

# Low Frequency Dielectric Relaxation Studies in the Nematic Phase of a Cyanobiphenyl Liquid Crystal

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**Abstract-** Low frequency dielectric relaxation studies are carried out in a nematic liquid crystal 4'-Heptyl-4-biphenylcarbonitrile (7CB). The anisotropic properties were observed for low frequency ranges using dielectric spectroscopic techniques. A parallel plate capacitor was filled with the liquid crystal material and the capacitance and dissipation factor were measured using an impedance analyzer. Both these parameters were observed to show anomalies at the isotropic–nematic transition temperature. Low frequency E-field response investigations are carried out in the range of 10 Hz to 10 MHz at various temperatures of nematic liquid crystal phase exhibited by the compound. Observed frequency variation in permittivity and loss at different temperatures in nematic phase are presented. The frequency at which loss exhibits a peak is argued to infer a relaxation. It is observed that the loss peak shifts to the higher side of the frequency with increase of temperature in nematic phase

**Keywords –** Nematic Liquid Crystals, Relative Permittivity, Dielectric Loss, Dielectric Relaxation, Relaxation Frequency

## I. INTRODUCTION

Thermotropic liquid crystals are mesogenic molecules in which the exhibited mesomorphism depends entirely on varying the surrounding temperature. Amongst the different types of thermotropic liquid crystals, the nematic phase is the least ordered. The nematic liquid crystalline phase is divided into uniaxial nematic, biaxial nematic, and cholesteric nematic in which the local nematic director rotates in space forming a helicoid. Some of the techniques used to characterize liquid crystals are polarized optical microscopy (POM), X-ray diffraction (XRD) and differential scanning calorimetry (DSC) [1]. Dielectric spectroscopy is used to study a number of properties of liquid crystals. This technique involves using an impedance analyzer that keeps a small amplitude sinusoidal voltage of some known frequency. The system responds with a voltage proportional to the applied voltage which can be shifted in time. If this is done for a range of frequencies, the impedance spectrum is obtained. This technique allows the determination of different processes occurring in the cell containing the liquid crystal such as charge transfer reaction, relaxation time, dielectric permittivity, dielectric loss, activation energy and accumulation of charges [2-6]. The liquid crystal being studied here is 4'-Heptyl-4-biphenylcarbonitrile (7CB), a compound in cyanobiphenyl class which exhibits nematic liquid crystal phase [7]. This compound is characterized by having the carbon nitrile tail and the transition from nematic to isotropic at 42.8oC. Nematic phase is quite fluid and can reorient and align themselves quickly in a magnetic and electric field, owing to their polarity nature. Thus, they can be used in liquid crystal displays (LCD) such as in calculators and monitors. When liquid crystal undergo heating, as the temperature rises the average spacing between the aligned molecules of a nematic phase increases and hence the phase of the material transforms from nematic to isotropic at temperature, TNI.

The paper is organized as follows. The material used and the description of the experimental techniques used for the dielectric studies is given in section II. Experimental results are presented in section III. Section IV is devoted for concluding remarks.

## II. MATERIALS AND METHODS

The liquid crystal under study, 7CB possess dissimilar local structural regions that can interact in an organized way with their neighbors. Over a certain range of temperatures, the interactive forces between neighboring molecules can lead to a degree of self-organization in which crystal-like order persists in some directions yet not in other directions. There are two benzene groups which makes the molecule polarized more in one plane and providing more interaction with the neighboring molecules. This planarity is enhanced in the presence of HC≡N. It also has a polar terminal group of H3C and hence more intermolecular attractions along the long axis with a hydrocarbon chain of 7 groups providing more elongation to the molecule. The chemical composition of 7CB is shown in Figure 1.

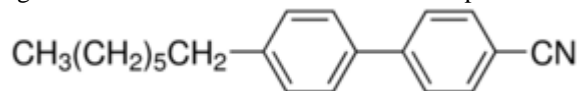


Figure 1: Chemical composition of liquid crystal 7CB

Commercially available (Devicetech, USA) cell made of two parallel plates with separation of  $9.0 \mu\text{m}$  was used for the study. The cell was made from optically transparent indium tin oxide (ITO) electrodes coating inside of the two glass plates. The capacitance of the empty cell and dissipation factor ( $\tan\delta$ ) were studied in the frequency range 10 Hz to 10 MHz over a temperature range of 20 – 100oC. The loss exhibited by the empty cell was found to exhibit no peaks in this frequency range. This indicates that neither the conductive coating of the cell plates, nor any trace level impurities in the cell are exhibiting any relaxation in this frequency and temperature range. The lead capacitance (Cleads) of the cell was measured by measuring the capacitance of air-filled capacitor (Cair), and the capacitance of the cell when filled with a liquid (Cliquid) of known dielectric constant (ethyl alcohol in the present case) which was subtracted from every capacitance measurements made.

The cell was filled with the liquid crystal by means of capillary action. The cell was placed in a specially built oven and the temperature was controlled to  $\pm 0.1\text{oC}$  using a temperature controller (Linkam, TMS 94). To conduct the study, the sample was heated at around 10oC above the nematic-isotropic transition temperature and then was cooled very slowly at around 0.5oC per minute to the temperature corresponding to the liquid crystal state. Dielectric investigations were performed using Wayne Kerr (WK 6500B) impedance analyzer along with test fixers. The dielectric permittivity ( $\epsilon'$ ) and dissipation factor ( $\tan\delta$ ) were studied with decreasing temperature in the range 50–30oC using 1Vpp oscillating level at 1.5 kHz frequency. The permittivity and dissipation factor were also studied with varying frequency (10 Hz to 10 MHz) at different temperatures in the nematic phase.

### III. RESULTS AND DISCUSSION

#### 3.1 Dielectric constant and dielectric loss variation with temperature –

When the temperature of the cell was decreased from 50oC while having an AC voltage of 1Vpp and constant frequency of 1.5 kHz, the permittivity and loss factor of the dielectric exhibited some variations as shown in Figure 2. The relative permittivity  $\epsilon_r'$  was having almost constant values until it reached the temperature of 42.6oC after which there is a sudden increase in its value. The rate became slower as the temperature was decreased further. On the other hand, the loss factor was assuming the same behavior, but started with a slow decrease in its value until it reached the same temperature of 42.6oC. At this temperature,  $\epsilon_r''$  showed a sudden drop in values that was shortly recovered. The values then started to decrease as in the case of  $\epsilon_r'$ , with a rate that was high in the beginning but slowly decreased with further decrease in temperature.

The temperature at which the anomalies are observed in the dielectric constant and the loss factor are where the liquid crystal is turning from isotropic liquid to a nematic liquid crystal. This can be considered as the nematic-isotropic transition temperature, TIN. The temperature TIN (42.6oC) obtained experimentally agreed with the literature value (42.8oC) to a high degree [8].

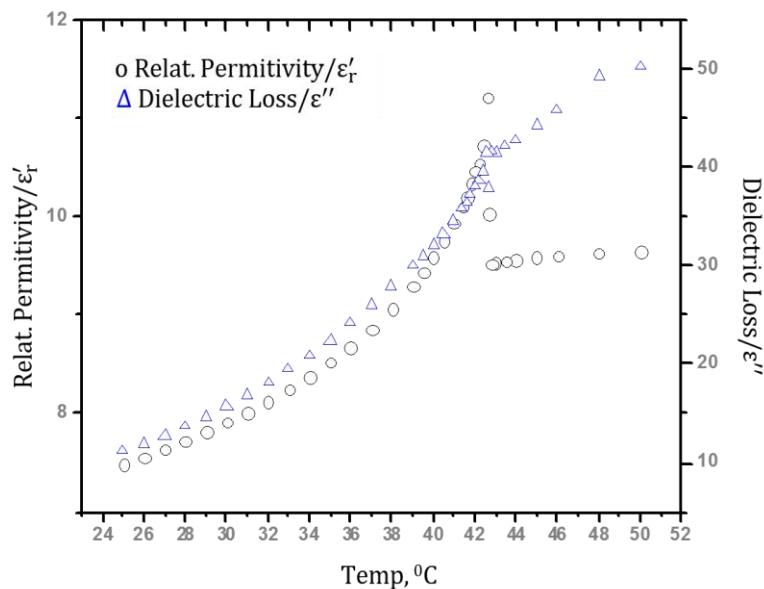


Figure 2: Temperature variation of dielectric constant and loss factor

The behavior of the dielectric constant,  $\epsilon_r'$ , could be interpreted by understanding the polarization and dipole properties of the dielectric, which is attributed to the motion of the individual molecules inside the sample and their

motion relative to each other. The investigation starts by heating the material inside the cell to a temperature of 50°C, which causes it to settle in the isotropic state, and then slowly cooling it to observe the transition temperature to the nematic phase,  $T_{IN}$ . The exact point at which the material turns to the nematic state, the  $\epsilon_r'$  is expected to increase at once because the orientation of the molecules which is basically the polarization inside the material is increasing since there is an increased alignment with the applied electric field. The more the alignment or polarization, the higher is the dielectric constant.

The decrease in  $\epsilon_r''$  is also attributed to the sudden rearrangement of molecules in the nematic phase. The loss factor is related to the loss rate of energy of a mode of oscillation in a dissipative system. When the molecules align with the electric field they assume a lower potential energy state than the time when they were before the alignment and hence they lose an amount of energy. This energy basically contributes to the overall energy of the system and helps in decreasing the energy that had to be supplied by the electric field, therefore, the energy dissipation of the system or loss factor would decrease at once. After the transition to the nematic phase, as the temperature is decreased, the alignment would be increasing as there is less thermal motion in the system that would interfere with the alignment of the molecules. The energy contributed by the increased alignment of the molecules basically reduces the loss factor.

### 2.2 Low frequency investigations in the nematic liquid crystal phase –

Low frequency E-field response investigations are carried out in the range of 10 Hz to 10 MHz at various temperatures of nematic liquid crystal phase exhibited by the compound. Observed frequency variation of permittivity and loss at different temperatures in nematic phase are presented in Figures 3 and 4.

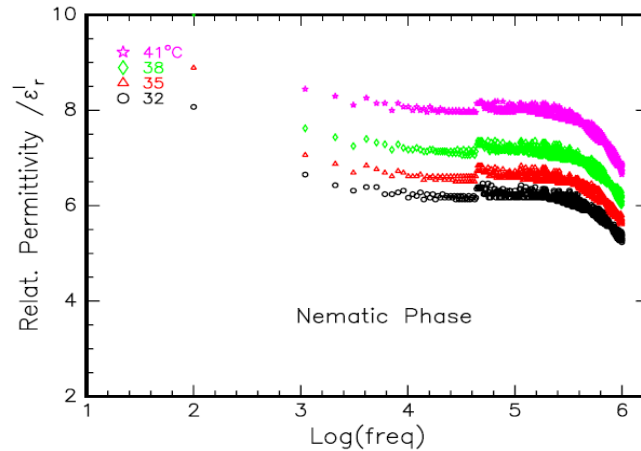


Fig 3: Low frequency variation of permittivity,  $\epsilon_r'$  at different temperatures of the nematic phase

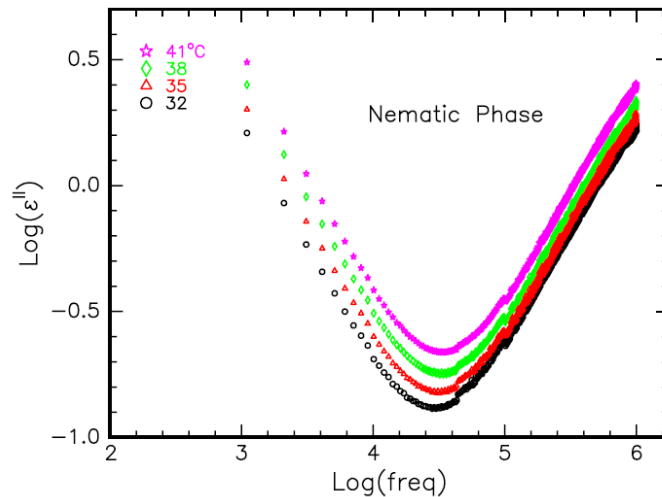


Fig 4. Low frequency variation of loss factor,  $\epsilon_r''$  at different temperatures of the nematic phase

Permittivity is observed to decrease with increasing frequency of the field. It implies the decreasing trend of dipolar orientational polarization of LC with increasing frequency. A meticulous analysis of Figure 3 reveals three falls in permittivity, i.e., for:

- i)  $\log(\text{freq}) < 4$ ;
- ii) between 4.5 and 5.2 of  $\log(\text{freq})$ , and
- iii)  $\log(\text{freq}) > 5.6$ .

Although each fall in permittivity needs a meticulous analysis to interpret the underlying dipole response in nematic phase, the corresponding loss  $\epsilon''(\omega)$  as presented in Figure 4 is to be further analyzed. It is observed that  $\epsilon''$  exhibits a monotonous decrease up to  $\log(\text{freq})$  equal to 4; and a monotonous increase with increasing frequency for  $\log(\text{freq}) > 5.2$ . In the back-drop of possible contributions, the former trend of loss decrease up to  $\log(\text{freq})$  equal to 4 is attributed to trace level ionic impurities in the sample. The latter trend of loss increase is attributed to the ITO coating contributions. However, a very careful observation of loss spectrum at all temperatures in the nematic phase reveals a peak in the vicinity of  $\log(\text{freq}) \sim 5$ . As such, its temperature trend is further analyzed by drawing loss against frequency spanning the range around  $\log(\text{freq}) \sim 5$  and presented as Figure 5. The frequency at which loss exhibits a peak is argued to infer a relaxation. Hence, the frequency is termed as relaxation frequency  $f_R$ . It is observed from Figure 5 that the loss peak shifts to the higher side of the frequency with increase of temperature in nematic phase. Loss magnitude at peak is also found to decrease with decreasing temperature. The observed shift of relaxation frequency is further argued as Arrhenius shift of orientational relaxation frequency  $f_R(T)$ . It is noticed that the observed  $f_R(T)$  (occurring at around  $\log f = 4.5$ ) agrees with the reported values [9,10].

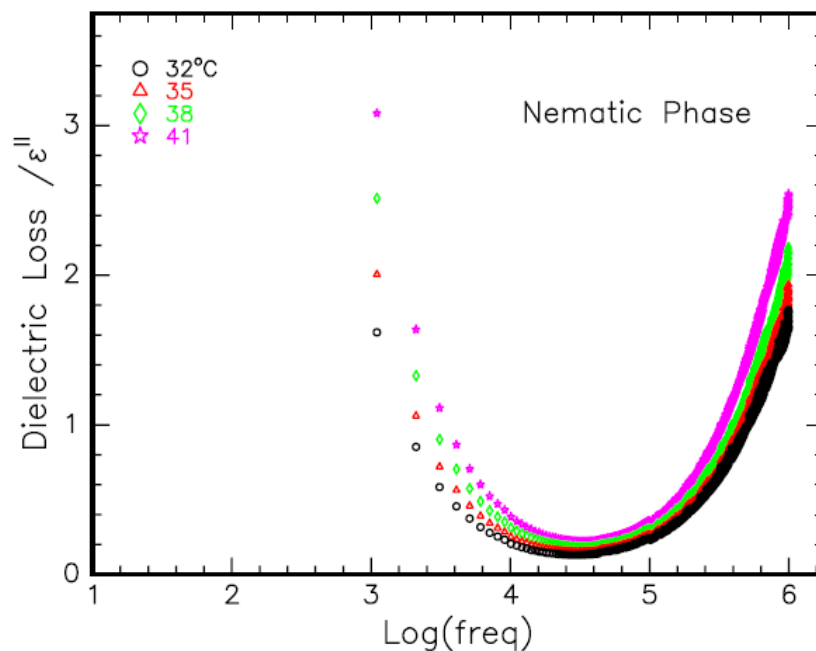


Figure 5: Low frequency variation of loss factor,  $\epsilon''$  at different temperatures of the nematic phase

The application of an alternating electric field in the dielectric spectrometer is the main reason of the so called relaxation behavior of dielectric material. The dipole nature of the molecules result in the separation with the other interacting molecules and eventually reorienting their polarization each time with the change in ac direction to contribute to the overall polarization of the dielectric. At different frequencies, the polarization which his described by the relative permittivity, shows differences as well. For example for a dipole molecules at low frequencies get sufficient time to orient themselves completely along the instantaneous direction of the field. The relaxation time is the average time it takes the molecules to orient themselves accordingly. The more the contribution to polarization, the more the relative dielectric constant. The relaxation phenomenon is an inherent property in materials since it is the result of the existence of forces between adjacent molecules that tend to prevent the alignment with electric field [9-11].

#### IV. CONCLUSION

Dielectric relaxation studies are carried out in the nematic phase of the liquid crystal 7CB. The permittivity and the loss factor exhibited variations in the vicinity of the isotropic-nematic phase transition temperature. Low frequency studies of permittivity and loss were carried out at various temperatures of the nematic phase. The frequency variation with the dielectric loss showed an inverted peak with an apex at the relaxation frequency, and the relaxation frequency was determined from this information.

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