction between molecules of different components [24]. Consequently binary system of Cholesteryl Pelargonate (cholesteric) and Nonyloxybenzoic Acid (nematic) gives rise to SmA\* (now known as TGBA) phase [25-27]. Liquid crystals possessing nematic and/or smectic phases are most commonly used in production of LCDs due to their unique physical properties and wide temperature range. By applying an electric or magnetic field the orientation of the molecules can be driven in a predictable manner. This mechanism provides the basis for LCDs. The dielectric parameters of liquid crystals play an important role in the development of electro-optical devices. Frequency and temperature dependent dielectric studies of LCs mixture give information, not only about bulk properties, but also about molecular parameters, and their mutual association and rotation under an applied electric field.

## **RESULTS AND DISCUSSION:**

MIXTURES PREPARATION AND THEIR PHASE SEQUENCES: Pure grade samples of ChM and DOBA have been provided by the Institute of Physics, National Academy of Sciences of Ukraine, Kiev, Ukraine.



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Binary mixtures of different mol ratios were prepared by mixing the required amount of pure samples and were homogenized before taking the measurements by heating to a temperature several degrees above the transition to the isotropic phase, stirring/shaking, and finally cooling. The homogeneous nature of the mixtures was checked under a Polarized light microcopy (PLM) and the mixtures were used as such for the present study. The chemical structures of the individual compounds investigated in this work are shown in the Figure 1. The different mol ratios of the binary mixtures of ChM and DOBA and their phase sequences and phase transition temperatures are shown in **Table 1.** 

Systems (Mol %)	Phase sequences and their phase transition temperatures K (70.6) SmA (78.6) N* (84.0) I		
0			
9.7 (M <sub>1</sub> )	K (55.5) K <sub>1</sub> (65.5) SmA (79.1) N* (79.4) I		
17.7 (M <sub>2</sub> )	K (57.1) K <sub>1</sub> (62.2) SmA (77.6) N* (78.9) I		
30.0 (M <sub>3</sub> )	K (48.5) K <sub>1</sub> (60.0) SmA (83.5) N* (84.5) I		
34.9 (M <sub>4</sub> )	K <sub>1</sub> (64.5) SmA (89.9) N* (94.7) I		
56.6 (M <sub>5</sub> )	K (63.8) K <sub>1</sub> (76.1) SmA (82.5) N* (97.0) I		
68.2 (M <sub>6</sub> )	K (64.1) K <sub>1</sub> (79.6) SmA (85.5) N* (99.0) I		
79.9 (M <sub>7</sub> )	K (60.8) K <sub>2</sub> (82.5) SmC (86.1) N* (116.0) I		
92.3 (M <sub>8</sub> )	K <sub>2</sub> (87.7) SmC (101.6) N* (128.7) I		
95.5 (M <sub>9</sub> )	K <sub>2</sub> (90.0) SmC (106.0) N* (130.8) I		
97.7 (M <sub>10</sub> )	K <sub>2</sub> (91.8) SmC (111.5) N* (134.9) I		

POLARIZED LIGHT MICROSCOPY STUDY: OPTICAL TEXTURE PROPERTIES: A liquid crystal phase has distinct texture and PLM is the most preferred technique for phase identification of liquid crystal sample. In a polarizing microscope there are two polarizing filters. The polarizer is situated below the specimen stage usually with its permitted vibration direction fixed in the east-west direction although this usually can be rotated through 360°. The analyzer usually aligned in north-south direction but again can be rotated through 360°. So in general both analyzer and polarizer are in the optical path and they are perpendicular to each other. In other words they are said to be crossed and dark field of view is present in the eye piece. Insertion of isotropic material does not change this because polarization of light is unchanged as it travels through isotropic material; whereas LCs normally appear bright when viewed between crossed polarizer as the polarized light makes an angle other than 0° and 90° with the director of the liquid crystal. The usual magnification 10X for both the ocular (eye-piece) and objective lenses giving a final magnification of 100X have been used for taking the optical textures. The most commonly observed SmA phase appearance is that of the fan-shaped texture, which is shown in Figure 2(a).

K (87.0) SmC (114.0) N (137.9) I

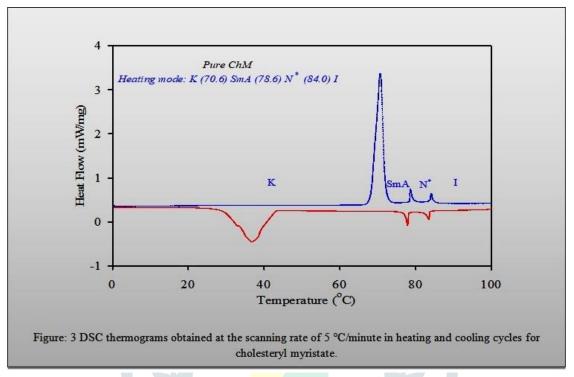


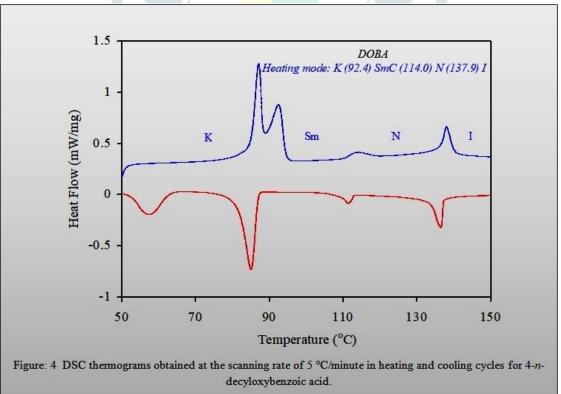
Figure: 2 Optical textures with total magnification of 100× observed for the binary mixtures M3 and M8 between two (unaligned) slides. Microphotograph (a) of the mixture M3 show SmA phase and Microphotograph (b) of the mixture M8 show transition from N\* to SmC phase.

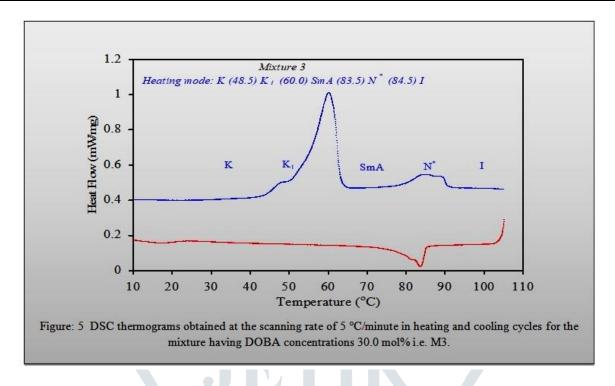
The smectic layers are arranged in so-called dupin cyclides [28-30], which contain a pair of focal conics. In fanshaped texture of SmA phase, the director basically lies in the plane of the substrate and the smectic layers are curved across the fans. We thus observe the projection of the confocal curves into the plane of the hyperbola with the ellipse degenerating to a line. Note that the backs of the fans are not as smooth in appearance as those of the cholesteric fan-shaped texture. One of the most commonly observed textures of the cholesteric phase prepared between two untreated glass substrates is the so-called oily streaks texture as shown partly in **Figure 2(b)**. The oily streaks can also appear in large bundles in which the director is basically anchored under planar conditions at the substrates, i.e. with the long molecular axis parallel to the bounding plates, which implies that the cholesteric helix axis is oriented perpendicular to the glass plates.

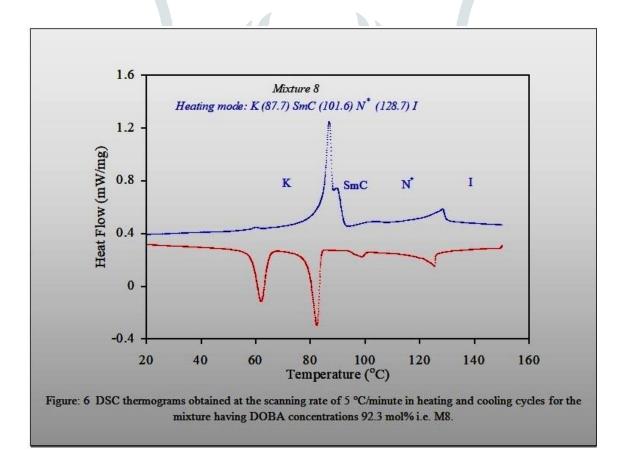
**DIFFERENTIAL SCANNING CALORIMETRY STUDY: BINARY PHASE DIAGRAMS AND EUTECTIC BEHAVIOUR:** Differential Scanning Calorimeter (DSC) thermograms in the heating and cooling cycles of the investigated pure compounds (i.e. ChM and DOBA) and their two specific mixtures 3 and 8 at the scanning rate of 5 °C/minute are shown in **Figures 3 to 6** respectively. Transition temperatures obtained at the scanning rate of 5 °C/min have been used to prepare the phase diagram in the heating and cooling cycles for the individual compounds and their mixtures (see **Figures 7** and **8**). From the phase diagrams, one can see enantiotropic SmA and N\* phases for ChM, i.e., observed phases in the cooling cycle are the same as that in the heating cycle. Phase sequence for ChM is K (70.6) SmA (78.6) N\* (84.0) Iso (83.3) N\* (77.8) SmA (36.7) K. For DOBA, the phase diagrams shows enantiotropic SmC and N phases having the phase sequence: K (92.4) SmC (114.0) N (137.9) Iso (136.4) N (111.3) SmC (84.9) K. Data in parentheses represent transition temperatures in °C as determined by DSC. These data are in good agreement with the literature [**18, 31**]. From **Figure 7**, it is clear that the melting of the mixtures from the solid phase exhibits two peaks which merge with each other at the eutectic composition i.e., at ~30 mol % of DOBA which is mixture M3. Near eutectic composition two melting

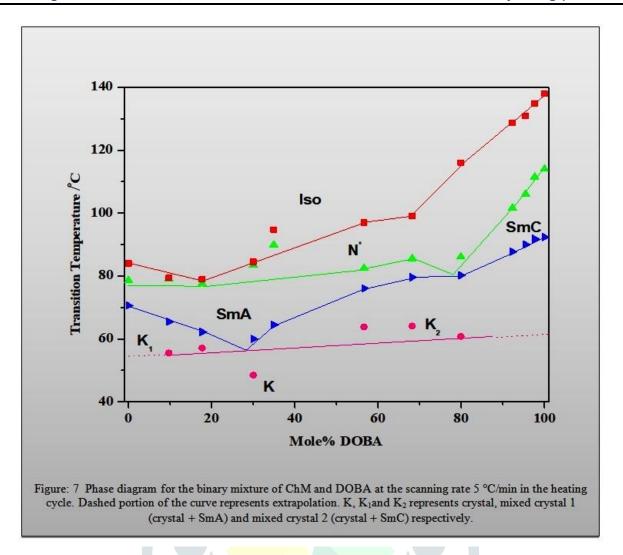
peaks overlap and they have been manually resolved into two curves. Transition enthalpies of the binary mixtures of ChM and DOBA have been determined by two methods: (i) by counting small squares (1 mm<sup>2</sup>) under the area covered by the peaks and (ii) by a weighing method [32]. Average transition temperature of crystal to mixed crystal phase increases slightly (see **Figure 7**) when the mol % of DOBA is increased to  $\sim$ 70. **Figures (7)** and (8) show simple eutectic phase diagrams with the eutectic temperature ( $T_e \sim 54$  °C) and eutectic composition  $30 \pm 4$  mol % of DOBA.











The eutectic composition has also been estimated by empirical relationship [33] as given below:

$$X_{e} = \frac{100 (T_{2} - T_{e})}{T_{1} + T_{2} - 2T_{e}}$$
 (1)

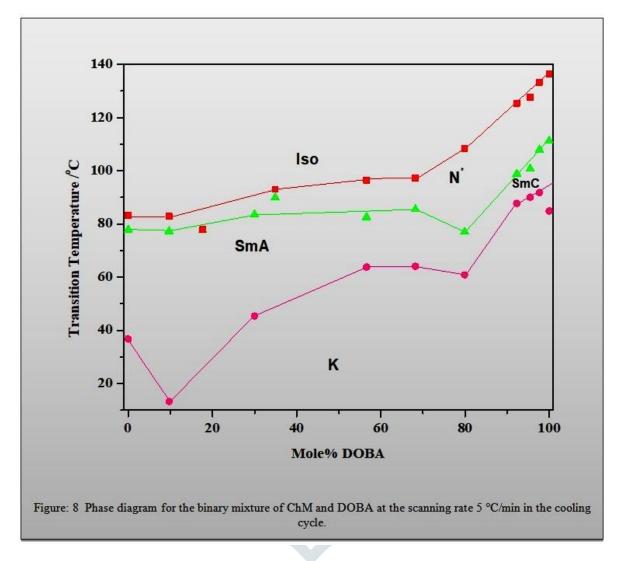
where  $T_1$  and  $T_2$  are melting points of the lower and higher melting components of the binary mixture, and  $X_e$  is the mol % of the lower melting component which is ChM. **Equation (1)** gives  $X_e = 74$  mol % of ChM (26 mol % of DOBA) i.e., approximately mixture M3.

Eutectic composition has also been estimated by Schroder-Van Laar equation [34, 35]:

$$\ln x_{e} = \frac{\Delta H}{R} \left( \frac{1}{T_{1}} - \frac{1}{Te} \right) - \ln f_{i}$$
 (2)

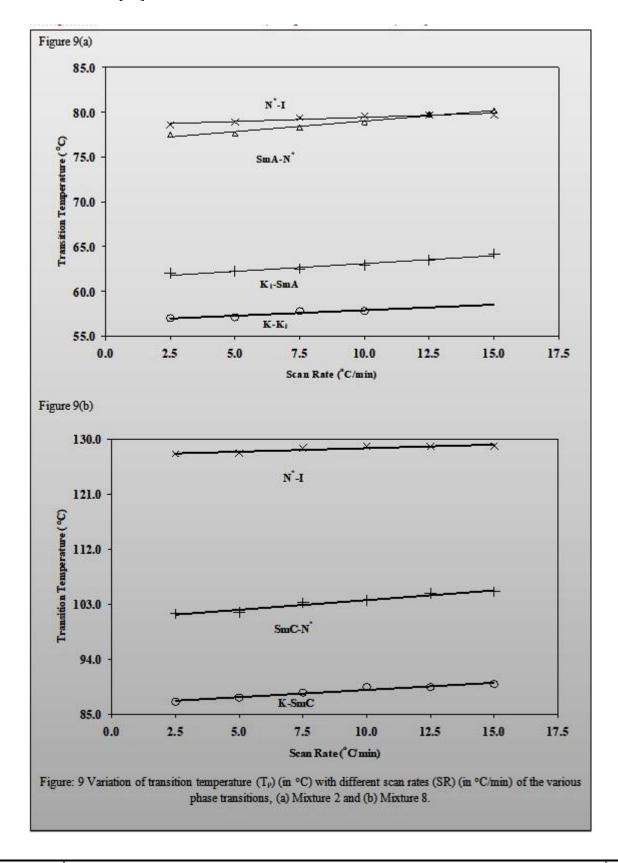
Where  $\Delta H$  is the crystal to mesophase transition enthalpy of ChM, R is the gas constant, and  $f_i$  is the activity coefficient. Value of  $f_i$  is 1 for ideal mixed phases [35]. Here  $\Delta H$  =124.8 J/g,  $T_1$  = 84.0 °C,  $T_e$  = 54.0 °C and R = 8.3 J deg<sup>-1</sup> mol<sup>-1</sup>. Taking  $f_i$  = 1,  $X_e$  comes out to be 64 mol % of ChM (36 mol % of DOBA), which marginally away from the experimental value (74 mol % ChM). However, one should note that the molecular length of ChM is large (almost twice) in comparison to that of DOBA; hence ChM–DOBA mixture may not be ideal one i.e.,  $f_i$  =

1 is not appropriate value. If we take experimental value of  $X_e$  i.e., 74 mol % of ChM then  $f_i$  comes out to be 0.87. In the studied system, SmA phase of ChM disappears when concentration of DOBA exceeds 80 mol % whereas on the other side, SmC phase of DOBA disappears when concentration of ChM exceeds 20 mol %, parting wide temperature range  $N^*$  phase (~ 20.0 °C) in heating and cooling cycles of the mixtures having DOBA concentrations approximately at ~ 80 mol % (see **Figures 7** and **8**).



Pure ChM shows the  $N^*$  and SmA phases which is characteristic property of ChM. As we increase the concentration of DOBA in ChM, it has been observed that the range of SmA phase increases in the heating cycle upto  $\sim 30$  mol % of DOBA (i.e., mixture M3). After this, as we increase the concentration of DOBA, the range of SmA phase remains constant upto  $\sim 68$  mol % of DOBA (i.e., mixture M6) but thereafter SmA phase disappears. The range of  $N^*$  phase is maximum at  $\sim 80$  mol % of DOBA due to the suppression of the SmA phase. In the cooling cycle also the range of SmA phase increases with increase of mol % of DOBA and it is maximum at 10 mol % of DOBA (i.e., mixture M1). After that, range of SmA phase is decreasing upto  $\sim 68$  mol % (i.e., mixture M6) and beyond that SmA phase disappears. The range of SmC phase decreases in the cooling cycle with increased concentration of ChM in DOBA and for  $\sim 20$  mol % of ChM (i.e., mixture M7); SmC phase disappears in the cooling cycle. The increase of the SmA phase in both the heating and cooling cycles can be explained by

the model given by Srivastava et al. [32]. In this model, for the binary mixtures of cholesteryl pelargonate (ChP) and 4-n-nonyloxy benzoic acid (NOBA), they have explained that NOBA molecules form doubly hydrogen-bonded dimer with a small percentage of monomer or dimer with one broken hydrogen bond [32]. Dimers of NOBA molecules in a specific arrangement increase the flexible tail of alkyl chains which helps in the formation of a layered SmA structure [32].



Long alkyl chains also help in increasing the stability of SmA phase by decreasing the repulsive dipole-dipole interaction around the rigid cores by increasing the intermolecular distances [32]. Hence, for the present mixtures also upto 30 mol % of DOBA (i.e., mixture M3) all the above factors are apparently responsible for the appearance and stabilization of the SmA phase. When concentration of DOBA molecules becomes approximately double of ChM, alternate stratum of ChM molecules and DOBA dimers rule out the possibility of the layered structure [32]. Perhaps the competition between ChM and DOBA molecules to form two different types of layered structure reduces the stability of the SmA phase. The SmC phase is observed for the pure DOBA and is destroyed by introducing even low concentration of ChM (~ 20 mol %) i.e., mixture M2. The reduction of the range of SmC phase with small concentration of ChM in DOBA can be explained on the basis of increased molecular length due to the addition of ChM [32]. Generally, the phase transition temperatures increase linearly with the increasing scan rate. Figure 9 (a-b) shows how the transition temperatures of various mesophases of the mixtures M2 and M8 (as representative cases) vary with the scan rate. In this plot, we have taken DSC observations of the mixtures M2 and M8 with different scan rates from 2.5 to 15 °C/min at an interval of 2.5. Using a least square fit method, we have obtained the linear equations for various mesophases of the above mixtures. The linear equations of the transition temperatures of the various mesophases with different scan rates for the mixtures M2 and M8 have been established as illustrated below:

# Mixture 2

For K- $K_1$  phase transition:

$$T_P = 0.124 \, SR + 56.65 \, and \, R^2 = 0.8467$$

For  $K_1$ -SmA phase transition:

$$T_P = 0.175 \, SR + 61.35 \, and \, R^2 = 0.9532$$
 3 (b)

For SmA-N\* phase transition:

$$T_P = 0.235 SR + 76.65$$
 and  $R^2 = 0.9703$ 

For N\*-I phase transition:

$$T_P = 0.0926 SR + 78.50$$
 and  $R^2 = 0.8773$  3 (d)

#### Mixture 8

For K-SmC phase transition:

$$T_P = 0.2343 \text{ SR} + 86.6 \text{ and } R^2 = 0.9477$$

For SmC-N\* phase transition:

$$T_P = 0.3166 \text{ SR} + 100.48 \text{ and } R^2 = 0.9586$$

For N\*-I phase transition:

$$T_P = 0.1154 \text{ SR} + 127.37 \text{ and } R^2 = 0.853$$

From **Equations 3** (a-d) and 4 (a-c), it has been seen that, the value of the slope of the various phase transitions are different, i.e., the lines do not indicates the same steepness. Also, it has been noticed that, the value of the

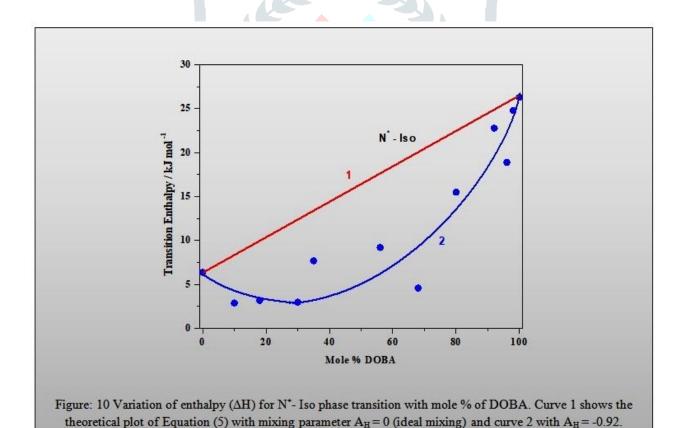
correlation coefficient (R<sup>2</sup>) of the various phase transitions are different. It describes that, the tendency of all the lines are not resembled to each other.

The transition enthalpies and entropies for  $N^*$  to Iso phase i.e.,  $[(\Delta H)_{N^*-Iso}]$  and  $(\Delta S)_{N^*-Iso}]$  have been fitted with the help of empirical equations [32] as given below:

$$\Delta H = X_1 \Delta H_1 + (1 - X_1) \Delta H_2 + A_H \sqrt{[X_1 \Delta H_1 (1 - X_1) \Delta H_2]}$$
 (5)

$$\Delta S = X_1 \Delta S_1 + (1 - X_1) \Delta S_2 + A_S \sqrt{[X_1 \Delta S_1 (1 - X_1) \Delta S_2]}$$
(6)

 $\Delta H_1$  and  $\Delta S_1$  are the enthalpy and entropy of  $N^*$  to Isotropic phase transition of ChM.  $\Delta H_2$  and  $\Delta S_2$  are the enthalpy and entropy of  $N^*$  to Isotropic phase transition of DOBA.  $A_H$  and  $A_S$  are the mixing parameters and their best fit values are  $-0.92 \pm 0.39$  and  $-0.62 \pm 0.35$  respectively showing deviation from ideal mixing (Curves 1 of **Figures 10** and **11**). Finite negative values of the mixing terms of **Equations (5)** and **(6)** suggest that two components of the mixture interact to produce excess disordering and destabilize  $N^*$  phase as observed in several other binary systems [9, 27].



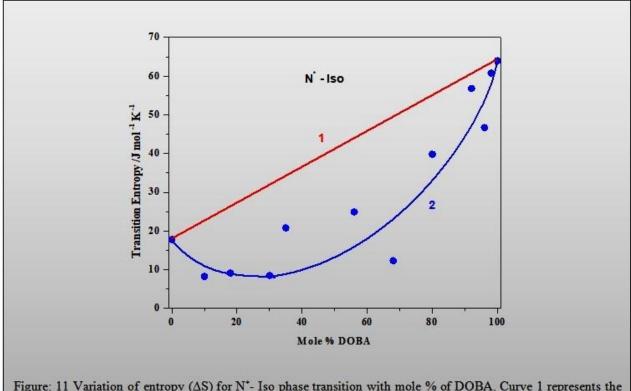


Figure: 11 Variation of entropy ( $\Delta S$ ) for N\*- Iso phase transition with mole % of DOBA. Curve 1 represents the theoretical plot of Equation (6) with mixing parameter  $A_S = 0$  (ideal mixing) and curve 2 with  $A_S = -0.60$ .

## IMPEDANCE SPECTROSCOPIC STUDY: DIELECTRIC PARAMETERS AND ANISOTROPY

**BEHAVIOUR:** The two principal components of the permittivities (ε'<sub>⊥</sub>: measuring electric field normal to the long molecular axis in planar configuration and  $\varepsilon'_{\parallel}$ : measuring electric field parallel to the long molecular axis in homeotropic configuration) have been determined for the typical mixtures having DOBA concentrations 30.0 and 92.3 mole % i.e. mixtures M3 and M8 respectively. M3 possess SmA phase and M8 possess SmC and N\* phases. Choice of these two mixtures is based on the logic that these mixtures lie approximately in the lower and upper concentration regions of the DOBA where wide ranges of the SmA phase (for M3) and SmC and N\* phases (in M8) have been observed. Anisotropy of the permittivity of the liquid crystal material is a necessary property for their possible use in devices. For both these mixtures M3 and M8, it has been observed that  $\epsilon_{\perp}^{'}$  and ε'<sub>||</sub> are almost invariant in the frequency range 100 Hz-100 kHz for all the temperatures between isotropic liquid to crystal phases, implying that no dipolar relaxation phenomenon occurs in this frequency range. In both the alignments of the samples,  $\epsilon'_{\perp}$  and  $\epsilon'_{\parallel}$  data are constant at least up to 100 kHz and therefore 10 kHz data have been used to determine the dielectric anisotropy  $\Delta \varepsilon' = (\varepsilon'_{\parallel} - \varepsilon'_{\perp})$  at different temperatures lying between isotropic liquid to crystal phases as shown in Figure 12. The dielectric losses are almost negligible and therefore not reported here. As anticipated, in the isotropic liquid phase,  $\Delta \varepsilon'$  has been found to be  $\cong 0$  showing that there is no preferred alignment of the molecules. Below isotropic liquid to SmA transition temperature ( $T_{Iso-SmA}$ ), both  $\epsilon'_{\perp}$ and  $\varepsilon_{\parallel}$  increases from isotropic liquid value with decrease in the temperature. However, increase in the value of  $\epsilon'_{\parallel}$  is less as compared to the value of  $\epsilon'_{\perp}$ . Thus M3 is showing negative dielectric anisotropy ( $\Delta\epsilon' = \epsilon'_{\parallel} - \epsilon'_{\perp} < 0$ )

in the SmA phase (see Figure 12 (a)). The dielectric anisotropy is maximum in magnitude ( $\sim$ 0.16) in the SmA phase at  $\sim$  45 °C (see Table 2).

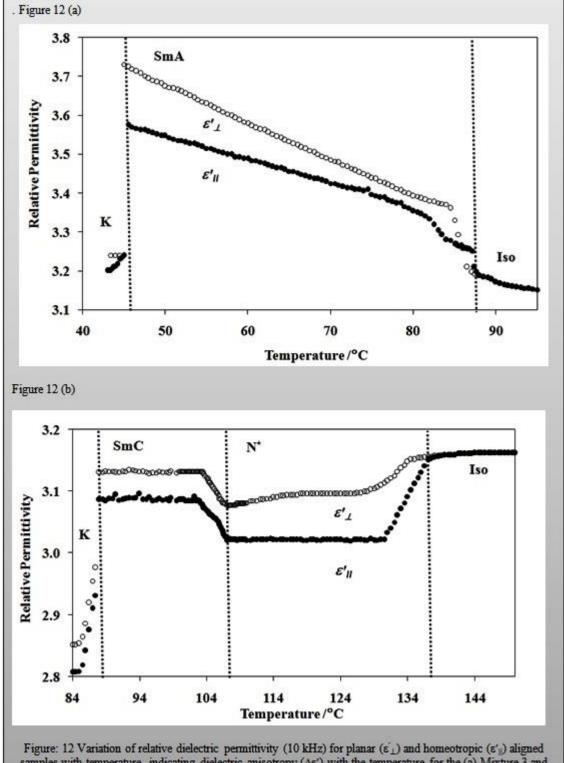


Figure: 12 Variation of relative dielectric permittivity (10 kHz) for planar (ε'<sub>⊥</sub>) and homeotropic (ε'<sub>||</sub>) aligned samples with temperature, indicating dielectric anisotropy (Δε') with the temperature for the (a) Mixture 3 and (b) Mixture 8. Vertical lines show the transition temperatures on the basis of dielectric studies.

Table: 2 The dielectric anisotropy  $\Delta \varepsilon' = \varepsilon'_{\parallel} - \varepsilon'_{\perp}$  in different mesophases at 10 kHz. The (+) and (-) represents positive and negative dielectric anisotropic of the individual material/mixtures respectively. × shows that the phase transition does not exist.

Dielectric anisotropy ( $\Delta \varepsilon'$ ) in different mesophases at 10 kHz					
Systems	Nematic (N)	Smectic C (SmC)	Smectic A (SmA)	Cholesteric (N*)	
Pure DOBA	(+) 0.07	(+) 0.33	×	×	
Pure ChM	×	×	(-) 0.65	(-) 0.20	
Mixture 3	×	×	(-) 0.16	×	
Mixture 8	X	(-) 0.045	×	(-) 0.055	

In the mixture M8 also,  $\Delta \varepsilon'$  has been found to be  $\cong 0$  in the isotropic liquid phase (as in mixture M3). Below  $T_{Iso}$  $_{N}^{*}$ , both  $\epsilon_{\perp}^{'}$  and  $\epsilon_{\parallel}^{'}$  decreases from the isotropic liquid value (unlike the case of M3), but the value of  $\epsilon_{\perp}^{'}$  is higher in the comparison to the value of  $\varepsilon_{\parallel}$  with decrease in the temperature showing negative dielectric anisotropy ( $\Delta\epsilon' = \epsilon'_{\parallel} - \epsilon_{\perp}' < 0$ ) in the  $N^*$  phases (see Figure 12 (b)). A clear change in the slopes of  $\epsilon'_{\perp}$  and  $\epsilon'_{\parallel}$ data has been observed at ~107 °C. This suggests macroscopic change in the structure of material at this temperature and confirms the existence of another phase below this temperature which has also been observed during the thermodynamic and polarized optical microscopic studies and confirms this phase as SmC.

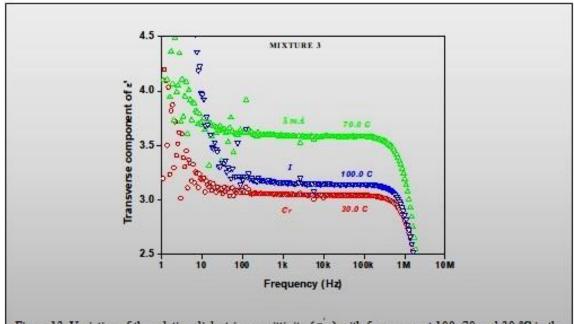
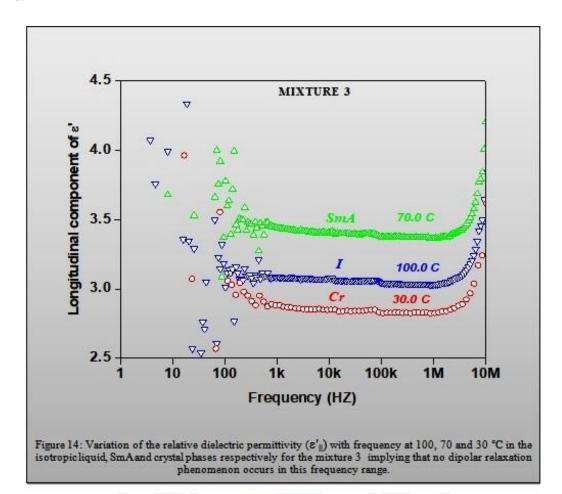
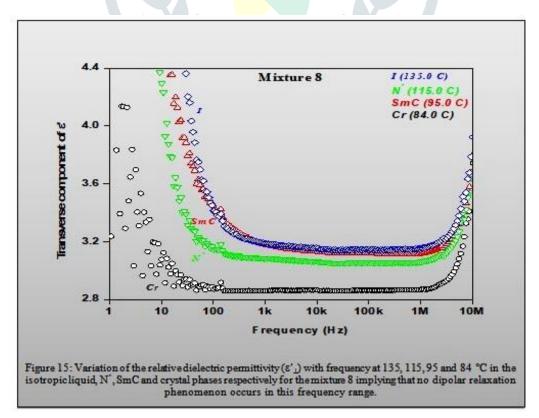
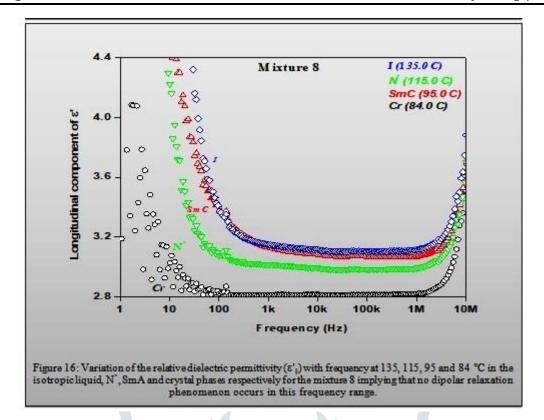


Figure 13: Variation of the relative dielectric permittivity (E) with frequency at 100, 70 and 30 °C in the isotropic liquid, SmA and crystal phases respectively for the mixture 3 implying that no dipolar relaxation phenomenon occurs in this frequency range.

The dielectric anisotropy has maxima (0.055) in  $N^*$  phase at ~107 °C and 0.045 in SmC phase at ~88 °C (see Table 2). It has been examined that the dielectric permittivity in planar and homeotropic configurations in the isotropic liquid to crystal phase is almost constant with the frequency in the frequency range 1 Hz to 10 MHz, implying that no dipolar relaxation phenomenon occurs in this frequency range and the same is evident from Figures 13 to 16.







**CONCLUSIONS:** Following lines summarize the result of the bicomponent mixtures of liquid crystals ChM and DOBA:

- \* Fan-shaped textures have been observed in the SmA phase and oily streaks in N\* phase under the polarized optical microscope for the mixtures having DOBA concentrations 30.0 and 92.3 mol %, respectively.
- \* In the variation of the transition temperatures of various mesophases with different scan rate, for the mixtures having DOBA concentrations 17.7 and 92.3 mol %, it has been established that, the slope of the lines for various phase transitions do not indicates the same steepness and also the tendency of the lines are not resembled to each other.
- \* In the binary system of ChM and DOBA, we have observed the phase diagram in heating and cooling cycles. The melting of the mixtures from the solid phase exhibits two peaks which merge with each other at the eutectic composition of 30 mol % of DOBA.
- \* The range of the SmA phase which is 8 °C in ChM, increases with mol % of DOBA and becomes maximum at the eutectic composition (~30 mol % concentration of DOBA). Above eutectic composition range of SmA phase is almost constant upto 68 mol % and disappears at ~ 80 mol % of DOBA. Thus around eutectic composition stability of the SmA phase is highest.
- \* The individual compounds DOBA and ChM are having positive and negative dielectric anisotropy respectively. However, the mixtures having DOBA concentrations 30.0 and 92.3 mole % show low value of negative dielectric anisotropy.

The dielectric permittivity in planar and homeotropic configurations in the isotropic liquid to crystal phase is almost constant with the frequency in the frequency range 1 Hz to 10 MHz, implying that no dipolar relaxation phenomenon occurs in this frequency range.

## **REFERENCES:**

- [1]. Collings P, Hird M. Introduction to liquid crystals, Taylor & Francis, London; 1997.
- [2]. Sage IC, Crossland WA, Wilkinson TD. Handbook of Liquid Crystals: Edited by Demus D, Goodby J, Gray GW, Spiess HW, Vill V. Ist vol., ch. IX.1–IX.2 Wiley: VCH, Weinheim; 1998.
- [3]. Chigrinov, V.G. "Liquid Crystal Devices: Physics and Application", Artech House, Boston, 1999.
- [4]. Bamezai, R.K.; Soni, A.; Vakhovskaya, Z.; Kresse, H. Russian Journal of Physical Chemistry A 2009, 83, 2283-2287.
- [5]. Wysocki JJ, Adams JE, Olechna DJ. Relaxation to the Cholesteric State: Liquid Crystals and Ordered Fluids, Edited by Johnson JF, Porter RS. Ist vol., 419-45 Plenum Press: New York; 1970.
- [6]. Nair CKS, Ramanaiah KV. Electro-Optic and Dielectric Studies in Cholesteric Liquid Crystal Mixtures.

  Mol Cryst Liq Cryst. 1983; 103:271-85.
- [7]. Gupta R, Vora RA. Exhibition of Non-Linear Behaviour and Smectic and Nematic Mesophases in the Binary Systems Where Both the Components are Non-Mesogenic. Mol Cryst Liq Cryst. 1984; 106:147-59.
- [8]. Lohar JM, Dave JS. Emergence of Smectic Mesophase in Binary Mixtures of Pure Nematogens. Mol Cryst Liq Cryst. 1983; 103:181-92.
- [9]. Dabrowski R, Wazynska B, Sosnowska B. Creation of a Nematic phase in mixtures of Smectic A1 phases. Liq Cryst. 1986: 1:415-28.
- [10]. Aliev DF, Bairamov GM, Cherkashina RM. Smectic C\* phase induced by cholesterol derivatives. Sov Phys Crystallogr. 1987; 32:1215-21.

- [11]. Pelzl G, Scholz C, Diele S, Deutscher HJ, Demus D, Sackman H. Reentrant Nematic Phases in Binary Systems of Terminal-Nonpolar Compounds III. Systems of Homologous n-Alkyloxyphenyl 4-[4-n-alkylcyclohexanoyloxy]-benzoates. Mol Cryst Liq Cryst. 1989; 168:197-208.
- [12]. Diele S, Pelzl G, Humke A, Wunsch S, Schafer W, Zaschke H, Demus D. New Binary Liquid Crystal Systems with the Phase Sequence SA SC SA. Mol Cryst Liq Cryst. 1989; 173:113-19.
- [13]. Cladis PE. New Liquid Crystal Phase Diagram. Phys Rev Lett. 1975; 35:48-51.
- [14]. Nounesis G, Garland CW, Shashaidhar R. Crossover from three-dimensional XY to tricritical behaviour for the nematic-smectic-A1 phase transition. Phys Rev A. 1991; 43: 1849-56.
- [15]. Patel P, Kumar S, Ukleja P. The case of missing incommensurate Smectic A phases. Liq Cryst. 1994; 16:351-71.
- [16]. Richard H, Mauzac M, Sigaud G, Achard MF, Hardouin F. Liquid crystal side chain polysiloxanes containing various proportions of non-mesogenic units. Liq Cryst. 1991; 9: 679-89.
- [17]. Pandey MB, Dhar R, Kuczynski W. Dielectric Investigations of Induced Twist Grain Boundary Phases in the Binary Mixtures of Cholesteryl Benzoate and Di-Heptyloxyazoxybenzene. Ferroelectrics 2006; 343:69-82.
- [18]. Dhar R, Srivastava AK, Agrawal VK. Induced twisted-grain-boundary phases in the binary mixtures of a Cholesteric and a Nematic compound. Phase Transitions 2003; 76: 959-74.
- [19]. Dhar R, Pandey MB, Agrawal VK. Twisted Grain Boundary Phases in the Binary Mixtures of 3β-Chloro-5-Cholestene and 4-N-Decyloxybenzoic Acid. Phase Transitions 2003; 76:763-80.
- [20]. Chilaya GS, Elashvili ZM, Ivchenko SP, Vinokur KD. New Nematic-Chiral Mixtures for Application in Thermography. Mol Cryst Liq Cryst. 1984; 106:67-71.

- [21]. Nagappa, Revannasidduiah D, Krisnamurti D. Optical Behaviour of Mixtures of Nematic and Cholesteric Compounds. Mol Cryst Liq Cryst. 1983; 101:103-27.
- [22]. Spier B, Stegemeyer H. Electric field-induced blue phases in liquid-crystalline systems of high chirality and negative dielectric anisotropy. Liq Cryst. 1991; 9:1-9.
- [23]. Heppke G, Kitzerow HS, Lotzsch D, Papenfeb C. Blue phase mixtures exhibiting low fractions of a chiral compound experimental observation of some unusual properties. Liq Cryst. 1990; 8:407-18.
- [24]. Fin PL, Cladis PE. Cholesteric Blue Phases in Mixtures and in an Electric Field. Mol Cryst Liq Cryst. 1982; 84:159-92.
- [25]. Chilaya GS, Lisetski LN. Cholesteric liquid Crystals: Physical Properties and Molecular-Statistical Theories. Mol Cryst Liq Cryst. 1986; 140:243-86.
- [26]. Lavrentovich OD, Nastishin YA. Quasi crystalline intermediate structure between Cholesteric and Smectic A phases. Ukr Fiz Zhurn. 1990; 35:221-23.
- [27]. Lavrentovich OD, Nastishin YA, Kulishov VI, Narkevich YS, Tolochko AS, Shiyanovskii SV. Helical Smectic A. Euro Phys Lett. 1990; 13:313-18.
- [28]. Friedel G, Grandjean F. Observations on the geometrical focal conic liquid. Bull Soc Fr Miner. 1910, 33:409-65.
- [29]. Kleman M. Points, Lines and Walls: Liquid Crystals, Magnetic Systems, and Various Ordered Media.

  John Willey & Sons Chichester; 1983.
- [30]. Bouligand YJ. Research on the textures of mesomorphic states: Arrangements in the Smectic focal: theoretical considerations and reminders. Phys Fr. 1972; 33:525-47.
- [31]. Srivastava SL, Dhar R, Kurik MV. Changes in Electrical & Thermodynamic Properties of Cholesteryl Myristate on Irradiation. Mol Mat. 1993; 2:261-73.

- [32]. Srivastava, S.L.; Dhar, R.; Mukherjee, A. Mol. Cryst. Liq. Cryst. 1996, 287, 139-154.
- [33]. Hsu ECH, Johnson JF. Prediction of Eutectic Temperatures, Compositions and Phase Diagrams for Binary Mesophase Systems. Mol Cryst Liq Cryst. 1974; 27:95-104.
- [34]. Demus D, Fietkau CH, Schubert R, Kehlen H. Calculation and Experimental Verification of Eutectic Systems with Nematic Phases. Mol Cryst Liq Cryst. 1974; 25:215-32.
- [35]. Griffen CW, Porter RS. Phase Studies on Binary Systems of Cholesteryl Esters A. Two Aliphatic Ester Pairs. Mol Cryst Liq Cryst. 1973; 21:77-98.

