

FREQUENCY AND TEMPERATURE DEPENDENT ELECTRICAL PARAMETERS OF THE BINARY MIXTURES OF THE CHOLESTERYL MYRISTATE AND 4-*n*-DECYLOXYBENZOIC ACID

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The present research article deals with the electrical parameters of the binary mixtures of cholesteryl myristate (ChM) and 4-*n*-decyloxybenzoic acid (DOBA). The present research article copes with the observed experimental electrical results on the above studied mixtures. This research article presents the determination of dielectric permittivity, dielectric anisotropy and conductivity by impedance spectroscopy.

INTRODUCTION: The frequency and temperature dependent dielectric method is considered to be a powerful tool [1-4] for studying the electrical properties of the mesophases. Such studies make it possible to characterize not only about bulk properties, but also about molecular parameters (dielectric permittivity, anisotropy etc.), and their mutual association and rotation under an applied electric field. Anisotropy of the dielectric permittivity of the liquid crystal material is a necessary property for their possible use in devices.

RESULTS AND DISCUSSION: Pure grade samples of ChM and DOBA have been provided by the Institute of Physics, National Academy of Sciences of Ukraine, Kiev, Ukraine. 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 microscopy (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**.

Figure 1(a)

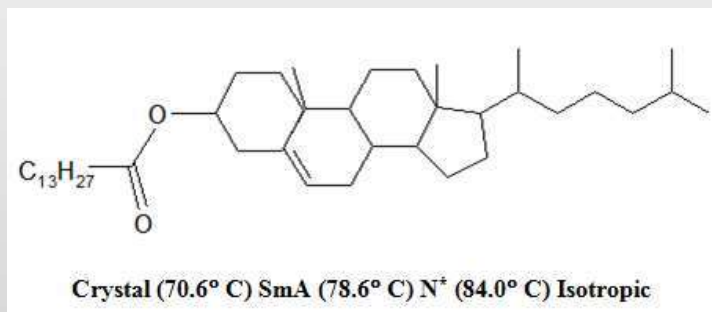


Figure 1(b)

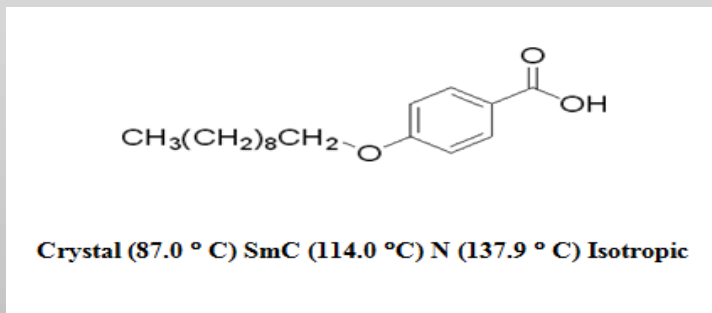


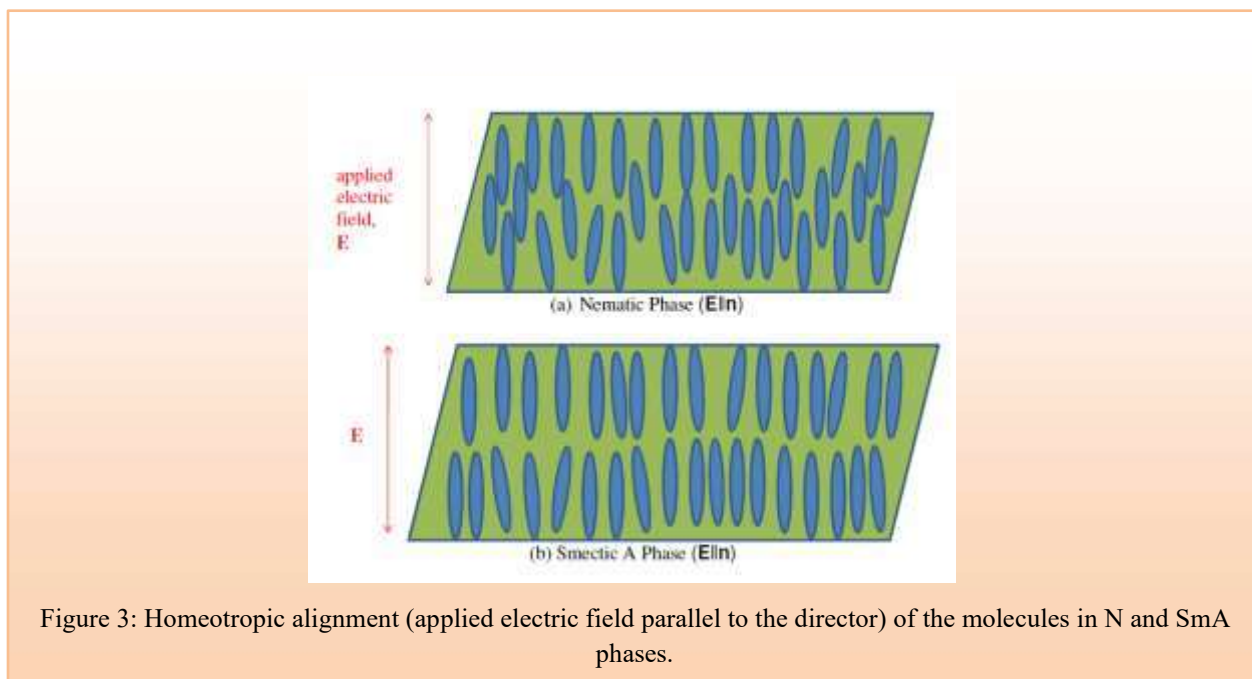
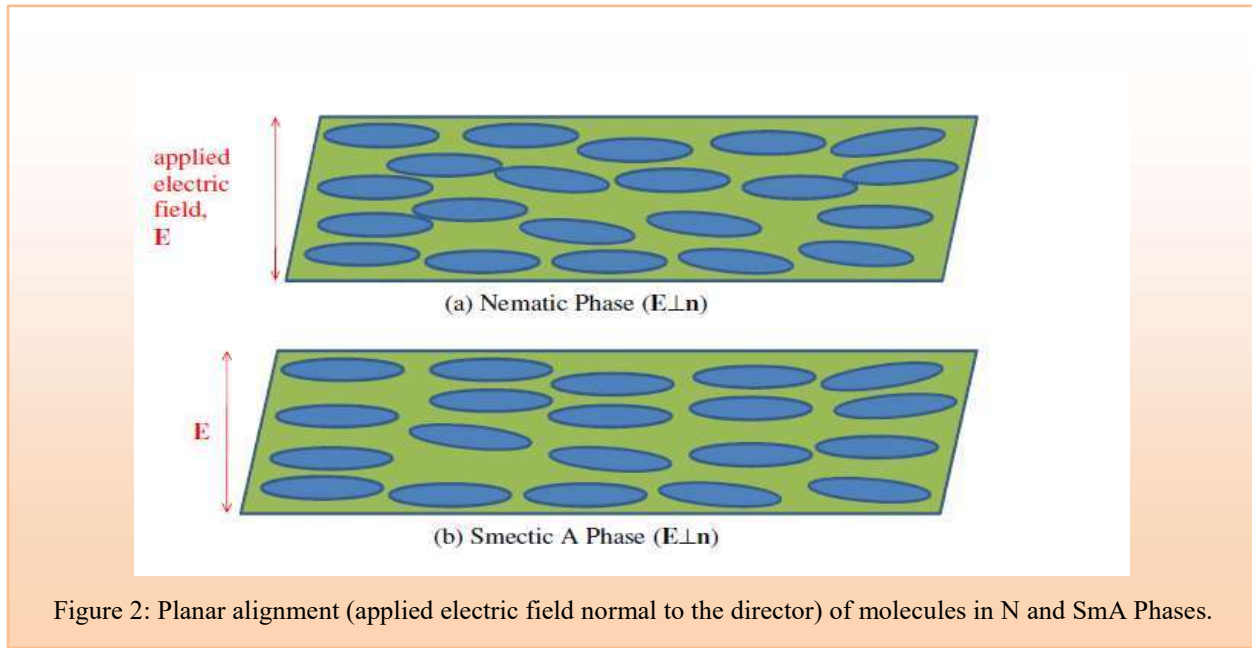
Figure 1: Chemical structures and phase transition temperatures of the liquid crystal materials (a) cholesteryl myristate (ChM) and (b) 4-*n*-decyloxy benzoic acid (DOBA) used for the preparation of the mixtures.

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**.

Table 1 Phase sequences and their phase transition temperatures (in °C) for different mole percents of DOBA in heating mode. K, K₁ and K₂ represents crystal, mixed crystal 1 (crystal + SmA), and mixed crystal 2 (crystal + SmC) respectively.

Systems (Mol %)	Phase sequences and their phase transition temperatures
0	K (70.6) SmA (78.6) N* (84.0) I
9.7 (M ₁)	K (55.5) K ₁ (65.5) SmA (79.1) N* (79.4) I
17.7 (M ₂)	K (57.1) K ₁ (62.2) SmA (77.6) N* (78.9) I
30.0 (M ₃)	K (48.5) K ₁ (60.0) SmA (83.5) N* (84.5) I
34.9 (M ₄)	K ₁ (64.5) SmA (89.9) N* (94.7) I
56.6 (M ₅)	K (63.8) K ₁ (76.1) SmA (82.5) N* (97.0) I
68.2 (M ₆)	K (64.1) K ₁ (79.6) SmA (85.5) N* (99.0) I
79.9 (M ₇)	K (60.8) K ₂ (82.5) SmC (86.1) N* (116.0) I
92.3 (M ₈)	K ₂ (87.7) SmC (101.6) N* (128.7) I
95.5 (M ₉)	K ₂ (90.0) SmC (106.0) N* (130.8) I
97.7 (M ₁₀)	K ₂ (91.8) SmC (111.5) N* (134.9) I
100	K (87.0) SmC (114.0) N (137.9) I

The two principal components of the permittivities (ϵ'_{\perp} : measuring electric field normal to the long molecular axis in planar configuration and ϵ'_{\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. The planar and homeotropic alignment of the N and SmA phases (as representative cases) are shown in **Figures 2** and **3**.



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. 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 4 to 7**.

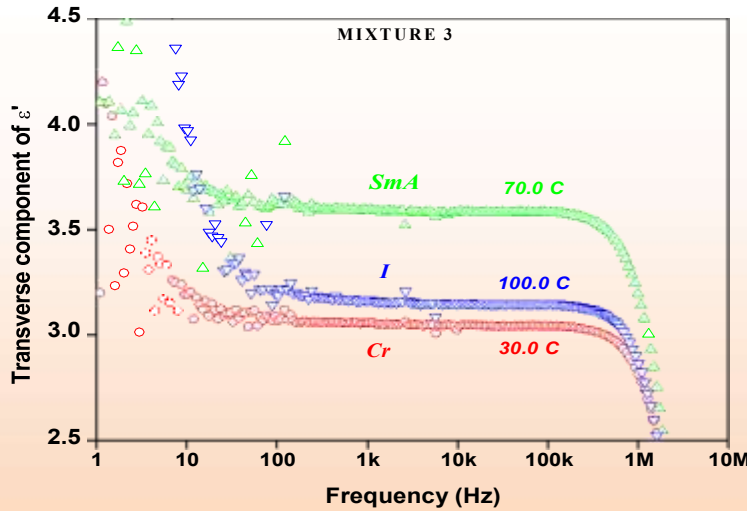


Figure 4: Variation of the relative dielectric permittivity (ϵ'_{\perp}) with frequency at 100, 70 and 30 °C in the isotropic liquid, SmA and crystal phases respectively for the mixture 3 implying that no dipolar relaxation phenomenon occurs in this frequency range.

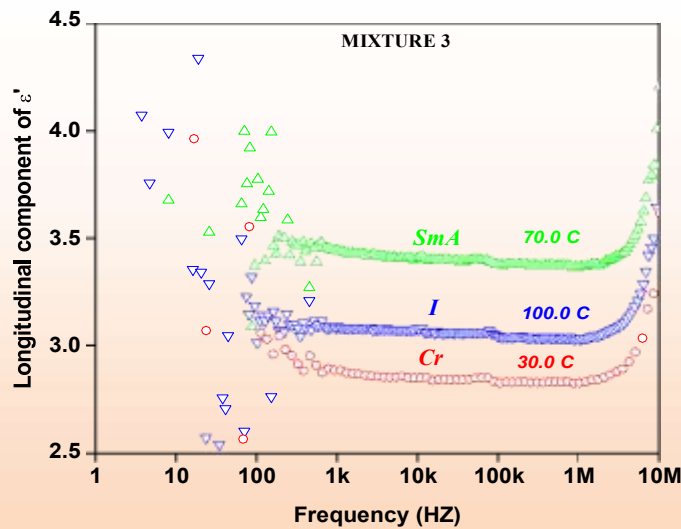


Figure 5: Variation of the relative dielectric permittivity (ϵ'_{\parallel}) with frequency at 100, 70 and 30 °C in the isotropic liquid, SmA and crystal phases respectively for the mixture 3 implying that no dipolar relaxation phenomenon occurs in this frequency range.

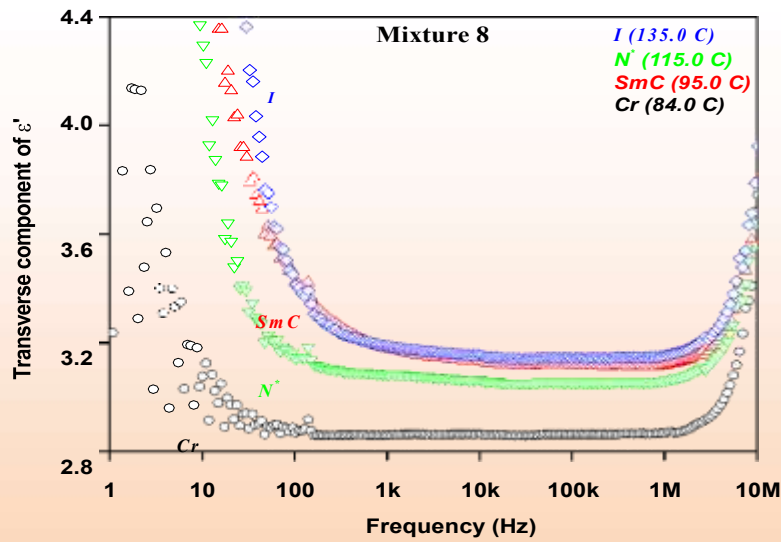


Figure 6: Variation of the relative dielectric permittivity (ϵ'_{\perp}) with frequency at 135, 115, 95 and 84 °C in the isotropic liquid, N , SmC and crystal phases respectively for the mixture 8 implying that no dipolar relaxation phenomenon occurs in this frequency range.

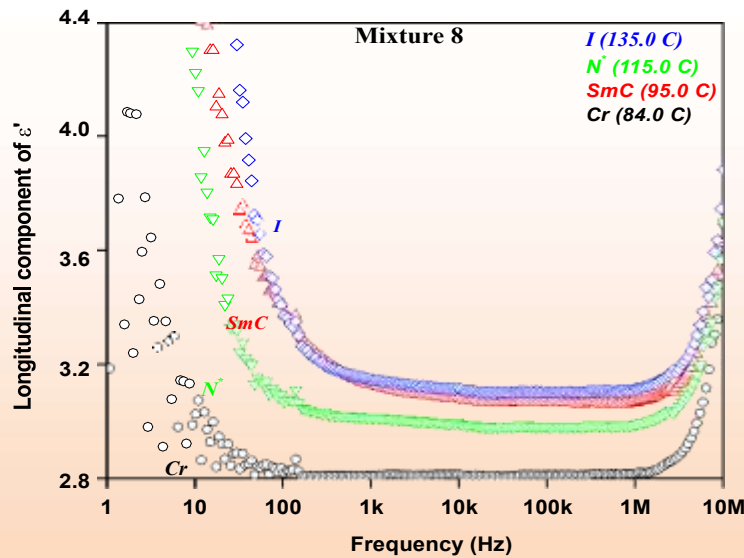


Figure 7: Variation of the relative dielectric permittivity (ϵ'_{\parallel}) with frequency at 135, 115, 95 and 84 °C in the isotropic liquid, N , SmA and crystal phases respectively for the mixture 8 implying that no dipolar relaxation phenomenon occurs in this frequency range.

As for both these mixtures M3 and M8, it has been observed that ϵ'_{\perp} and ϵ'_{\parallel} 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, ϵ'_{\perp} and ϵ'_{\parallel} data are constant at least up to 100 kHz and therefore 10 kHz data have been used to determine the dielectric anisotropy $\Delta\epsilon' = (\epsilon'_{\parallel} - \epsilon'_{\perp})$ at different temperatures lying between isotropic liquid to crystal phases as shown in **Figure 8**. The dielectric losses are almost negligible and therefore not reported here. As anticipated, in the isotropic liquid phase, $\Delta\epsilon'$ has been found to be $\cong 0$ showing that there is no preferred alignment of the molecules. Below isotropic liquid to SmA transition temperature ($T_{\text{Iso-SmA}}$), both ϵ'_{\perp} and ϵ'_{\parallel} increases from isotropic liquid value with decrease in the temperature. However, increase in the value of ϵ'_{\parallel} is less as compared to the value of ϵ'_{\perp} . Thus M3 is showing negative dielectric anisotropy ($\Delta\epsilon' = \epsilon'_{\parallel} - \epsilon'_{\perp} < 0$) in the SmA phase (see **Figure 8 (a)**). The dielectric anisotropy is maximum in magnitude (~ 0.16) in the SmA phase at $\sim 45^{\circ}\text{C}$ (see **Table 2**).

Figure 8 (a)

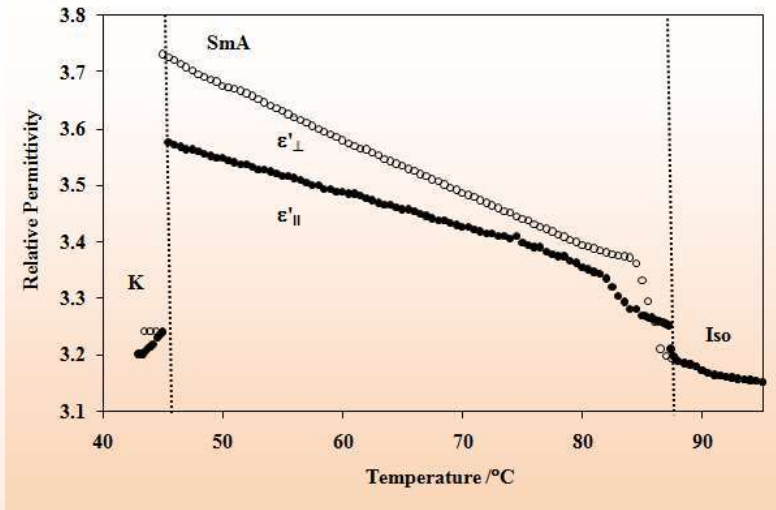


Figure 8 (b)

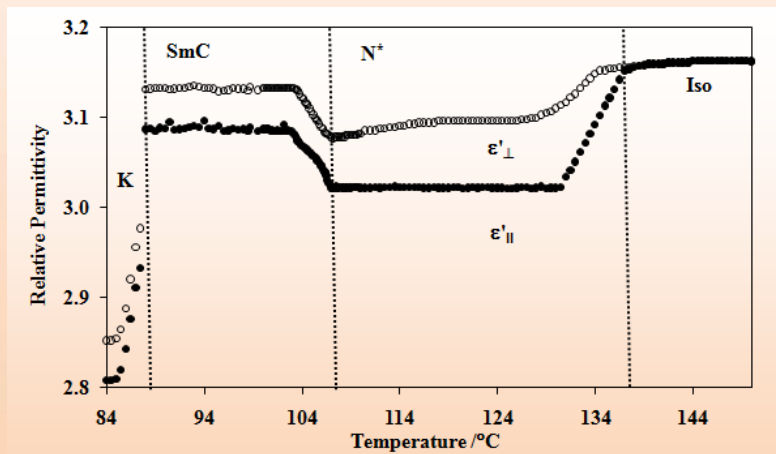


Figure: 8 Variation of relative dielectric permittivity (10 kHz) for planar (ϵ'_{\perp}) and homeotropic (ϵ'_{\parallel}) aligned samples with temperature, indicating dielectric anisotropy ($\Delta\epsilon'$) with the temperature for the (a) Mixture 3 and (b) Mixture 8. Vertical lines show the transition temperatures on the basis of dielectric studies.

Table 2 The dielectric anisotropy $\Delta\epsilon' = \epsilon'_{\parallel} - \epsilon'_{\perp}$ 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 ($\Delta\epsilon'$) 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	×	(-) 0.045	×	(-) 0.055

In the mixture M8 also, $\Delta\epsilon'$ has been found to be $\cong 0$ in the isotropic liquid phase (as in mixture M3). Below T_{Iso-N^*} , both ϵ'_{\perp} and ϵ'_{\parallel} decreases from the isotropic liquid value (unlike the case of M3), but the value of ϵ'_{\perp} is higher in the comparison to the value of ϵ'_{\parallel} with decrease in the temperature showing negative dielectric anisotropy ($\Delta\epsilon' = \epsilon'_{\parallel} - \epsilon'_{\perp} < 0$) in the N^{*} phases (see **Figure 8 (b)**). A clear change in the slopes of ϵ'_{\perp} and ϵ'_{\parallel} data has been observed at $\sim 107^{\circ}C$. 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. The dielectric anisotropy has maxima (0.055) in N^{*} phase at $\sim 107^{\circ}C$ and 0.045 in SmC phase at $\sim 88^{\circ}C$ (see **Table 2**). In the mixture M3, good planar and homeotropic alignments have not been observed throughout the SmA phase. In the mixture M8 also, the good planar alignment could not be observed just below T_{Iso-N^*} but as temperature decreased, the molecular alignment improved and that is why ϵ'_{\perp} increases sharply with decrease in temperature. In general, it is difficult to get good homeotropic alignment in N^{*} phase but we have got good homeotropic alignment in the N^{*} phase of M8. Initially, ϵ'_{\parallel} decreases below T_{Iso-N^*} and then sharply increases at T_{N^*-SmC} with decrease in temperature (see **Figure 8 (b)**).

The optical anisotropy (Δn) is defined as:

$$\Delta n = n_{\parallel} - n_{\perp} \tag{1}$$

Where n_{\parallel} and n_{\perp} are the parallel and perpendicular refractive indices, respectively.

The variation of refractive index (10 kHz) for planar (n_{\perp}) and homeotropic (n_{\parallel}) aligned samples with temperature, indicating optical anisotropy (Δn) with the temperature for the mixture 3 and mixture 8 are shown in **Figure 9**.

Figure 9 (a)

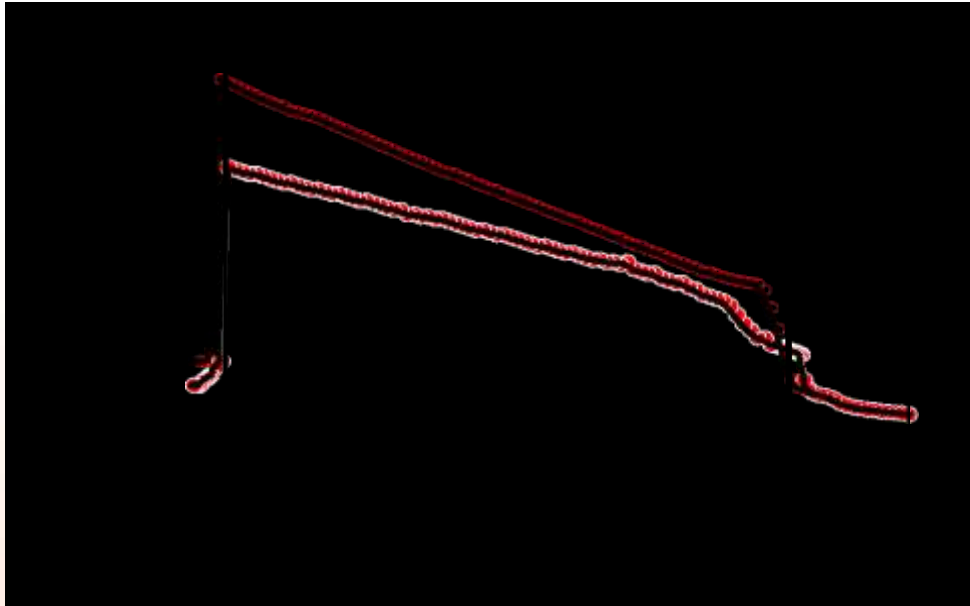


Figure 9 (b)



Figure: 9 Variation of refractive index (10 kHz) for planar (n_{\perp}) and homeotropic (n_{\parallel}) aligned samples with temperature, indicating dielectric anisotropy (Δn) with the temperature for the (a) Mixture 3 and (b) Mixture 8. Vertical lines show the transition temperatures on the basis of dielectric studies.

For electro- optic devices, typically, the time to switch on the display is proportional to the viscosity but inversely proportional to the dielectric anisotropy and a combination of the elastic

constant whereas the time taken for the display to turn off is only proportional to the viscosity and a combination of the elastic coefficient i.e. the dielectric anisotropy does not affect the off time. Similarly, the transmission of light through a device is related to the optical anisotropy and the device thickness and inversely to the wavelength of light, as shown in **Equation 2**:

$$I_{\parallel} = I_0 \cos^2 \theta \left(\frac{d}{\lambda} \right) \left(n_{\parallel} - n_{\perp} \right) \quad (2)$$

Where the relative phase retardation is $\frac{d}{\lambda} (n_{\parallel} - n_{\perp})$, I_{\parallel} is the transmission intensity of two parallel polarizers, θ is the angle between the input light polarization and the nematic optic axis, d is the film thickness and λ the wavelength of the light.

The magnitude of the optical anisotropy ($|\Delta n| = n_{\parallel} - n_{\perp}$) in different mesophases at 10 kHz for pure ChM and DOBA as well as mixtures are shown in **Table 3**.

Table: 3 Magnitude of the optical anisotropy ($|\Delta n| = n_{\parallel} - n_{\perp}$) in different mesophases at 10 kHz. × shows that the phase transition does not exist.

System	Nematic (N)	Smectic C (SmC)	Smectic A (SmA)	Cholesteric (N [*])
Pure DOBA	0.26	0.57	×	×
Pure ChM	×	×	0.81	0.45
Mixture 3	×	×	0.40	×
Mixture 8	×	0.21	×	0.23

Ionic conductivity (σ_{ion}) has been determined from the measured conductivity data in different phases of the mixtures 3 and 8 for planar and homeotropic alignments of the material.

The variation of ionic conductivity with frequency in SmA phase of the mixtures 3 for the planar and homeotropic aligned material are shown in **Figure 10**.

The variation of ionic conductivity with frequency in various phases of the mixtures 8 for the planar aligned material is shown in **Figure 11**.

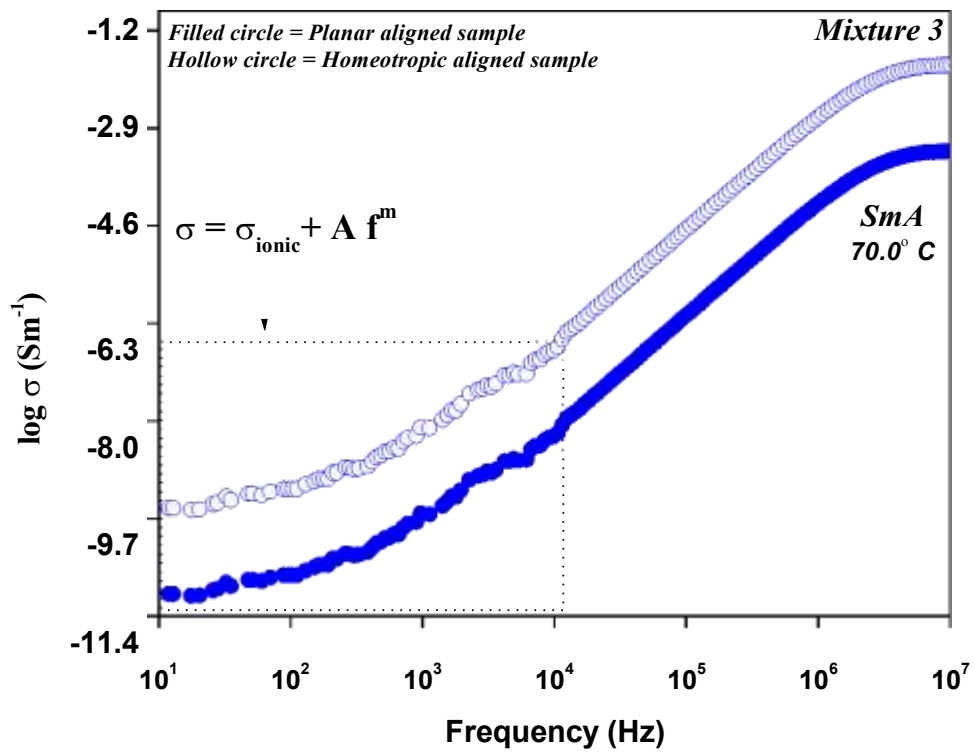


Figure: 10 The variation of ionic conductivity with frequency in SmA phase of the mixtures 3 for the planar and homeotropic aligned material.

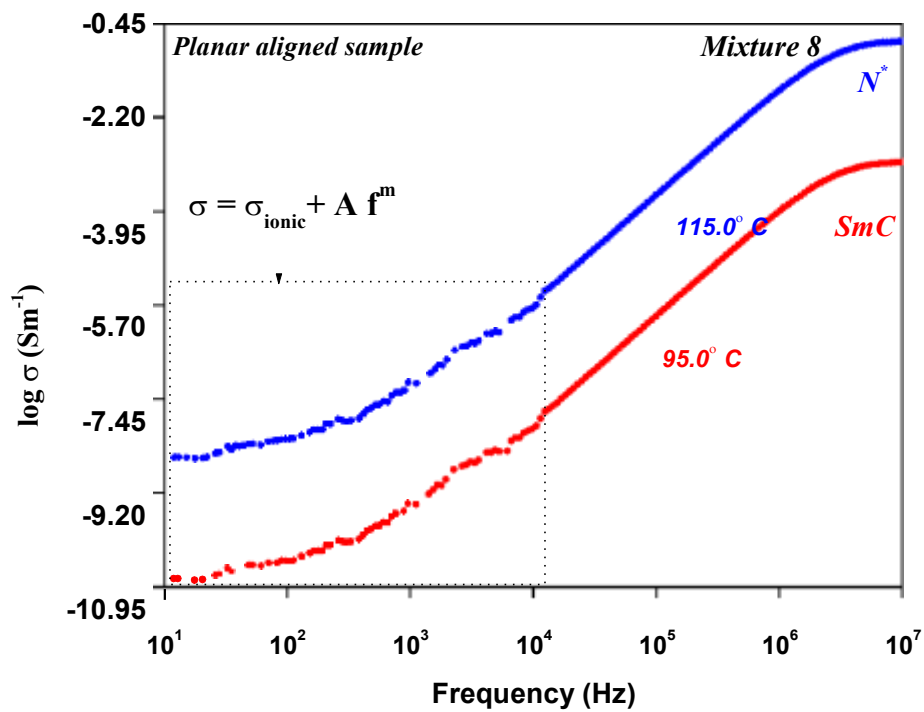


Figure: 11 The variation of ionic conductivity with frequency in SmA phase of the mixtures 8 for the planar and homeotropic aligned material.

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

- 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 for the mixtures having DOBA concentrations 30.0 and 92.3 mole %, implying that no dipolar relaxation phenomenon occurs in this frequency range. Thus frequency range 1 Hz to 10 MHz is the usable frequency range for display purpose.
- We have observed 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. Therefore it is extremely beneficial in construction of LCDs.

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