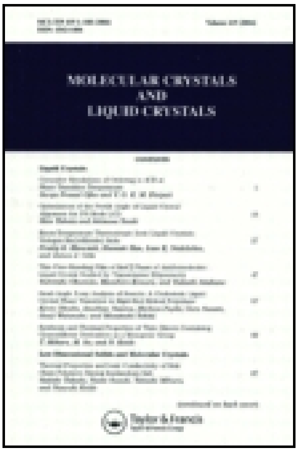


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

# Dielectric Relaxation Study of Two Different Mesogenic Cinnamates with a Substituted Ethyl Terminal Chain

R. Manohar [a], S. Gupta [a], A. K. Prajapati [b] & H. N. Patel [b]

[a] Department of Physics, Lucknow University, Lucknow

[b] Department of Applied Chemistry, Faculty of Technology and Engineering, The M.S. University of Baroda, Kalabhavan, Vadodara, India

Version of record first published: 07 Oct 2011

To cite this article: R. Manohar, S. Gupta, A. K. Prajapati & H. N. Patel (2011): Dielectric Relaxation Study of Two Different Mesogenic Cinnamates with a Substituted Ethyl Terminal Chain, Molecular Crystals and Liquid Crystals, 548:1, 86-95

To link to this article: http://dx.doi.org/10.1080/15421406.2011.590370

*Mol. Cryst. Liq. Cryst.*, Vol. 548: pp. 86–95, 2011
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.590370

# Dielectric Relaxation Study of Two Different Mesogenic Cinnamates with a Substituted Ethyl Terminal Chain

R. MANOHAR,[1,*] S. GUPTA,[1] A. K. PRAJAPATI,[2]
AND H. N. PATEL[2]

[1]Department of Physics, Lucknow University, Lucknow
[2]Department of Applied Chemistry, Faculty of Technology and Engineering,
The M.S. University of Baroda, Kalabhavan, Vadodara, India

*Dielectric studies of liquid crystals are important as they provide information about their molecular structure, intermolecular interaction, and molecular dynamics. The dielectric relaxation has been investigated for two different mesogenic cinnamates with a substituted ethyl terminal chain, β-methoxyethyl [4-(4′-n-octyloxycinnamoyloxy) benzoates (ME8OCB), and β-chloroethyl [4-(4′-n-octyloxycinnamoyloxy) benzoates (CE8OCB). The ME8OCB exhibits an enantiotropic smectic A (SmA) and a nematic mesophase whereas CE8OCB exhibits only an enantiotropic SmA mesophase. The real and imaginary parts of permittivity and dielectric anisotropy have been measured using an impedance/gain phase analyzer in the frequency range 100–10 MHz. The measurements have been carried out in the temperature range 80°C–136°C. The measurement in the smectic phase indicates dielectric dispersion. The relaxation time and activation energies have also been determined. The result suggests that there is a molecular rotation about molecular axis. The dielectric anisotropy falls with a rise in temperature but mean dielectric permittivity increases with a rise in temperature.*

**Keywords** Dielectric loss; dielectric permittivity; liquid crystal.

## 1. Introduction

The nematic phase (N) is used extensively in commercially available liquid crystal displays (LCDs). The molecules in the nematic phase tend to align nearly to parallel each other resulting in a net long-range orientational order. The preferred direction of orientation is called the director, represented by a unit vector **n**. Due to the thermal fluctuations, the long axis of a single molecule deviates from the average director given by **n**. In the nematic phase, the components of different macroscopic properties in the plane perpendicular to the director **n** are degenerate, thus, the nematic phase is a uniaxial phase. If we cool a nematic phase, we may get a smectic A (SmA) phase. In the smectic phases, the molecules are assembled in layers and are arranged with their molecular long axes perpendicular to the planes of the layers [1].

The SmA phase may be described as a stack of two-dimensional (2D) liquid layers, which can easily be curved and flow over one another, keeping the interlayer thickness

---

[*] Address correspondence to R. Manohar, Department of Physics, Lucknow University, Lucknow. Tel.: +91 9415000687. E-mail: rajiv.manohar@gmail.com

constant. The rod-like molecules in the SmA have their long axis oriented normal to the layers. This makes the systems optically uniaxial with a large optical anisotropy [2]. Dielectric spectroscopy is a powerful technique to study molecular dynamics and molecular ordering in liquid crystals in general [3].

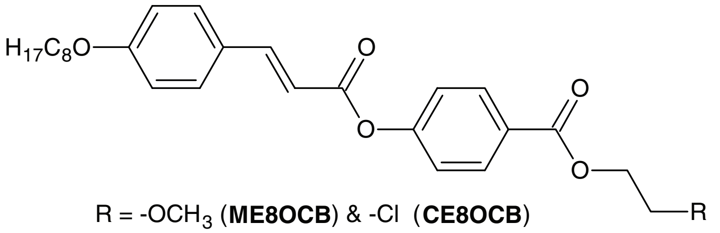
A number of studies have been made on the low-frequency dielectric relaxation [4] of nematic liquid crystals. Most of the experiments have been concentrated on the low-frequency relaxation process, which can be attributed to the hindered rotation of the long molecular axis around its short axis [4–6]. The nematic liquid crystals dielectric behavior at low frequency has been linked to cells without an alignment layer for the electrode polarization [7]. Thus, these mechanisms depend upon the materials used and the cell manufacturing process, which can vary significantly.

De Jeu et al. [8, 9] have calculated the dipole–dipole correlation between the molecules for nematic and smectic-A phase. The importance of the dipole–dipole interaction in dielectric permittivity and phase diagram measurements of liquid crystalline phases has been demonstrated [10,11]. The dipole correlation plays an important role in such phenomenon as the occurrence of smectic phases, re-entrancy and smectic induction [8,12,13]. The dipole correlation is affected by the presence of different side chains and these substituted side chains can produce a large change in dielectric and other properties of liquid crystals.

Therefore, in this article, we report the dielectric spectroscopy results of two different mesogenic cinnamates with a substituted ethyl terminal chain, showing a SmA and a nematic phase. The nature of phase changes occurring in the samples, are also verified by dielectric anisotropy and activation energies estimated from the dielectric study. The SmA and nematic phase was encountered in the sample having methoxyethyl tail while the nematic phase is not present in the sample having a chloroethyl tail.

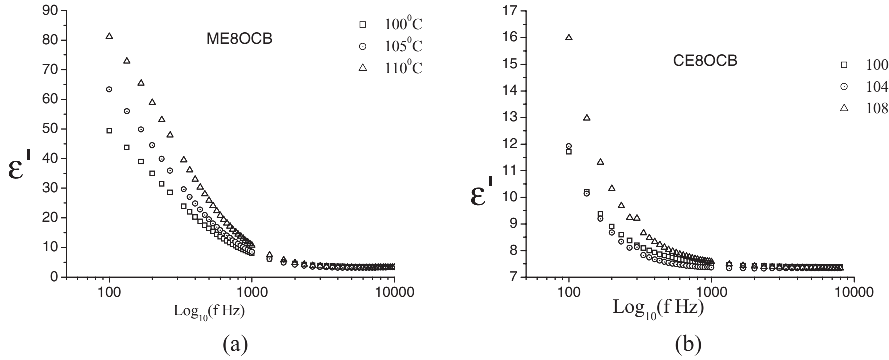
## 2. Experimental Details

The detailed synthesis of both the compounds used in the present study is described elsewhere [14]. General structural formula and the transition temperatures of the samples are as follow:



**ME8OCB**: Cr 84°C SmA 124°C N 128°C Iso. & **CE8OCB**: Cr 82°C SmA 119°C Iso.

Two similar cells have been prepared by using highly conducting Indium Tin Oxide (ITO) coated optically flat glass substrates, which were used as electrodes. These electrodes allow us to align the liquid crystal molecules. To get planar alignment all of the electrodes were pretreated with adhesion promoter and polymer(nylon 6/6), and rubbed unidirectionally with velvet cloth. The thickness of the cell was maintained at 5 $\mu$m by means of Mylar spaces. The cells were calibrated using standard AR grade liquids like benzene ($C_6H_6$) and carbon tetrachloride ($CCl_4$). The materials **ME8OCB** and **CE8OCB** were introduced into the cell by capillary action at 5°C above their isotropic transition temperature, and then



(a) (b)

**Figure 1.** The variation of dielectric permittivity ($\varepsilon'$) with Log$_{10}$ ($f$) Hz at different temperature for (a) **ME8OCB**, and (b) **CE8OCB** samples in the SmA phase.

cooled slowly in the presence of a small electric field. Well-aligned cells were obtained and their alignment was confirmed by observing them under a polarizing microscope, model [**CENSICO (7626)**].

The dielectric behavior of materials **ME8OCB** and **CE8OCB** has been studied in the frequency range 100–10 MHz using a computer controlled Impedance/gain phase analyzer (HP4194A). Measurements in the high frequency range have been limited to 10 MHz because of dominating effect of ITO coated on the glass plates [15]. The dielectric parameters were measured as a function of temperature and frequency by keeping the sample on a hot stage of computer controlled refrigerated circulator (Julabo F25). The experiments were done at very slow heating rate and temperature was measured with the accuracy of ±0.01°C.

## 3. Results and Discussion

The samples **ME8OCB** and **CE8OCB** used in this article were enantiotropic liquid crystals. All the measurements have been taken in the heating cycle.

The frequency dependence of dielectric permittivity for both the samples of same type of series is given in Fig. 1(a) and (b). It is clear from the figures that the dielectric permittivity for both the samples **ME8OCB** and **CE8OCB** increases with an increase in temperature below 1 kHz and shows an almost constant trend beyond 1 kHz in the SmA phase. The variation of dielectric permittivity with frequency for both the samples is found to be similar to the earlier reported studies. The same behavior is also observed in the nematic phase for **ME8OCB** sample as shown in Fig. 2.

The variation of dielectric permittivity with temperature for both samples **ME8OCB** and **CE8OCB** is shown in Fig. 3(a) and (b). From the figures it is clear that the dielectric permittivity increases slowly with an increase in temperature, but it decreases as the frequency is increased. The magnitude of dielectric permittivity for **ME8OCB** sample is higher than that of **CE8OCB** sample. This may be due to the longer tail at one end of the molecule, which may increase the overall polarizability of the molecules of compound **ME8OCB** as compared with the molecules of compound **CE8OCB**. The higher value of the dielectric constant at higher temperature indicates that the molecular dipole has more freedom of movement as we increase the temperature. The phase changes are not demonstrated clearly by sharp discontinuity of the dielectric permittivity for the case of **ME8OCB**. But in the

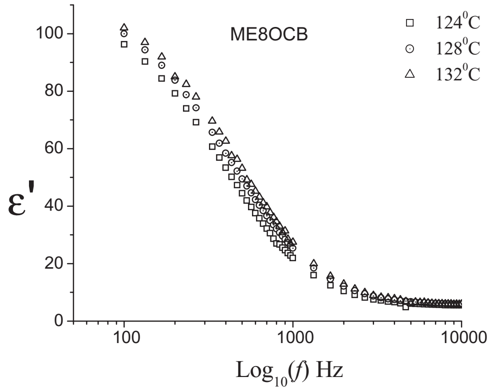


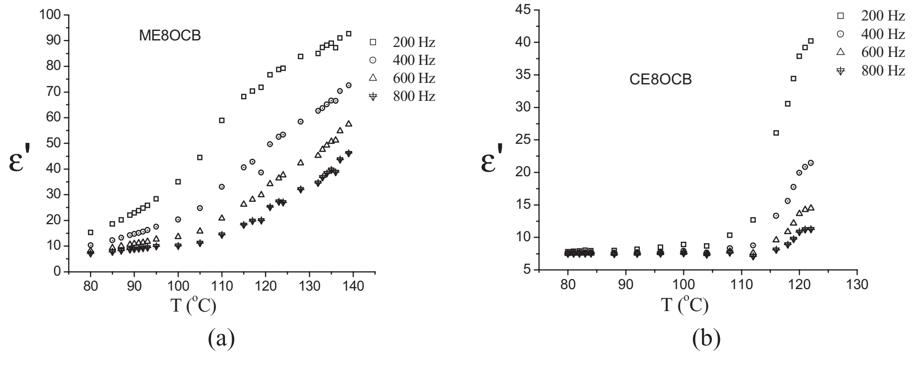
**Figure 2.** The variation of dielectric permittivity ($\varepsilon'$) with Log$_{10}$ ($f$)Hz at different temperature for **ME8OCB** in the nematic phase.

case of **CE8OCB,** the sample goes into the isotropic phase at 119°C and the $\varepsilon'$ increases sharply, clearly indicating a phase change.

Figure 4(a) and (b) represent the dielectric permittivity measured in parallel and perpendicular directions of the electric field, i.e., $\varepsilon'_\perp$ and $\varepsilon'_{||}$ at two different frequencies 400 Hz and 800 Hz for **ME8OCB** and **CE8OCB** samples. The value of dielectric anisotropy ($\Delta\varepsilon$) for both the samples is positive and is given by $\Delta\varepsilon = \varepsilon'_\perp - \varepsilon'_{||}$. The variation of $\Delta\varepsilon$ with temperature can be explained qualitatively by taking into account the Maier and Meier [16] formula given as

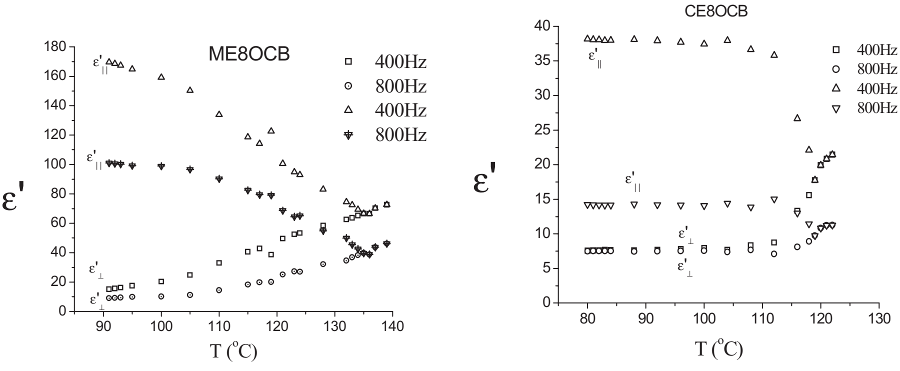
$$\Delta\varepsilon = \varepsilon'_{\|} - \varepsilon'_{\perp} = N_{\mathrm{o}} FH \left[ \Delta\alpha - F\frac{\mu^2}{2KT}(1 - 3\cos^2\beta) \right] \mathrm{S}$$

where, $N_{\mathrm{o}}$ denotes the number of molecules per unit volume, $S$ is the order parameter, $\Delta\alpha$ is anisotropy of the molecular polarizability, and $\beta$ represents the angle between the total dipole moment and long axis of molecules.



(a) (b)

**Figure 3.** The variation of dielectric permittivity ($\varepsilon'$) with temperature at different frequencies, i.e., 200 Hz, 400 Hz, 600 Hz, and 800 Hz for (a) **ME8OCB**, and (b) **CE8OCB** sample.

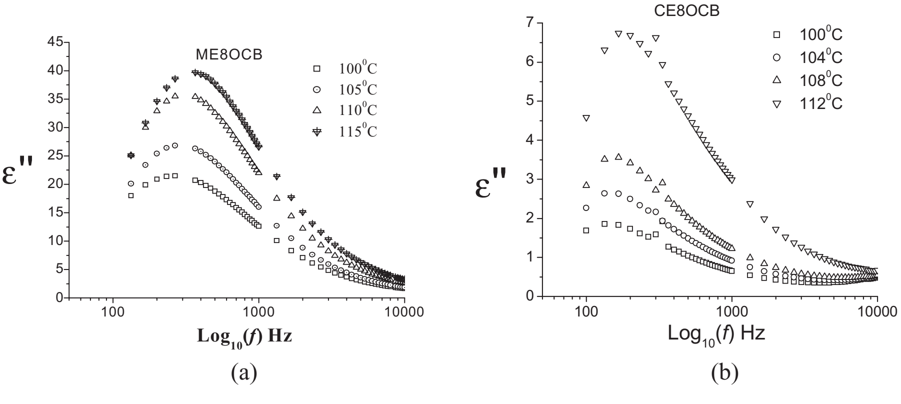


(a) (b)

**Figure 4.** The variation of dielectric permittivity ($\varepsilon'$) in parallel and perpendicular direction with temperature for (a) **ME8OCB**, and (b) **CE8OCB**.

The value of $\Delta\varepsilon$ is higher at the lower frequency and decreases for the higher frequency for both the samples. The value of $\Delta\varepsilon$ is higher for **ME8OCB** as compared with **CE8OCB** due to the larger side chain size. The higher side chain hinders the movement of the molecule in one direction and therefore the difference of $\varepsilon'_\perp$ and $\varepsilon'_{||}$ is higher for the compound with higher side chain. This behavior has also been reported previously [17].

The variation of dielectric loss with frequency at different temperature is shown in Fig. 5. The $\varepsilon''$ peak actually increases with an increase of temperature in the smectic A phase and thus there are a larger number of free molecules with a corresponding enhancement of the effective dipole moment at higher temperature [18]. The magnitude of peak value of $\varepsilon''$ in SmA phase for **ME8OCB** sample is larger in comparison to that of **CE8OCB** sample. The relaxation frequency increases with an increase in temperature. This type of behavior has also been reported by other workers [19, 20]. It is also clearly observed that the dielectric loss falls with a decrease in temperature and frequency. The loss peak has also been observed for the nematic phase of **ME8OCB** sample but the amplitude of the peak is not changing much with the variation of temperature for this phase (Fig. 6).



(a) (b)

**Figure 5.** The variation of dielectric loss ($\varepsilon''$) with Log $_{10}(f)$Hz at different temperature for (a) **ME8OCB**, and (b) **CE8OCB** samples in the SmA Phase.

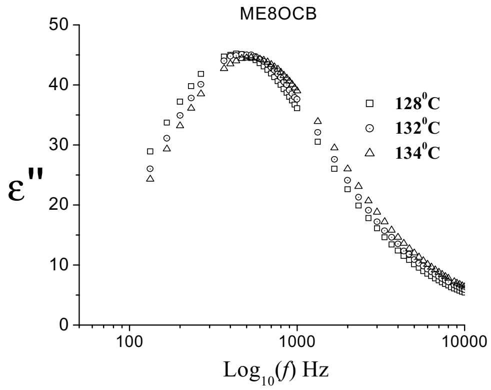


**Figure 6.** The variation of dielectric loss ($\varepsilon''$) with log $_{10}$ ($f$) Hz at different temperature for **ME8OCB** sample in the nematic phase.

We have determined the relaxation frequency of the samples using the Cole–Cole presentation. The Cole–Cole dispersion equation may be given as [21, 22]

$$\varepsilon * = \varepsilon'(\infty) + \frac{\delta\varepsilon'}{1 + (j\omega\tau)^{(1-\alpha)}} \tag{1}$$

where, $\delta\varepsilon'$ is dielectric strength of material; $\varepsilon_\infty$ is high frequency of electric permittivity of free space, and $\alpha$ is distribution parameter. If $\alpha$ is small the above equation will satisfy the Debye type of relaxation phenomenon, and as $\alpha$ increases beyond 0.5 the above equation suggests the existence of more than one relaxation process [23].

Generally, the measured dielectric data for such type of sample holder are affected due to ionic conductance and electrode polarization effect in low-frequency region [14]. Whereas data are affected due to the combined effect of lead inductances and electrode surface resistances in high frequency region [24, 25]. Therefore, the experimental results extremely required a low- and high-frequency correction. On separating real and imaginary parts of the Equation (1), one may get after adding high- and low-frequency correction parameters

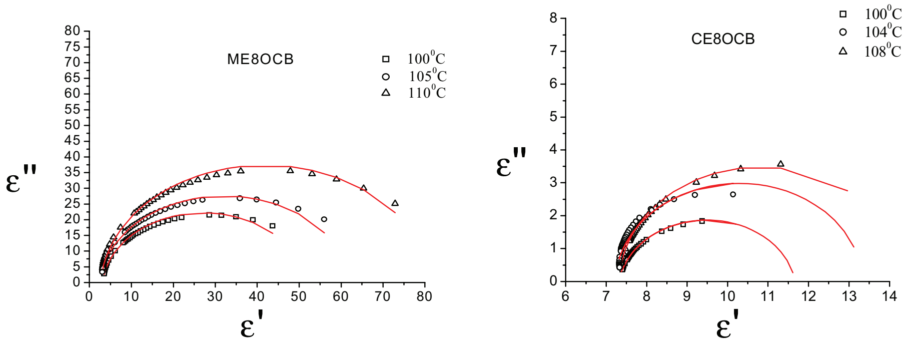
$$\varepsilon' = \varepsilon'(dc)f^{-n} + \varepsilon'(\infty) + \frac{\delta\varepsilon'[1 + (2\pi f\tau)^{(1-\alpha)}\sin(\alpha\pi/2)]}{1 + (2\pi f\tau)^{2(1-\alpha)} + 2(2\pi f\tau)^{(1-\alpha)}\sin(\alpha\pi/2)} \tag{2}$$

and

$$\varepsilon'' = \frac{\sigma(dc)}{\varepsilon_0 2\pi f^k} + \frac{\delta\varepsilon'(f\tau)^{(1-\alpha)}\cos(\alpha\pi/2)}{1 + (2\pi f\tau)^{2(1-\alpha)} + 2(2\pi f\tau)^{(1-\alpha)}\sin(\alpha\pi/2)} + Af^m \tag{3}$$

where, $\sigma$ (dc) is ionic conductance, $\varepsilon_o$ is free space permittivity, $k$ is the fitting parameter, and $\omega$ is angular frequency. The term $\varepsilon$ (dc)/$f^{-n}$ and $\sigma$ (dc)/$\varepsilon_0\omega$ are added in Equations (2) and (3) for low-frequency effect due to the electrode polarization, capacitance, and ionic conductance. The term $Af^m$ is added in Equation (3) for high-frequency effect due to the ITO resistance and lead inductance. By the least square fitting of Equation (3) into experimental data, we have removed the low- and high-frequency errors.

Figure 7 represents the plots of $\varepsilon'$ versus $\varepsilon''$ to give the Cole–Cole arcs for different temperatures. The points lie on a semicircle with its center below $\varepsilon'$-axis. With increasing



(a) (b)

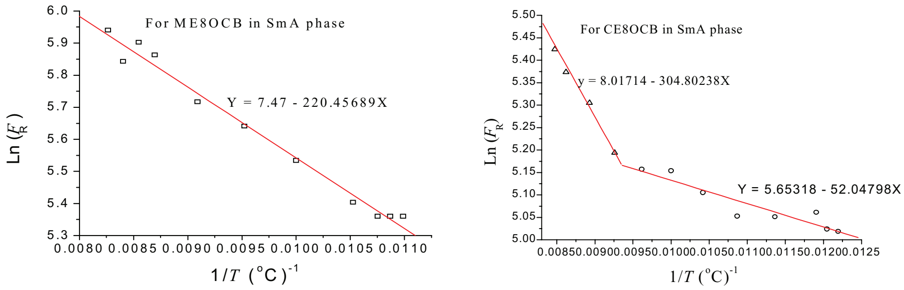
**Figure 7.** The Cole–Cole plot for (a) **ME8OCB**, and (b) **CE8OCB** in the SmA phase.

temperature the radius of semicircle increases and the center shifts toward $\varepsilon'$-axis. According to Debye's relaxation theory [26], this describes a single relaxation with relaxation time $(\tau_R)$ determined by the maximum of $\varepsilon''$, which decreases with increasing temperature. The Cole–Cole plots have been used to determine the values of relaxation frequency, dielectric strength and distribution parameter. The dielectric strength and distribution parameter are given in Table 1. It can be observed that the dielectric strength increases with an increase in temperature for both the samples while the distribution parameter decreases with the increase in temperature, which suggests that the relaxation behavior approaches the ideal Debye's type at higher temperature.

Figure 8 shows the relaxation frequency ($F_R$) versus $1/T$ for (a) ME8OCB and (b) CE8OCB in the SmA phase.

Figure 9 shows the relaxation frequency ($F_R$) versus $1/T$ for ME8OCB sample in the nematic phase.

The activation energies of both the samples have been evaluated using frequency versus $1/T$ curves. The activation energies [27,28] are found to be 0.019 eV in the SmA phase for **ME8OCB** and 0.0263 eV for the nematic phase of **ME8OCB**. However, the sample **CE8OCB** shows two different values of activation energies, i.e., 0.0045 eV and 0.0263 eV for lower-and higher-temperature range for the SmA phase. This may suggest existence of



(a) (b)

**Figure 8.** The plot of relaxation frequency ($F_R$) with temperature for (a) **ME8OCB**, and (b) **CE8OCB** in SmA phase.

**Table 1.** Variation of dielectric strength ($\Delta\varepsilon$) and distribution parameter in SmA phase of both ME8OCB and CE8OCB

| Temperature (°C) | Dielectric strength ($\Delta\varepsilon$) | Distribution parameter |
|---|---|---|
| | ME8OCB | |
| 91 | 32.054 | 0.064 |
| 92 | 33.145 | 0.062 |
| 93 | 35.782 | 0.064 |
| 95 | 37.301 | 0.066 |
| 100 | 48.079 | 0.051 |
| 105 | 59.563 | 0.049 |
| 110 | 78.355 | 0.030 |
| 115 | 85.809 | 0.031 |
| 117 | 87.202 | 0.032 |
| 119 | 87.202 | 0.032 |
| 121 | 90.129 | 0.030 |
| | CE8OCB | |
| 82 | 3.016 | 0.294 |
| 83 | 3.138 | 0.286 |
| 84 | 2.365 | 0.359 |
| 88 | 1.738 | 0.075 |
| 92 | 1.908 | 0.013 |
| 96 | 2.725 | 0.029 |
| 100 | 367 | 0.100 |
| 104 | 5.803 | 0.008 |
| 108 | 7.007 | 0.004 |
| 112 | 1863 | 0.043 |
| 116 | 40.744 | 0.014 |
| 118 | 4777 | 0.014 |
| 119 | 47.955 | 0.014 |

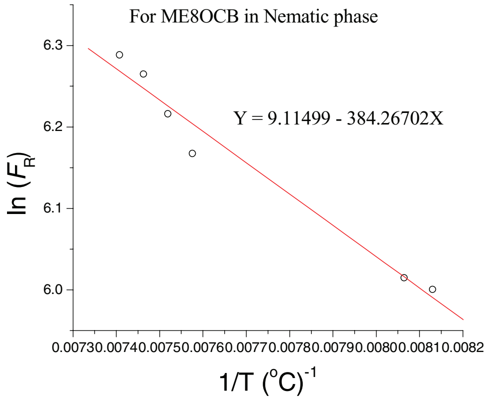


**Figure 9.** The plot between the relaxation frequency ($F_R$) and temperature for **ME8OCB** in the nematic phase.

biphase region in the SmA phase of this sample but it could not be ascertained by dielectric or texture studies.

## 4. Conclusion

In the present study, we have investigated the dielectric properties of two different mesogenic cinnamates with a substituted ethyl terminal chain, $\beta$-methoxyethyl [4-(4′-n-octyloxycinnamoyloxy) benzoates (**ME8OCB**) and $\beta$-chloroethyl [4-(4′-n-octyloxycinnamoyloxy) benzoates (**CE8OCB**) as a function of temperature and frequency.

The entire study can be summarized as follows:

1. The dielectric study of the samples shows dielectric relaxation in the frequency range covered in the present study.
2. The dielectric anisotropy is positive and is high in the SmA phase. The relaxation frequency of the Cl attached compound occurs in the low-frequency range while the relaxation frequency of the $OCH_3$ attached sample lies in the high-frequency range in comparison to earlier one.
3. The dielectric study of the samples shows dielectric relaxation in the frequency range covered in the present study.
4. The dielectric anisotropy is positive and is high in the SmA phase.
5. The $OCH_3$ attached sample contains the smectic A and the nematic mesophase while the Cl attached sample has only the smectic A phase.

## Acknowledgments

The authors are sincerely thankful to BRNS (DAE), RESPOND (ISRO), and DST for providing a grant in the form of a project.

## References

[1] Gray, G. W., & Goodby, J. W. (1984). *Smectic liquid Crystals (*Textures *and Structures)*, Leonard Hill: London.
[2] Rout, D. K., & Choudhary, R. N. P. (1989). *Mol. Cryst. Liq. Cryst.*, *166*, 75–90.
[3] Zywucki, B., Kuczynski, W., & Malecki, J. (2003). *Ferroelectrics*, *297*, 91–105.
[4] Maier, W., & Meier, G. (1961). *Nat. Forsch.*, *16a*, 1200.
[5] Diguet, D., & Schadt, F. M. (1972). *J. Chem. Phys.*, *6*, 1494.
[6] Rondelez, C. R., & Durand, G. (1970). *Acad. Sci. Ser.*, *B271*, 954.
[7] Murakami, S., & Naito, H. (1997). *Jpn. J. appl. Phys.*, *36*, 2222.
[8] de Jeu, W. H., Lathouwers, Th. W., & Bordewijk, P. (1974). *Phys. Lett.*, *32*, 40.
[9] de Jeu, W. H., Goossens, W. I. A., & Bordewijk, P. (1974). *J. Chem. Phys.*, *61*, 1985.
[10] Madhusudana, N. V., & Chandrasekhar, S. (1973). *International. Liquit Crystal Conference*, Bangalore, Pramana Supplement1.57.
[11] Szabon, J. (1984). *MCLC*, 10th International LC Conference, York.
[12] Hardouin, F., Levelut, A. M., Sigaud, G., Tink, N. H., & Achard, M. F. (1982). 9th *International LC Conference*, Bangalore.
[13] Bock, M., & Heppke, G. (1980). *Advances in LC Research and Applications, Budapest*, 131.
[14] Prajapati, K., & Patel, H. N. (2007). *Liq. Cryst.*, *34*(8), 903.
[15] Srivastava, S. L., & Dhar, R. (1991). *Ind. J. Pure & Appl. Phys.*, *29*, 745–751.
[16] Meier, W., & Meier, G. (1961). *Z. Naturforsch.*, *16a*, 262.
[17] Manohar, R., Srivastava, A. K., Shukla, J. P., Prajapati, A. K., & Bonde, N.L. (2006). *International J. of Physical Science*, *1*(3), 147–153.

[18] Madhsudana, N. V., Srikanta, B. S., & Subramanya Raj Urs, M. (1984). *Mol. Cryst. Liq. Cryst.*, *108*, 19–37.
[19] Drudn, & Wacrenier, J. M. (1984). *Mol. Cryst. Liq. Cryst.*, *108*, 291.
[20] Simon, R., & Cales, H. J. (1986). *Mol. Cryst. Liq. Cryst.*, *30*, 49.
[21] Hill, N. E., Vaughan, W. E., Price, A. H., & Davies, M. (1969). *Dielectric Properties and Molecular Behaviour*, Van Nostrand Reinhold: London.
[22] Bottcher, J. F., & Bordewijk, P. (1978). *Theory of Electric Polarization*, Vol. II, Elsevier: Amstrerdam.
[23] Majumder, P., Mitra, M., & Roy, S. K. (1994). *Physical Review E*, *50*, 4796.
[24] Srivastava, S. L. (1993). *Proct. Natl. Acad. Sci. (India)*, *63*, 311.
[25] Dhar, R. (2004). *Ind. J. Pure & Appl. Phys.*, *42*, 56–61.
[26] Debye, P. (1929). *Polar Molecules*, Chemical Catalog Co.: New York.
[27] Schadt, M. (1972). *J. Chem. Phys.*, *56*, 1494.
[28] Meier, G., & Saupe, A. (1966). *Mol. Cryst. Liq. Cryst.*, *1*, 515.