REPRINTS
Dielectric Studies on Benzothiazole Based Liquid Crystals at Radio Frequency Region

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Abstract: The phase transition temperatures and textural changes in homologous series of 2-(4- n alkanoyloxy benzylidenamino) benzothiazoles (n BABTH), where n=12 and 16, were studied by using Polarisng Optical Microscope (POM). The temperature and frequency dependence of dielectric constant and dielectric loss were made out in the frequency range 1 kHz to 1 MHz. Anomalies in dielectric properties were recorded near phase transitions when dielectric constant and dielectric loss have been measured as a function of frequency and temperature. Changes in dielectric constant and loss are at low frequencies, but constant at higher frequencies. The variation of activation energy and relaxation times were studied in smectic phase.

Keywords: Liquid crystals, benzothiazoles, phase transitions, dielectric constant, dielectric loss, Relaxation times, Activation energy.

I. INTRODUCTION

Generally matter exists in three states, viz., solid, liquid and gas. Certain organic compounds show intermediate phases between crystalline solids and isotropic liquids, which are thermodynamically stable. These phases exhibit rheological behavior similar to liquids but have anisotropic properties of crystalline solids and hence they are termed as liquid crystal (LC) phases [1-3]. Liquid crystals have been extensively investigated due to increasing importance in science, technology, industry, consumer product, and other medical applications [4-7]. Azobenzene based liquid crystalline (LC) materials, either low molecular weight or polymeric in nature, are fascinating and promising class of compounds due to their unique electrical, optical and mechanical properties. Amongst the wide variety of experimental methods used to study the molecular dynamics of liquid crystals (LCs), the low frequency dielectric spectroscopy assumes special importance due to the utility of the relevant data in electro-optic devices. These LC devices are known to operate in the frequency region of a few Hz to several MHz that involves different modes of their molecular motions. [8]. Heterocyclic mesogens are usually incorporated with hetero atoms such as N,O and S, resulting a reduced geometry in the overall molecule as well as generation of strong polar induction. Inclusion of the hetero atom can considerably change the polarities, polarizabilities, and to a certain extent the geometry of the molecule. Thus it influences the type of mesophase transition temperature, dielectric constants and other properties of the liquid crystals [9]. Examples of liquid crystals with incorporated heterocyclic rings are pyridine, thiophene, oxadiazole and benzoxazole. Although many compounds having a heterocyclic core exhibit mesomorphic properties, mesogenic samples derived from benzothiazole are relatively less. Benzothiazole, another kind of heterocyclic fused ring system, exhibits good hole-transporting properties with a low ionisation potential, making it of potential interest as hole-transporting materials in organic light-emitting devices (OLEDs) [10]. Therefore, the benzothiazole ring is chosen as the mesogenic core in this study. The present study emphasises at textural, phase transitions and dielectric properties of homologous series of 2-(4- n alkanoyloxy benzylidenamino) benzothiazoles mesogens where n = 12 and 16 at starting from room temperature to above to its isotropic temperatures and in the frequency range 1Hz to 1 M Hz region.
II. EXPERIMENTAL

A. Materials:

2-(4- n alkanoyloxybenzildenamino) benzothiazoles (where n=12 and 16) mesogens are synthesized [11]. Chemical structure of the compound is shown in Figure 1.

![Molecular structure of n BABTH](image)

B. Methods:

Textural and phase transition temperatures were recorded using a Meopta Polarising Optical Microscope (POM) with hot-stage as described by Gray [12]. These compounds were filled in LC1 ITO coated liquid crystal cells- 90° twist aligned (5mm X 5 mm X 6 μm) -obtained from Instec, Inc. USA. The cells were filled through capillary action method at their above isotropic temperature. The temperature and frequency dependence of Capacitance C, Resistance R, Inductance L were measured by using Newton’s 4th Ltd., LCR meter model. In this study the cells filled with samples were placed in an Instec hot and cold stage (HCS 302) being equipped with microscope (Olympus BX50) and DP10 camera setup. The temperature was monitored and controlled through a computer by a software program to an accuracy of ± 0.1°C. The sample was heated to isotropic state and held until to attain thermal equilibrium. The data were taken during cooling process. The measuring signal is the square form with amplitude of 2V. The frequency range of measurement was from 1 Hz to 1 MHz, and calculated the different dielectric parameters [13, 14]. The accuracy in dielectric constant and loss may be to the extent of 1% and 2% respectively.

III. DETERMINATION OF DIELECTRIC PARAMETERS

A. Calculation of dielectric constant($\varepsilon'$): The dielectric constant of a material is the ratio of the capacitance of a capacitor containing the material to the capacitance of the same electrode system with vacuum. Using the following equation the dielectric constant($\varepsilon'$) was calculated.

$$\varepsilon' = \frac{(C_p - C_o)}{\varepsilon_o A} + 1 \tag{1}$$

where A is area of the cell, d thickness of the cell, $\varepsilon_o$, permittivity of free space $8.85\times10^{-12}$ Fm$^{-1}$, $C_p$, capacitance with sample and $C_o$, capacitance without sample.

B. Calculation of temperature coefficient of dielectric constant ( $\tau_{\varepsilon}$): The temperature coefficient of dielectric constant ( $\tau_{\varepsilon}$) was calculated using equation (2).
$\tau_\varepsilon = \frac{\varepsilon (T_{\text{final}}) - \varepsilon (T_{\text{initial}})}{\varepsilon (T_{\text{ref}})} \times 10^6 \left[ \frac{\text{ppm}}{\degree C} \right] \tag{2}$

where $T_{\text{initial}}$ is starting LC phase temperature value, $T_{\text{final}}$, ending LC phase temperature value, $\varepsilon (T_{\text{initial}})$; $\varepsilon (T_{\text{final}})$ are the corresponding dielectric constant respectively and $\varepsilon (T_{\text{ref}})$, dielectric constant at some reference temperature (50°C). The $\tau_\varepsilon$ value has units of parts per million per degree Celsius [ppm/°C].

C. Calculation of dielectric loss ($\varepsilon''$):

The simplest model for a capacitor with a lossy dielectric is a capacitor with a perfect dielectric in parallel with a resistor giving the power dissipation. The dielectric loss angle (tan δ) values were directly measured from the experimental technique, and the imaginary part of permittivity (dielectric loss, $\varepsilon''$) was calculated using the equation (3) for the compound series studied.

$$\varepsilon'' = \varepsilon' \tan \delta \tag{3}$$

D. Calculation of relaxation time ($\tau$) and activation energy ($\Delta G$):

Slater’s perturbation equations [15, 16] were used to find the relaxation time ($\tau$) and activation energy ($\Delta G$) from equations 4 and 5 respectively

$$\tau = \frac{\tan \delta}{\omega} \tag{4}$$

where $\omega$ is $2\pi f$, and $f$ the frequency. These frequency domain measurements needed a new frequency each time and hence,

$$\Delta G = 2.303RT \log \left( \frac{\tau KT}{h} \right) \tag{5}$$

where $R$ is the molar gas constant, $h$ the Plank’s constant, $k$ the Boltzmann constant, $T$ the absolute temperature and $\tau$ the relaxation time derived from eq. (4).

IV. RESULTS AND DISCUSSION

A. Textural and Phase Transition Studies:

The phases and their transition temperatures (K) obtained from POM are shown below which are enantiotropic.

<table>
<thead>
<tr>
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<td>For 12 BABTH</td>
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<td>S$_A$</td>
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</table>

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<td>Cr$_2$</td>
<td>Cr$_3$</td>
<td>S$_A$</td>
</tr>
</tbody>
</table>

(Note: I = Isotropic, S$_A$ = Smectic, Cr= Crystal)
The textural observation for 2-(4- n alkanoxybenzylidnamino) benzothiazoles (where n= 12 and 16) mesogens made through POM have shown enantiotropic Smectic A phase as shown in Figure 2. The transition temperatures were also determined by differential scanning calorimetry technique. The data of the phase transition temperatures measured from both POM and DSC are in good agreement. [11]

**B.Dielectric Studies:**

The variation of dielectric constant, temperature coefficient dielectric constant, dielectric loss as a function of frequency, for 12 BABTH and 16 BABTH mesogens at different phases are shown in figures 3 to 5.

![Fig 2: Smectic A phase in 16 BABTH](image)

**Fig3.** Frequency dependence of dielectric constant \( \varepsilon' \) for (a) 12 BABTH and (b) 16 BABTH at different temperatures.
Fig 4: Frequency dependence of thermal coefficient of dielectric constant $\tau_\varepsilon$ for (a) 12 BABTH and (b) 16 BABTH.

Fig 5: Frequency dependence of dielectric loss for (a) 12 BABTH and (b) 16 BABTH at different temperatures.
The dielectric permittivity ($\varepsilon'$) and loss ($\varepsilon''$) as a function of frequency at different temperatures for both samples is shown in figure 3(a) and 3(b). The figure shows that the dielectric constant value ($\varepsilon'$) is high at low frequencies and decreasing gradually with increasing frequency but increasing with increasing temperature. The higher value of ($\varepsilon'$) at low frequencies is due to the effect of space charge polarization [17]. The decrease in permittivity with frequency can be explained on the basis of Koop’s theory [18], in which dielectric materials are treated as two layer structure of Maxwell-Wagner type [19]. In this model the grains represent a conducting layer, while grain boundaries represent a poorly conducting layer. The grain possesses small value of dielectric constant and have dominant role at high frequencies [20]. The grain boundaries possess high value of dielectric constant, and mainly influence the dielectric properties.

At higher frequencies, the temperature coefficient dielectric constant stability was noticed rather at low frequencies in both compounds which are shown in figure 4. As the $\tau_\varepsilon$ is the combination of thermal and dielectric constant values the results produced by $\tau_\varepsilon$ as a function of frequency are corresponding to variations in dielectric constant and change in structural properties. It is observed that $\tau_\varepsilon$ was maximum around 100 Hz for these samples which represents the existence of orientational polarization of liquid crystal molecule with temperature.

The figure 5 indicated the dielectric loss for 12 BABTH and 16 BABTH mesogens. The low dielectric loss is at high frequencies showing similarity with that of the variation of dielectric constant (figure 3) on owing to smaller angle of rotation. The loss factor on frequency dependence is in similar way as the dielectric constant. The variation in relaxation peaks is observed for both the compounds within the frequency range covered. The data of dielectric loss clearly show that low frequency data are affected due to ionic conductance, where as high frequency data are affected due to ITO resistance. As usual relaxation frequencies are seen to shift towards lower side with decreasing temperature.

Variation of relaxation time and activation energies at different temperatures are shown in fig 6 and fig 7.
The observed temperature variation of the relaxation frequency was analysed through the corresponding Slater’s perturbation equations as shown in Figures 6. It shows that the relaxation times in solid phase are increased slowly, and they are increase rapidly in liquid crystal phase up to isotropic phase. The activation energy can be interpreted as the energy required to make reorientation of molecule and the energy necessary to make the dissociation [21]. The relatively higher value of the activation energy is suggestive of the higher potential barrier witnessed by the molecular dipole moment to orient to the field at high frequencies the activation energies decreases so that it has a relatively high dielectric strength. From the figure 7, it is evident that the activation energy is increased with temperature, but relatively decreased with applied frequency. The activation energy showed similar tendencies for both samples, while increase with increasing temperature and decreased with increase of frequency as shown in Figure 7. This effect, is due to role of the surface activity of dispersed particles on local order of the liquid crystal as a result of elastic distortions associated with the liquid crystal on following increased the frequencies. At low frequencies the increase in activation energy has led to restricted mobility of charged carriers resulting in low conductivity. At higher frequencies, the decrease in the activation energy is due to high mobility of charged transports.

V. CONCLUSIONS
The phase transition temperatures and phases of homologous series of 2-(4- n alkanoyloxy benzylidenamino) benzothiazoles (n BABTH), where n=12 and 16, were studied using polarizing microscope (POM). Thermal microscopic studies revealed enantiotropic SmA phase. The data of the phase transition temperatures measured from both POM and DSC are in good agreement. The dielectric spectrum of frequency dependent dielectric constant and the loss for both samples were analysed and space charge polarisation observed at low frequencies. The sharp changes on measured dielectric parameters in the temperature region are corresponding to the
respective phase transitions in the liquid crystal materials. In addition, the variation in relaxation times and activation energy at different regions of temperature as a function of frequencies are observed.

ACKNOWLEDGEMENTS

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Abstract—The phase transition temperatures and textural changes in homologous series of 6-methoxy-2-(4-n-alkanoyloxybenzylidenamino) benzothiazoles mesogens (n MBABTH) for n=14 and 16 were studied using polarizing optical microscope. The temperature and frequency dependence of dielectric constant and dielectric loss were observed at near phase transitions when dielectric constant and dielectric loss had been examined as a function of frequency and temperature. Changes in dielectric constant and loss are observed at low frequencies, whereas at high frequencies they are nearly constant. Temperature dependence of activation energy and relaxation frequency studies was made for smectic and nematic phases.

Keywords: Liquid crystals; benzothiazoles; phase transitions; dielectric constant; dielectric loss; Relaxation frequencies; Activation energy.

1. INTRODUCTION

Liquid crystals in the nematic group are most commonly used in production of liquid crystal displays (LCD) due to their unique physical properties and wide temperature range. A great number liquid crystalline compounds containing heterocyclic units have been synthesized and Interest in such structures is constantly growing [1–3], because of the greater possibilities with heterocyclics in the design of new liquid crystal molecules, but also because the insertion of heteroatoms strongly influences the formation of mesomorphic phases. The effect of heteroatoms (S, O and N) are able to change considerably the polarizability and sometimes the geometric shape of the molecule, thereby influencing the type of mesophase, the phase transition temperatures, and the dielectric and other properties of the mesogens [4]. The incorporation of heterocyclic rings such as pyridine [5], thiophene [3, 6] and 1,3,4-thiazolone [7] as the core in liquid-crystalline materials has been widely reported. However, very little information on the incorporation of benzothiazole as a core in liquid-crystalline compounds is available [8–15]. Benzothiazole derivatives have been studied as photoconductive materials [16–18]. A benzothiazole core is found in fluorescent compounds, which is useful in applications as a result of its high fluorescence quantum yields in the presence of the rigid core structure [19–20]. Lately, benzothiazole derivatives have been continuously investigated for application in thin-film and organic field-effect transistors [21]. In the nematic phase, liquid crystal molecules are usually oriented on average along a particular direction. By applying an electric or magnetic field the orientation of the molecules are to be manipulated 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 different phases give information not only about bulk properties but also about molecular parameters and their mutual association and rotation under an applied electric field. Substances with high dielectric constants are widely used in the electronics industry [22]. The dielectric materials that are used as inter layers in electronic chips they significantly increase the speed of propagation of electric impulses and reduce dielectric losses. The effect of frequency on dielectric properties offers valuable information about the localized charge carrier that helps to explain the mechanism responsible for charge transport phenomona and dielectric behavior.

The aim of present work is to report the dielectric properties as a frequency and temperature dependence for compounds of homologous series of 6-methoxy-2-(4-n-alkanoyloxy benzylidenamino)benzo thiazoles mesogens (n MBABTH) [23] where n=14 and 16, to understand the phase transitions undergoing with temperature.

II. EXPERIMENTAL DETAILS

2.1. Materials

Textural and phase transition temperatures were measured using Meopta Polarising Optical Microscope with hot-stage as described by Gray [24]. These compounds were filled in LC1 homogenously aligned ITO coated liquid crystal cells, (5mm X 5 mm X 6 μm) obtained from M/s Instec, USA. The temperature and frequency dependence of dielectric constant and dielectric loss were measured in the frequency range 1Hz to 1MHz of using Newton’s 4th Ltd., LCR meter model PSM1700. In this study the cells filled with samples were placed in the Instec hot and cold stage (HCS 302). The temperature was monitored and controlled through a computer by a software program. The sample was heated to isotropic state and kept until to attain thermal equilibrium.
The data was taken during heating and cooling cycles but the results are shown in cooling process. The measuring signal was the square form with 2V amplitude. The accuracy for dielectric constant and loss were maintained to the error of 1% and 2% respectively and the temperature accuracy to ±0.1°C.

The selected LCs for present studies are 6-methoxy-2-(4-alkanoyloxybenzylidenamino)benzothiazoles mesogens (nMBABTH for n=14 and 16) while their molecular structure is presented below.

![Structure of 6-methoxy-2-(4-alkanoyloxybenzylidenamino) benzothiazoles](Structure.png)

2.2. Computational Details

The dielectric constant of a material is the ratio of the capacitance of a capacitor containing the material to the capacitance of the same electrode system with vacuum. Using the following equation the dielectric constant, (ε') was calculated.

$$\varepsilon' = \frac{(C_p - C_o) d}{\varepsilon_o A} + 1$$  \hspace{1cm} (1)

where A = area of the cell, d = thickness of the cell, \(\varepsilon_o\) = permittivity of free space 8.85×10^{-12} Fm^{-1}, \(C_p\) = capacitance of the same electrode system with vacuum. Using \(C_o\) = capacitance with sample and \(C_c\) = capacitance without sample. The temperature coefficient of dielectric constant \(\tau_\varepsilon\) was calculated using equation (2).

$$\tau_\varepsilon = \frac{\varepsilon(T_{\text{final}}) \varepsilon(T_{\text{initial}})}{\varepsilon(T_{\text{ref}}) \varepsilon(T_{\text{ref}})} * 10^9 \left(\frac{\text{ppm}}{\text{C}}\right)$$  \hspace{1cm} (2)

where \(T_{\text{initial}}\) = starting LC phase temperature value, \(T_{\text{final}}\) = ending LC phase temperature value, \(\varepsilon(T_{\text{initial}})\) and \(\varepsilon(T_{\text{final}})\) are the corresponding dielectric constant respectively and \(\varepsilon(T_{\text{ref}})\) = dielectric constant at some reference temperature (50°C). The \(\tau_\varepsilon\) value has units of parts per million per degree Celsius [ppm/C].

The simplest model for a capacitor with a lossy dielectric is as a capacitor with a perfect dielectric in parallel with a resistor giving the power dissipation. The dielectric loss angle (tan δ) values were directly measured from experimental technique, and the imaginary part of permittivity (dielectric loss ε’’) was calculated using the equation (3) for the series of compounds studied.

$$\varepsilon^{**} = \varepsilon^1 \tan \delta$$  \hspace{1cm} (3)

With the ε’’ data the sample conductivity σ (Siemens per meter) was estimated using equation (4). The changes in the electrical conductivity and charge transferring at different temperatures and isotropic phase, the ac conductivity at 1 KHz to 1MHz frequencies, in the LC region is measured from equation (4)

$$\sigma_{ac} = 2\pi \varepsilon_o \varepsilon^{11} f$$  \hspace{1cm} (4)

where \(\varepsilon_o\) = permittivity of free space 8.85×10^{-12} Fm^{-1}, \(f\) = corresponding frequency in Hz and ε’’ = dielectric loss.

The widely adopted form of the Arrhenius equation [25] to study the effect of temperature on conductivity is shown in equation (5). The activation energy is viewed as an energetic threshold for a fruitful electric field production generated by the LC molecules orientation. It is possible to calculate activation energy by Arrhenius equation by just using the conductivity at two temperatures. It would be more realistic and reliable if more data of conductivity is taken at deferent temperatures. Hence, by using the ac conductivity values measured from equation (4) in the LC temperature region at 1KHz to 1MHz, the activation energy (W) was calculated by using equation (5).

$$\sigma_{ac} = \sigma_o \exp \left(\frac{-W}{KT}\right)$$  \hspace{1cm} (5)

where W = activation energy KJ/mol, K = Boltzmann constant in eV/K, T = temperature relative to the conductivity value calculated using a reference temperature and as well considering temperature values of corresponding phases, \(\sigma_{ac}\) = conductivity in LC phase and \(\sigma_o\) = conductivity in the isotropic phase at different frequencies.

### III. RESULTS AND DISCUSSION

3.1 Textures and phase transition temperatures

The phases and their transition temperatures obtained from POM are shown in Table 1. The textural observation of 6-methoxy-2-(4-alkanoyloxybenzylidenamino) benzothiazoles mesogen (n=14 and 16) made through POM have shown enantiotropic smectic C and nematic phase as shown in plate 1 and plate 2. The data for phase transition temperatures measured from both POM and DSC [23] are in good agreement.
Table 1. Phase transition temperatures of $n$ MBABTH

<table>
<thead>
<tr>
<th>S.no</th>
<th>Compound</th>
<th>Textures</th>
<th>Transition Temperatures ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$n=14$</td>
<td>I - N</td>
<td>109.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N - SmC</td>
<td>79.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SmC - Cr$_2$</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>Cr$_2$ - Cr$_1$</td>
<td>65.6</td>
</tr>
<tr>
<td>2</td>
<td>$n=16$</td>
<td>I - N</td>
<td>107.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N - SmC</td>
<td>88.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SmC - Cr</td>
<td>83.7</td>
</tr>
</tbody>
</table>

Note: Iso = Isotropic, SmC = Smectic C. N=Nematic Cr= crystal

Plate 1. Nematic phase in 14 MBABTH

Plate 2. Smectic C phase in 16 MBABTH

3.2 Dielectric studies

The frequency dependence of dielectric constant, temperature coefficient of dielectric constant, dielectric loss is shown in figures 1 to 3.

The dielectric constant for both samples as a function of frequency at different temperatures is shown in figure 1. It is observed that the dielectric constant value is high at low frequencies and decreasing gradually with increased frequency and increasing with increased temperature. The observed higher value of dielectric constant at low frequencies is due to effect of space charge polarization. Figure 2 depicts the information about the frequency dependence of temperature coefficient of dielectric constant at higher frequencies. The temperature coefficient of dielectric constant stability is noticed rather to low frequencies in both compounds which are shown in figure 2. As the $\tau_e$ is the combination of thermal and dielectric constant values the results produced by $\tau_e$ as a function of frequency are corresponding to variations in dielectric constant and change in structural properties. It is observed that $\tau_e$ is maximum around 100 Hz for these samples which...
represents the existence of orientational polarization of liquid crystal molecule with temperature.

**Figure 2.** Frequency dependence of thermal coefficient of dielectric constant $\varepsilon$ for (a) 14 MBABTH and (b) 16 MBABTH

**Figure 3.** Frequency dependence of dielectric loss for (a) 14 MBABTH and (b) 16 MBABTH at different temperatures

Figure 3 indicates the dielectric loss for 14 MBABTH and 16 MBABTH mesogens, the reported low dielectric loss at high frequencies is showing similarity with that of the variation of dielectric constant (figure 1) on owing to smaller angle of rotation. It is clear from this figure that the relaxation is shifted towards the higher frequency side as the temperature increased in both the samples. Molecules forming a nematic mesophase are rod like structures in their orientation, tending with long axes towards mutual parallelism and each molecule remaining free to rotate about its long axis and free to translate in an isotropic liquid. That the intermolecular forces are responsible for the mutual parallelism in the molecular long axes resulted in a long-range order, has been the subject of a large number of studies [26-31]. One particularly illuminating experiment [32] has been the dielectric relaxation of nematic liquid crystals for an external electric field directed either parallel or perpendicular to the local optic axis. Maier and Meier [32] reported that the dielectric loss associated with dipolar reorientation about the molecular long axis has occurred at frequencies comparable to isotropic liquids at the same temperature. The loss associated with reorientation about the short axis, however, occurred at frequencies nearly three orders of magnitude lower. This unusually low loss frequency reflects the cooperative nature of the molecular orientation. The static dielectric behavior of liquid crystals has also been of significant interest because of the importance of the dielectric anisotropy in describing the reorientation of liquid crystals in the presence of electric fields. This description has been particularly useful for applications involving electro optic devices [33,34].
Figure 4. Temperature dependence of dielectric constant for (a) 14MBABTH and (b) 16 MBABTH at different Frequencies

From the figure 4 it is observed that the values of dielectric constant remain almost constant up to solid phase and thereafter there is a sharp increase when the transition from solid to Smectic C. It shows a small dip at smectic C to nematic transition. So, the transition temperatures mentioned above are 78.8 °C for phase (Cr→SmA), 79.7 °C for phase (SmA→SmC) and 109.6°C for phase (N→I) for 14 MBABTH and 83.7°C for phase (Cr→SmA), 88.3°C for phase (SmA→SmC), 107.2°C for phase (N→I) for 16 MBABTH which are confirmed significantly through dielectric constant curves.

The temperature dependence of conductivity, relaxation frequency and activation energies are shown in figures from 5 to 7.
The conductivity as shown in figure 5 has increased with increasing temperature in both samples. This is due to the restriction of charge carrier at low temperatures, as the temperature increased the mobility of charge carriers are increased so that the conductivity increases up to isotropic phase in both samples. Temperature dependence of relaxation frequency is shown in Figures 6. It shows that the relaxation frequency has increased with the increase of temperature up to isotropic phase. From Table 2, it is observed that the relaxation times were decreased with increasing temperature in both the samples so that from this result we say that because of the easy orientation of the molecules are tend to align to original direction within a short period of time. The activation energy is the energy required to make reorientation of molecule and necessary to cause for dissociation. The relatively higher value of the activation energy is suggested to the higher potential barrier witnessed by the molecular dipole moment to orient to the field. At high frequencies the activation energy decreases so that it will have a relatively high dielectric strength. From figure 7, it is evident that the activation energy is increased with increased temperature. The activation energy has showed similar tendencies for both samples, it is increased with increasing temperature. This effect is due to role of the surface activity of dispersed particles on local order of the liquid crystal as a result of elastic distortions associated with the liquid crystal molecules.
The variations between dielectric constant and dielectric loss plotted at different temperatures for both samples are shown in Figures 8. From these Figures, the relaxation frequency ($f_R$) corresponding to the peak value of the curve is determined and then, the relaxation time is calculated with the equation $\tau = 1/\omega$ where $\omega = 2\pi f_R$. These cote-cote plots showed Debye relaxation. The observed relaxation times from the cote cote plots and relaxation curves are in good agreement. Because of the chain length increasing in 16 MBABTH compound shows relatively high relaxation times when compared with 14 MBABTH.

Table 2. Relaxation times at different temperature for 14MBABTH and 16 MBABTH

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Relaxation time (m sec)</th>
<th>Temperature (°C)</th>
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IV. CONCLUSIONs

The phases and phase transition temperatures of homologous series of (6-methoxy-2-(4-n-alkanoyloxybenzylidenamino) benzothiazoles mesogens ($n$ MBABTH for $n=14$ and 16 mesogens) are shown enantiotropic smectic C and nematic phases. The phase transition temperatures measured from both POM and dielectric studies are in good agreement. From dielectric studies space charge polarization is observed at low frequencies. $\tau_R$ is maximum around 100 Hz for these samples which represents the existence of orientational polarization. Molecules forming nematic mesophase the intermolecular forces are responsible for the mutual parallelism in the molecular long axes resulted in a long-range order. The low loss frequency reflects the cooperative nature of the molecular orientation. The dielectric study reveals that these compounds are useful for applications involving electro optic devices.

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Research Article

Dielectric Studies on Fe$_3$O$_4$ Nanodoped p-n-Alkyloxybenzoic Acids

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The stability of phase transition temperatures and textural changes for thermotropic pure and nanodoped p-n-alkyloxybenzoic acid mesogens were aimed to study at considerable time periods. Frequency and temperature dependent dielectric constant and dielectric loss for the pure and nanodoped liquid crystals were carried out. Significant anomalies in dielectric studies were observed near phase transitions when dielectric constant and dielectric loss had been measured as a function of temperature and frequency. Changes in dielectric constant and loss were observed and there were no apparent changes at high frequencies instead maintaining constant values. The variations in conductivity, activation energy, and relaxation times had also been studied in the nematic and smectic phases. The temperature dependent dielectric constant stability (temperature coefficient of dielectric constant $\tau_\varepsilon$) had shown shift in the observed frequency range of thermotropic liquid crystals corresponding to the change in the dielectric constant values.

1. Introduction

Nanodoped liquid crystal (LC) research has emerged an important potential area in scientific and technological applications especially in liquid crystal displays [1]. The liquid crystalline materials doped with nanoparticles have indeed attracted much scientific and technological interest mainly because the incorporation of nanomaterials enhances the physical properties of the liquid crystal itself [2]. Low doping concentrations (<3% by weight) are usually preferred to get a more stable and for an even distribution in the LC, which will lower the interaction forces between particles [3, 4]. p-n-alkyloxybenzoic acids are extensively studied earlier and gained interesting results [5–8]. Various experimental techniques are being done on these alkyloxybenzoic acids on individual members and on mixed compounds [6, 8–10].

Dielectric spectroscopy [11, 12] is an effective experimental tool to understand the doping of nanoparticles in liquid crystals. It all depends on intrinsic properties of charged material distribution in molecules and also the intermolecular interactions. The LC anisotropy is proven to have substantially increased due to introduction of nanoparticles (magnetic nanoparticles, basically ferric oxides) [13]. However, enhancement of the electrooptical properties of LC is dependent on the size, type, concentration, and intrinsic characteristics of nanoparticles that are used for doping [14, 15].

The present study aims to examine the stable conditions for the properties of textural, phase transitions, and dielectric properties from room temperature to more than its isotropic temperatures on nanodoped p-n-alkyloxybenzoic acids.
2. Materials and Methods

$p-n$-Alkylxybenzoic acids (nOBA) from $n = 3$ to 10 and 12 are procured from Frinton Laboratories, Inc., USA. The ferric oxides ($\text{Fe}_3\text{O}_4$) nanoparticles of 20 nm size are procured from Indian Institute of Technology, Chennai. Magnetite ($\text{Fe}_3\text{O}_4$) nanoparticles of 0.1% are doped through continuous stirring for nearly 3 hours in their isotropic phase of $p-n$-alkyloxybenzoic acids and after cooling the nanodoped $p-n$-alkyloxybenzoic acids (NnOBA) are subjected to study.

Textural and phase transition temperatures are measured using a Meopta polarising optical microscope (POM) with hot stage as described by Gray [16]. The pure and nanodispersed thermotropic LCs are filled in LCI ITO coated cells, for 90° twist aligned (5 mm × 5 mm × 6 μm), which are obtained from M/s Instec Inc., USA. The compounds in their isotropic state are filled in these cells through capillary action method. Textural and phase transition temperatures are studied after preparation of the sample and observations are made again after a gap of period to understand the stability of Fe$_3$O$_4$ nanoparticles.

The temperature and frequency dependence of capacitance $C$, resistance $R$, and inductance $L$ were measured by using Newton’s 4th Ltd. LCR meter model PM1700. The cells filled with pure and nanodoped samples are placed in an Instec hot and cold stage (HCS 302) equipped with microscope (Olympus BX50) having DP10 camera setup. The temperature is monitored and controlled through a computer by a software program to an accuracy of ±0.1°C. The sample is heated to isotropic state and held until attaining thermal equilibrium. The data of $C$, $L$, and $R$ is taken during cooling process. The measuring signal is the square form with amplitude of 2 V. The frequency range of measurement is from 100 Hz to 1 MHz. The accuracy of dielectric constant and loss are estimated to the error of 1% and 2%, respectively.

3. Results and Discussion

3.1. Textures and Phase Transition Temperatures. The phases and their transition temperatures shown in Table 1 are obtained from POM for nanodoped $p-n$-alkyloxybenzoic acids which exhibit enantiotropic behavior.

The phase transition temperatures for different series of those pure $p-n$-alkyloxybenzoic acids [17] recorded immediately after preparation of NnOBA are not similar as shown in Table 1. The clearing temperatures have decreased for nanodoped liquid crystals when compared to pure liquid crystals [18]. This decrease is due to increase in the van der Waals attraction among nanoparticles that disturbed the orientational properties of director in the LCs medium. Hence, the interaction among them excluding the neighbourhood molecules has formed strong anchoring conditions that influenced the specific orientation to the director resulting in topological defects [19, 20].

The nanoparticles appeared to be stabilized after many interactions among themselves within the liquid crystal medium. The mobility of these nanoparticles in liquid crystal medium is limited forming stable dispersions in alkylxybenzoic acids. It means the surface anchoring properties became weak such that there is no director distortion in the liquid crystal phase. On the other hand, these features reveal clearly that the elastic energy dominates the magnetic one as long as the orientation of director is fixed [21]. The textures of nematic and smectic phases of pure and doped samples are shown in Figure 1. All the nOBA samples have exhibited both threaded nematic and smectic C [22] from $n = 7$ to 10 and 12, whereas $n = 3$ to 6 samples show only threaded nematic. In addition, the observed nanodoped nOBA liquid crystals have displayed threaded nematic and Sm C for $n = 6, 7, 9$, and 12 and cholesteric phase in nanodoped 8OBA and the phases of Sm A and Sm B in nanodoped 10OBA.

These changes can be attributed to the increase in chain length, surface anisotropy, and even-odd effect which are commonly existing in homologous series [23]. The textural changes start playing into effect in nanodoped samples for $n = 6$. This is a self-explanatory showing the effect of chain length increase on textures. The existence of cholesteric phase in N8OBA particularly is due to electroconvection that is usually existing in nematic liquid crystals of short range Sm C order [24]. Comparatively, among all in the selected homologous series of nOBA, the 8OBA has displayed short range Sm C (from 90.5°C to 98.5°C). Hence, only in 8OBA, the presence of nano has made it modified to cholesteric. With the order of chain length increase, the nanoparticles effect the alignment of LC molecules and try to bring them into layering which is identified as Sm A and Sm B. These textures corresponding to different phases are shown in Figures 1(e)–1(g).

The aggregation of magnetite nanoparticles appearing in the textures shown in Figure 2 is attributed to a large contribution to the magnetic anisotropy, which is likely to be located on the particle surface by overcoming randomly oriented molecules with uniaxial symmetry of mesophases.

The UV-visible spectroscopic studies have also confirmed the presence of magnetite nanoparticles in the lattice of samples.

The UV-visible spectra of pure and nanodoped 7OBA mesogen samples are shown in Figure 3. It is observed that the spectrum for pure 7OBA does not exhibit any absorption
peaks in the wavelength range of 200 nm–2000 nm. However, the spectrum of nanodoped 7OBA shows three significant peaks at 418 nm, 681 nm, and 821 nm, which are the characteristic peaks of Fe$^{3+}$ ion [25]. So, the UV-visible spectral study confirms the presence of Fe$_3$O$_4$ nanoparticles in the prepared nanodoped mesogens.

3.2. Dielectric Spectral Studies for Series of Pure and Nanodoped p-n-Alkylxybenzoic Acids

3.2.1. Frequency Dependence of Dielectric Constant and Temperature Coefficient of Dielectric Constant $\tau_\varepsilon$. The dielectric constant of a material is numerically the ratio of the capacitance of a capacitor containing that material to the capacitance of the same electrode system with vacuum. Using (1), the dielectric constant ($\varepsilon^1$) for series of pure and nanoalkyloxybenzoic acids is calculated:

$$\varepsilon^1 = \frac{(C_p - C_o) d}{\varepsilon_o A} + 1,$$

where $A$ = area of the cell, $d$ = thickness of the cell, $\varepsilon_0$ = permittivity of free space $8.85 \times 10^{-12}$ Fm$^{-1}$, $C_p$ = capacitance with sample, and $C_o$ = capacitance without sample.

The temperature coefficient of dielectric constant ($\tau_\varepsilon$) is calculated using (2). Values of $\tau_\varepsilon$ can be positive or negative, indicating an increasing or decreasing dielectric constant, respectively, with an increasing temperature [26]. As these are thermotropic liquid crystals, their temperature stability with respect to other materials is low [26]. To determine $\tau_\varepsilon$, the measured dielectric constant at isotropic temperature considered as reference temperature is compared with the values recorded at both initial and final phases given for temperature range of liquid crystal. Consider

$$\tau_\varepsilon = \frac{(\varepsilon (T_{\text{final}}) / \varepsilon (T_{\text{ref}})) - (\varepsilon (T_{\text{initial}}) / \varepsilon (T_{\text{ref}}))}{T_{\text{final}} - T_{\text{initial}}} * 10^6 \text{[ppm/°C]},$$

where $T_{\text{initial}}$ = initial LC phase temperature value, $T_{\text{final}}$ = final LC phase temperature value, $\varepsilon(T_{\text{initial}})$, $\varepsilon(T_{\text{final}})$ = the corresponding dielectric constant, and $\varepsilon(T_{\text{ref}})$ = dielectric
constant at reference temperature (50°C). The $\tau_e$ value has units of parts per million per degree Celsius [ppm/°C].

Figure 4 represents the calculated $\varepsilon'_1$ variation using (1) as a function of frequency ($f$) for pure and nanodoped LCs compounds in different phases. $n$OBA and $Nn$OBA series have shown the same path in the graphical chart showing a decrease in $\varepsilon'_1$ at low frequencies and almost constant $\varepsilon'_1$ at high frequencies. It infers that doping ferroelectric nanoparticles to liquid crystal for a small amount (0.1%) has affected slightly the dielectric properties of the system at low frequencies.

At high frequency, both compounds exhibit constant $\varepsilon'_1$ and also show lower values. These are associated with the lowest electrical loss characteristics. The high orientation of liquid crystal molecules in isotropic phase shows high value of $\varepsilon'_1$ when compared with another phase. On doping nanoparticles, the strong anchoring forces developed among nanoparticles and liquid crystal molecules caused decrease in dielectric permittivity. Fixed orientations of molecules have brought low values in liquid crystalline phase.

More stability in the dielectric constant at temperatures for high frequencies is significantly relative to low frequencies for both compounds as shown in Figure 5. $\tau_e$ is the product of thermal and dielectric constant; properties of the results produced by $\tau_e$ as a function of frequency are corresponding to variations in dielectric constant and structural properties.

The lower values of $\tau_e$ closer to zero indicate stable dielectric constant with temperature. While compared with dielectric constant variation of pure and nano LCs, the $\tau_e$ variation is high since it consists of important role of thermal and alignment stabilities with respect to applied field. From Figure 5 ($n = 3$ and 8), the instability thermal properties showing high value of $\tau_e$ are observed for $n = 3$ to 6 (both $n$OBA and $Nn$OBA) mesogens at lower frequencies. The high transition temperatures and orientational order of
the nematic molecules are attributed to that property as a result of the dominating frequency applied. With increasing chain length, the smectic translation order decreased in the transition temperatures. Surface anchoring by nanoparticles would also bring instability in thermal and dielectric properties resulting in decrease for owng molecules aligned with respect to applied high frequencies.

3.2.2. Frequency Dependence of Dielectric Loss, Conductivity, and Activation Energy. The simplest model for a capacitor with a lossy dielectric is the capacitor with a perfect dielectric in parallel with a resistor giving power dissipation. The dielectric loss angle (tan δ) values are directly measured from the experimental technique, and the imaginary part of permittivity (dielectric loss, $\varepsilon^{11}$) is calculated using (3) for the chosen series:

$$\varepsilon^{11} = \varepsilon^1 \tan \delta.$$ (3)

Based on $\varepsilon^{11}$ data, the sample conductivity $\sigma$ (siemens per meter) is estimated using (4). Changes in electrical conductivity and charge transferring for low concentration dispersion of Fe$_3$O$_4$ nanodoped in alkloxybenzoic acids and for pure compounds are studied. At different temperatures and isotropic phase, the ac conductivity in the LC region is measured from (4) from 1 kHz to 1 MHz frequencies:

$$\sigma_{ac} = 2\pi \varepsilon_0 \varepsilon^{11} f,$$ (4)

where $\varepsilon_0$ = permittivity of free space $8.85 \times 10^{-12}$ Fm$^{-1}$, $f$ = corresponding frequency in Hz, and $\varepsilon^{11}$ = dielectric loss.

The most widely adopted form of the Arrhenius equation [27] to study for the effect of temperature on conductivity is shown in (5). The activation energy is viewed as an energetic threshold for a fruitful electric field production generated by the LC molecules orientation or by dispersed nanoparticles structure. It is possible to calculate activation energy with the Arrhenius equation simply by using the conductivity at two temperatures. It would be more realistic and reliable if more data of conductivity is taken at different temperatures. Hence, by using the ac conductivity values calculated from (4) in the LC temperature region from 1 kHz to 1 MHz, the activation energy ($W$) is calculated by following

$$\sigma_{ac} = \sigma_o \exp\left(-\frac{W}{KT}\right),$$ (5)

where $W$ = activation energy KJ/mol, $K$ = Boltzmann constant in eV/K, $T$ = temperature relative to the conductivity value calculated using a reference temperature and the temperature values at corresponding phases, $\sigma_{ac}$ = conductivity in LC phase, and $\sigma_o$ = conductivity in the isotropic phase at different frequencies.

Figure 6 has indicated the dielectric loss for nanodoped system that is increased when compared to pure compounds (LC phase) because of more conducting nature in nanodoped particles. Low dielectric loss at high frequencies has shown similarity with the variation of dielectric constant (Figure 4) owing to smaller angle of rotation. The loss factor on frequency dependent is also the same behavior in a similar way as the dielectric constant (which is known when the loss experimental data is analyzed). The positional variation of relaxation peaks within the frequency range studied is observed only for a particular compound of even series of $n$OBA and $n$OBA.

Figure 7 represents the conductivity variation with temperature from isotropic to crystal at specific frequencies and shows the results for 12OBA and 112OBA as a representative case. The other members of $n$OBA and $n$OBA
mesogens have been shown in a similar pattern but with a different magnitude. For the frequency increased from 12.3 Hz to 1 MHz, the conductivity rapidly increased. Hence, the variation at lower frequencies is not significant in the graph. However, the low frequencies variation is prominent for both 12OBA and N12OBA compounds as depicted on right side graph. The conductivity has increased with the increased frequency of 1 MHz. The maximum conductivity values studied at 1 MHz are $1.25 \times 10^{-4}$ (S/m) in isotropic state for nanodoped LCs N3OBA and $1.07 \times 10^{-4}$ (S/m) for 3OBA. Having the lowest carbon chain length in the series, the mobility of molecular rotation in 3OBA has led to increase in flow of current in anisotropic LCs matrix compared to that in other compounds upon their gradual increased chain lengths in the series. The presence of higher conductivity for nanodoped LCs than pure compounds is known through the higher dielectric constant recorded for pure LCs than for nanodoped as shown in Figure 4.
Figure 7: Relative conductivity $\sigma$ (S⋅m$^{-1}$) versus inverse temperature $1/T$ (1/K) for pure and nanodoped LCs of 12OBA ((a) and (c)) at various frequencies and ((b) and (d)) for the variations at low frequencies.

The anomalies at near transition temperatures are observed. A nearly invariant temperature affecting ac conductivity is noticed in the smectic to crystal transition. A sharp decrease in nematic phase is observed with respect to increase in inverse temperature. As discussed earlier, the high conductivity value is exhibited at high frequency; therefore, for pure and nanodoped LCs, high frequency relative conductivity dominates than other lower frequencies.

The calculated activation energy ($W$) for conduction in entire LC region by using (5) as function of frequency at LC temperatures for nematic and smectic regions is shown in Figure 8. The results shown here are representing 5OBA and 8OBA and their nanocomplexes as a case study and conclusions are drawn for other members of $n$OBA mesogens.

The activation energy also showed similar tendencies in the nanodispersed samples that is decreasing with increasing frequency in the smectic and solid phases. Figure 8 indicates that there are three levels present in the frequency range in nematic phase. Firstly, the frequency increased with the increase of activation energy; secondly, on further increase
Figure 8: Frequency dependence of activation energy in nematic and smectic phases for (a) nanodoped and (b) pure LCs of 5OBA and (c) nanodoped 8OBA and pure 8OBA.

in frequency, there exists a broad frequency region where the activation energy is nearly constant and finally started decreasing until approaching 0 (KJ/mol). This effect is raised due to the role of the surface activity of dispersed particles in local order of the liquid crystal as a result of elastic distortions associated with the liquid crystal on following increased frequencies.

By analyzing the activation energy results, it can be concluded that the energy values for both compounds in nematic phase are in the range from −100 to 250 (KJ/mol). The values of activation energy in smectic phase at a particular frequency region are more than 250 (KJ/mol), which is similar to the relative conductivity (σ) that showed steep slope in nematic as in smectic phase. This can be explained by considering two reasons while using long and short molecular axis rotation in the liquid crystal matrix in the presence or absence of the suspended nanoparticles with respect to applied field. Firstly, at low frequencies, the increase in activation energy in nematic phase for $n = 3$ to 6 (both pure and nano) has led to restricted mobility of charged carriers resulting in low conductivity (Figure 7). At higher frequencies, the decrease in the activation energy (Figure 8) is related to high mobility of
charged transports. This is confirmed by correlating the high conductivity (Figure 7) and low temperature coefficient of dielectric constant (Figure 5) at higher frequencies. Therefore, the distortion in rotation and in alignment of LC molecules with respect to the field will bring on increase in the conductivity on lowering its active potential energy.

3.2.3. Temperature Dependence of Dielectric Constant and Loss for Pure and Nanodoped Alkyl oxybenzoic Acids. Temperature dependent dielectric studies for the prepared nOBA nanodoped particles are carried out to analyze its response to an applied low ac voltage (2 V). The variations in dielectric constant and loss with temperature at various frequencies are shown in Figure 9. Increase in the ionization of the sample with temperature increases the processes of conductivity and dissipation factor simultaneously, and it is vice versa in case of higher frequencies.

A nearly similar trend of dielectric constant with temperature is also observed in dielectric loss. These different variations at low and high frequencies due to temperature may be attributed to conformational vibrations of mobile molecular fragments, like vibrations of flexible alkyl oxy groups and vibrations of the benzene rings together of nOBA mesogens. From Figure 9(a) (1 kHz), it is observed that an increase

![Graphs showing temperature dependence of ε₁ and ε₁₁ for nanodoped and pure nOBA at 1 kHz and 1 MHz.](image-url)
in dielectric constant on increasing temperature has suggested that the dipoles are oriented perpendicularly towards the director at high temperatures, whereas in Figure 9(b) (1 MHz), nearly, constant is observed at high temperatures. The difference in dielectric constant and loss of pure and nanodoped LCs as shown in Figure 9 is due to variations in thermal transition temperatures.

3.2.4. Cole-Cole Plots of $\varepsilon^1$ and $\varepsilon^{11}$ for Nematic and Smectic Phases between 1 kHz to 1 MHz for Pure and Nanodoped p-n-Alklyloxybenzoic Acids. By using the dielectric data (dielectric constant and loss) from LCR meter, the Cole-Cole plots [28] are drawn for different temperatures. The relaxation time $\tau$ (Sec) can be found from the arc plot by using

$$\omega = \left( \frac{\nu}{\omega_c} \right)^{1/(1-\alpha)},$$

(6)
where \( \alpha = \theta/90 \) (distribution parameter), \( \omega = 2\pi f \) (angular frequency, Hz), and \( u, v \) values are determined from the drawn Cole-Cole plots.

Figure 10 (as representative case) illustrates a few characteristic results showing typical Cole-Cole plots at several temperatures (in LC region). The symbols used in it are representing the experimental data and the solid line is representing the semicircle fitting. Table 2 provides the subset relaxation time values at different frequencies and phases. Same relaxation times are observed at all frequencies on semicircle curvature at a particular temperature on varied \( u, v \) values. From Figure 10, conclusions are drawn that the dielectric dispersions (curvature) for nanodoped LCs are exhibited better at the frequency studied when compared to pure composites. These plots are drawn to analyze the dielectric dispersion spectra of the LC phases with respect to isotropic phase relaxation times and variations in dipoles orientation variation as a function of temperature. Even though there is a fixed temperature and having same nematic or smectic order with same molecular structure in these series, there are different relaxation times observed at different relaxation frequencies for variation in their carbon chain length. Table 2 shows the calculated values of relaxation times using Cole-Cole plots in isotropic, nematic, and smectic phases at particular temperatures.

Among all these series, the pure 7OBA compound does not show any relaxation but the 7OBA nanodoped compound shows relaxation. This phenomenon is reversed in the case of 4OBA compound as given in Table 2. It is concluded that the Fe₃O₄ particles hindered the free rotations in the liquid crystal matrix and showed better relaxation times at studied frequencies when compared to pure compounds. In some cases of pure and nanodoped LCs, have displayed nearly equal dispersions and relaxation times as that of the isotropic phase [12] and showing the reorientation of molecular dipoles dominating the ordering in LC phases. The presence of nano not only effected the molecular ordering but also influenced the dielectric parameters like \( \varepsilon' \), \( \varepsilon'' \), \( \tau \), and activation energy. These changes can be attributed to the dipole moment contribution of magnetite nanoparticles to the liquid crystal molecules [29, 30].

4. Conclusions

The dielectric spectrum of frequency dependent dielectric constant and the loss for both pure and nanodoped alkoxybenzoic acids in perpendicular alignment are analyzed. The sharp changes in measured dielectric parameters in the temperature region are corresponding to the respective phase transitions in the liquid crystal materials. Two regions of dispersion observed on dielectric charts, that is, one at low frequency dispersion and the other at high-frequency, are related to the rotation of molecules about the short axis in the former case and about the long axis in the latter case. In addition, the variation in activation energy at different regions of temperature corresponds to conductivity as a function of frequency. The strong interaction between the Fe₃O₄ nanoparticles and the liquid crystal anisotropic matrix has brought obvious effects on thermal transition behavior and dielectric properties of LCs. Therefore, when the nanoparticles are dispersed in the anisotropic liquid crystalline medium, the particle resonance, depending on the angle of the director and the surface reactivity, is identifiable.

### Table 2: Subset values of relaxation time (Sec) with temperature variation at different frequencies for nOBA.

<table>
<thead>
<tr>
<th>Phases</th>
<th>Relaxation times (frequency (Hz)) (Sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nematic</td>
<td>Isotropic ( 0.185 \times 10^{-3} (8.69 \times 10^{2}) )</td>
</tr>
<tr>
<td></td>
<td>Nanopropoxybenzoic acids ( 0.191 \times 10^{-4} (1.10 \times 10^{3}) )</td>
</tr>
<tr>
<td>Nematic</td>
<td>Nematic ( 0.116 \times 10^{-3} (4.16 \times 10^{2}) )</td>
</tr>
<tr>
<td></td>
<td>Nanobutoxybenzoic acids ( 0.311 \times 10^{-2} (8.69 \times 10^{2}) )</td>
</tr>
<tr>
<td>Nematic</td>
<td>Isotropic ( 0.227 \times 10^{-3} (1.15 \times 10^{3}) )</td>
</tr>
<tr>
<td></td>
<td>—</td>
</tr>
<tr>
<td>Pentyloxybenzoic acids</td>
<td>Isotropic ( 0.183 \times 10^{-3} (8.69 \times 10^{2}) )</td>
</tr>
<tr>
<td></td>
<td>Nanopentyloxybenzoic acids ( 0.192 \times 10^{-3} (8.69 \times 10^{2}) )</td>
</tr>
<tr>
<td>Nematic</td>
<td>Nematic ( 0.116 \times 10^{-4} (4.16 \times 10^{2}) )</td>
</tr>
<tr>
<td></td>
<td>Nanobutoxybenzoic acids ( 0.131 \times 10^{-3} (1.21 \times 10^{2}) )</td>
</tr>
<tr>
<td>Nematic</td>
<td>Hexyloxybenzoic acids ( 0.245 \times 10^{-3} (8.69 \times 10^{2}) )</td>
</tr>
<tr>
<td></td>
<td>Nanohexyloxybenzoic acids ( 0.100 \times 10^{-2} (1.60 \times 10^{2}) )</td>
</tr>
<tr>
<td>Nematic</td>
<td>Pentyloxybenzoic acids ( 0.251 \times 10^{-3} (4.94 \times 10^{2}) )</td>
</tr>
<tr>
<td></td>
<td>Nanoheptloxybenzoic acids ( 0.126 \times 10^{-2} (1.60 \times 10^{2}) )</td>
</tr>
<tr>
<td>Nematic</td>
<td>Heptloxybenzoic acids ( — )</td>
</tr>
<tr>
<td></td>
<td>—</td>
</tr>
<tr>
<td>Nematic</td>
<td>Octyloxybenzoic acids ( 0.138 \times 10^{-3} (2.02 \times 10^{2}) )</td>
</tr>
<tr>
<td></td>
<td>Nanooctyloxybenzoic acids ( 0.308 \times 10^{-3} (8.69 \times 10^{2}) )</td>
</tr>
<tr>
<td>Nematic</td>
<td>Nematic ( 0.227 \times 10^{-3} (1.15 \times 10^{2}) )</td>
</tr>
<tr>
<td></td>
<td>Nematic ( 0.131 \times 10^{-2} (1.21 \times 10^{2}) )</td>
</tr>
<tr>
<td>Nematic</td>
<td>Nonyloxybenzoic acids ( 0.131 \times 10^{-2} (3.14 \times 10^{2}) )</td>
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<tr>
<td></td>
<td>Nonoxyloxybenzoic acids ( 0.563 \times 10^{-3} (2.12 \times 10^{2}) )</td>
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<tr>
<td>Smectic</td>
<td>Isotropic ( 0.995 \times 10^{-3} (1.60 \times 10^{2}) )</td>
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<td>Nonoxyloxybenzoic acids ( 0.563 \times 10^{-3} (2.12 \times 10^{2}) )</td>
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<tr>
<td>Smectic</td>
<td>Nonyloxybenzoic acids ( — )</td>
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<td></td>
<td>—</td>
</tr>
<tr>
<td>Nematic</td>
<td>Decyloxybenzoic acids ( 0.398 \times 10^{-3} (1.15 \times 10^{2}) )</td>
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<td></td>
<td>Nanodecyloxybenzoic acids ( 0.426 \times 10^{-3} (3.73 \times 10^{2}) )</td>
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<td>Nematic</td>
<td>Nematic ( 0.584 \times 10^{-3} (2.81 \times 10^{2}) )</td>
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<td>Nanodecyloxybenzoic acids ( 0.312 \times 10^{-3} (8.69 \times 10^{2}) )</td>
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<tr>
<td>Smectic</td>
<td>Smectic ( 0.186 \times 10^{-3} (8.69 \times 10^{2}) )</td>
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<td>Nanodecyloxybenzoic acids ( 0.224 \times 10^{-3} (1.53 \times 10^{3}) )</td>
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<tr>
<td>Dodecyloxybenzoic acids</td>
<td>Isotropic ( 0.988 \times 10^{-3} (2.81 \times 10^{2}) )</td>
</tr>
<tr>
<td></td>
<td>Dodecyloxybenzoic acids ( 0.162 \times 10^{-3} (2.68 \times 10^{2}) )</td>
</tr>
<tr>
<td>Nematic</td>
<td>Nematic ( 0.991 \times 10^{-3} (2.81 \times 10^{2}) )</td>
</tr>
<tr>
<td></td>
<td>Nematic ( 0.160 \times 10^{-3} (2.68 \times 10^{2}) )</td>
</tr>
<tr>
<td>Smectic</td>
<td>Smectic ( 0.098 \times 10^{-2} (6.55 \times 10^{2}) )</td>
</tr>
<tr>
<td></td>
<td>Smectic ( 0.520 \times 10^{-3} (2.68 \times 10^{3}) )</td>
</tr>
</tbody>
</table>

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.
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