

Dielectric anisotropy and dielectric relaxation dynamics in chiral and non-chiral salicylaldimine – nematic crystal composites

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The dielectric anisotropy and dielectric relaxation dynamics in 4-cyano-4'-pentylbiphenyl and salicylaldimine compounds 5-octyloxy-2-[(4-hexyloxyphenylimino)methyl]phenol (LC1) and (S)-5-octyloxy-2-[(4-(2-methylbutoxy)phenylimino)methyl]phenol (LC2) composites have been investigated. The polarizing microscopy and differential scanning calorimetry results show that salicylaldimine compounds LC1 and LC2 exhibits enantiotropic SmC and SmC* mesophases, respectively. The dielectrical anisotropy of 5CB, 5CB/LC1 and 5CB/LC2 liquid crystals changes from the positive dielectric anisotropy to negative with the frequency of the applied voltage. The critical frequency f_c values of dielectrical anisotropy for 4-cyano-4'-pentylbiphenyl and salicylaldimine compounds LC1 and LC2 liquid crystal composites were found to be 693.84, 573.77 and 562.41 kHz, respectively. The dielectric relaxation mechanism of the liquid crystals was analyzed using Cole-Cole plots and the dielectric relaxation mechanism is a non-Debye type relaxation behavior.

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1. Introduction

Ferroelectric liquid crystals (FLCs) exhibiting the chiral smectic C* phase (SmC*) have been reported for the first time by Meyer et al. [1]. Over the last few years, there has been considerable interest in the experimental and theoretical studies of the SmC* phase including chemical aspects. These studies have been carried out in efforts to understand the ferroelectric properties of the SmC* phase, thus enabling the development of electro-optical devices. 4-cyano-4'-pentylbiphenyl (5CB) is one of the best-known liquid crystalline substances. 5CB, as well as other members of the *n*CB homologous series, is important from the point of view of applications due to the possession of a strong dipole moment, good chemical stability and a convenient temperature range of the nematic phase [2]. Dielectric spectroscopy can be applied to investigate the dynamic properties of liquid crystals. This method is used to obtain the valuable information about the molecular properties of nematic liquid crystals. The relationship between static dielectric permittivity and molecular properties of liquid crystals has long been an objective of dielectric studies [3]. The anisotropic dielectric properties of liquid crystals play an important role in determining the electro-optical response of liquid crystal devices. Liquid crystal mixtures with positive dielectric anisotropy are used for most active matrix displays

(LCDs) is strongly dependent on the dielectric anisotropy of the LC [4].

The physical and optical properties of liquid crystals can be developed by doping of different liquid crystals and thus, new liquid crystals modified electronic and optical properties may be prepared. The aim of this study is to prepare new liquid crystal material and determine dielectric dynamics and dielectric anisotropy properties.

2. Experimental

The salicylaldimine compounds LC1 and LC2 were prepared by the *p*-toluenesulfonic acid catalyzed condensation of the corresponding aldehydes and anilines. The preparation procedures and spectroscopic dates for LC1 and LC2 salicylaldimines are given by us in [5, 6] and [6-8], respectively. Transition temperatures were measured using a Linkam THMS 600 hot stage and a Linkam TMS 93 temperature control unit in conjunction with a Leitz Laborlux 12 Pol polarizing microscope, and these were confirmed using differential scanning calorimetry (Perkin-Elmer DSC-7, heating and cooling rate: 10 K min⁻¹). The chemical structure of the 5CB, LC1 and LC2 are shown in Fig. 1. (a) 4-cyano-4'-pentylbiphenyl (5CB), (b) salicylaldimine compounds LC1 and (c) LC2.

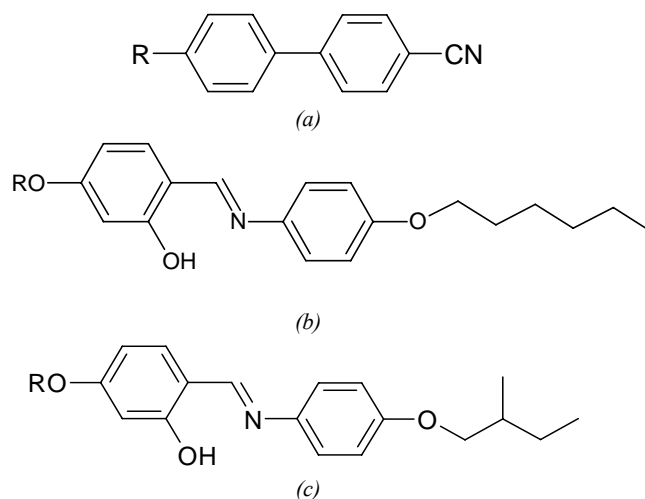


Fig. 1. The chemical structures and phase transition temperatures of the liquid crystals: (a) 5CB: $R = C_3H_{11}$; Cr 25 N 34 Iso; (b) LC1: $R = C_8H_{17}$; Cr 55.8 SmC 127.4 Iso; (c) LC2: $R = C_8H_{17}$; Cr 31.2 SmC* 84.3 Iso.

Measurement cells were made up of two indium tin oxide (ITO) conductive glass plates with planar alignment having $\sim 5.2 \mu\text{m}$ thicknesses. The prepared 5CB, 5CB+LC1 1% (w/w) and 5CB+LC2 1% samples were mixed in ultrasonic water bath for 30 minutes. The cells were filled in capillary action with the 5CB, 5CB+LC1 1% (w/w) and 5CB+LC2 1% (w/w) samples.

3. Results and discussion

3.1 Liquid crystalline properties of the salicylaldimine LC1 and LC2

The salicylaldimine LC1 and LC2 exhibit liquid crystalline properties and show thermotropic enantiotropic mesophase [5-8]. The compound LC1 show SmC mesophase with broken fan texture. When cooled from its isotropic phase, LC2 displays a fingerprint texture of chiral smectic C*. The transition temperatures and the thermodynamic data for the LC1 and LC2 are given in Table 1.

Table 1. Phase transition temperatures T ($^{\circ}\text{C}$)^a and transition enthalpies ΔH° (kJ mol^{-1}) of LC1 and LC2; Cr: crystalline, SmC*: chiral smectic, SmC: smectic and Iso: isotropic phase.

	$T/^{\circ}\text{C}$ ($\Delta H/\text{kJ mol}^{-1}$)
LC1	Cr 55.8 (60.2) SmC 127.4 (17.4) Iso
LC2	Cr 31.2 (24.8) SmC* 84.3 (11.4) Iso

^aPerkin-Elmer DSC-7; heating rates 10 K min^{-1} for the melting and clearing process.

3.2 Dielectrical anisotropy properties of the liquid crystals

The capacitance-voltage characteristics of the liquid crystals under various frequencies are shown in Fig. 2. As seen in the figures, at lower voltages, the capacitance of the liquid crystals is almost constants and after a certain voltage, it increases drastically and reaches saturation due to molecular reorientation of the liquid crystals. The minimum value of the capacitance corresponds to original orientation of the molecules. Once the voltage applied is increased, the molecular orientation starts and in turn, the capacitance increases with voltage applied. The 5CB/LC1 liquid crystal has the highest Frederiks threshold voltage with respect to other LC samples. This suggests that the LC1 molecules have the lower molecular orientation ability.

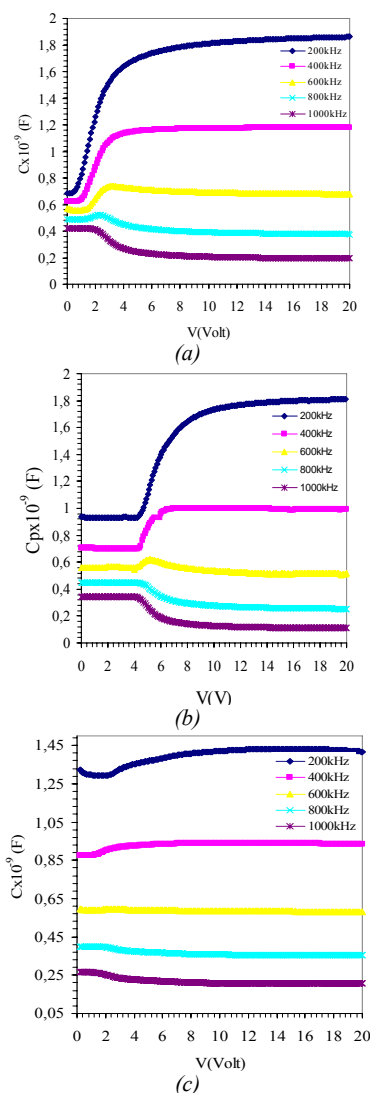


Fig. 2. Plots of capacitance–voltage (C – V) of the liquid crystals for $\Delta\epsilon > 0$ at different frequencies: (a) 5CB, (b) 5CB/LC1 (c) 5CB/LC2.

The dielectric constant of the liquid crystals is dependent of external effects due to the anisotropic nature of their.

There are two types of dielectric anisotropy in LCs:

- positive or p-type, when $\Delta\varepsilon > 0$ in which the molecules align parallel to the applied electric field;
- negative or n-type, when $\Delta\varepsilon < 0$, in which the molecules align perpendicular to the applied field [9-10].

The dielectric anisotropy for the liquid crystals is determined by the following relationship [11]:

$$\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp} \quad (1)$$

where ε_{\parallel} is the parallel and ε_{\perp} is the perpendicular part of the dielectric constant. The dielectric anisotropy values were calculated via C-V characteristics and are shown in Fig. 3. As seen in Fig. 3, the dielectrical anisotropy of 5CB, 5CB/LC1 and 5CB/LC2 liquid crystals changes from the positive dielectric anisotropy to negative with the frequency of the applied voltage. When the LCs are biased by external voltage, the applied electric field creates a torque and this torque acts on the molecule and the molecule starts to align the parallel to the field. Once the electric field is strong enough, the molecule will be aligned from perpendicular state to parallel to the field. Thus, the liquid crystals indicate a p-type dielectric anisotropy. The $\Delta\varepsilon$ values of the 5CB liquid crystal are higher than that of 5CB/LC1 and 5CB/LC2 liquid crystal composites and 5CB/LC2 liquid crystal has the lowest $\Delta\varepsilon$ value. This is indicative the strong interactions occurred between the 5CB molecules and LC2 rather than LC1. This interaction results from the large dipole moment and high polarizability of the LC2 molecules. The LC2 molecules affect both dielectric losses and the dielectric permittivity of the LC system. The decrease in dielectrical anisotropy is due to the permanent dipole moments of the LC2 molecules.

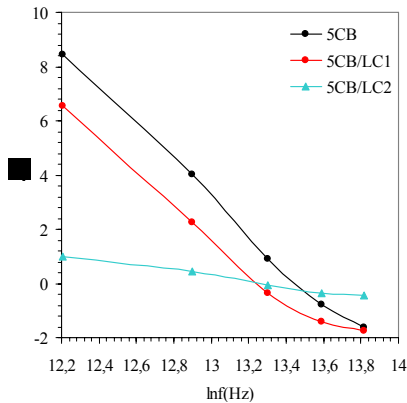


Fig. 3. The dielectric anisotropy dependence on frequency for the 5CB, 5CB/LC1, 5CB/LC2.

Electrical conductivity plays an important role in electro optical applications of liquid crystals, because the physical properties of them are highly dependent on the direction and the frequencies of the field. Thus, in order to determine the electrical properties of the 5CB and 5CB/LC1 and 5CB/LC2 liquid crystals is very important. The electrical conductivity for the liquid crystals is expressed by the well-known relation

$$\sigma_{\perp} = A\omega^{S_{\perp}} \quad (2)$$

$$\sigma_{\parallel} = B\omega^{S_{\parallel}} \quad (3)$$

where σ_{\parallel} and σ_{\perp} are respectively the parallel and perpendicular conductivities, A and B are constants, S_{\parallel} is a constant for parallel conductivity, S_{\perp} is a constant for perpendicular conductivity, ω is the angular frequency. Fig. 4 shows plots of $\ln \sigma_{\parallel}$ and $\ln \sigma_{\perp}$ versus $\ln f$ of the liquid crystals. As seen in Fig. 4, at lower frequencies, the σ_{\perp} conductivity of the liquid does not change with frequency, whereas at higher frequencies, the conductivity increases with frequency. Thus, the conductivity at lower and higher frequencies correspond to direct current and alternating current conductivities, respectively. The S_{\parallel} and S_{\perp} values for the 5CB, 5CB/LC1 and 5CB/LC2 liquid crystals were obtained from the linear region of $\ln \sigma_{\perp}$ vs. $\ln f$ plots. The S_{\parallel} and S_{\perp} values of the 5CB, 5CB/LC1 and 5CB/LC2 liquid crystals were determined and are given in Table 2. The S_{\perp} values of 5CB liquid crystal decrease with LC1 and LC2 dopants, whereas S_{\parallel} values do not indicate any regular trend.

Table 2. The S_{\perp} and S_{\parallel} values of alternating current conductivity of the liquid crystals.

	S_{\perp}	S_{\parallel}
5CB	1.87	1.80
5CB/LC1	1.71	1.75
5CB/LC2	1.65	1.84

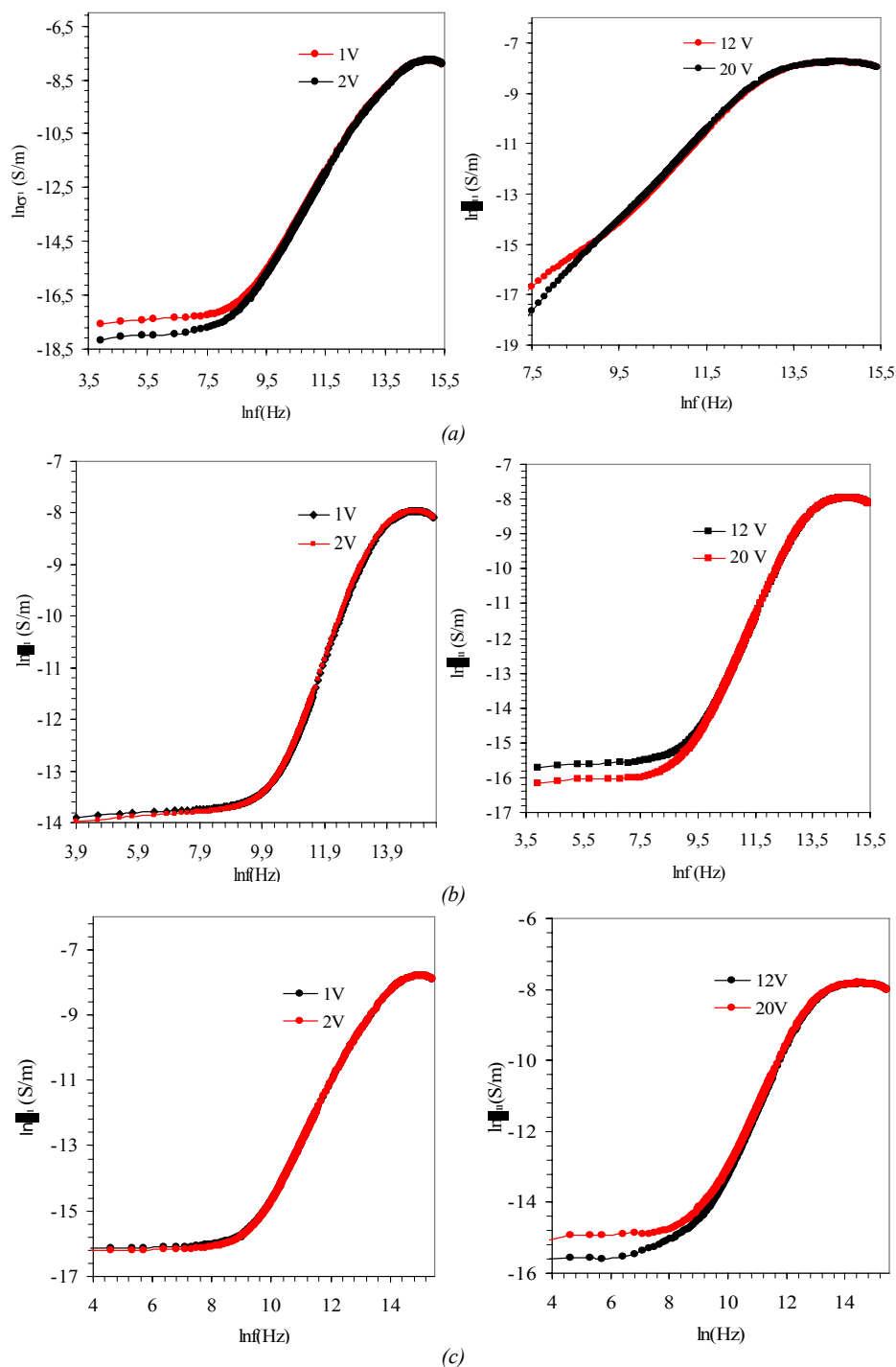


Fig. 4. Perpendicular and parallel conductivities at different frequencies. a) 4-cyano-4'-pentylbiphenyl (5CB), b) 5CB/LC1 c) 5CB/LC2.

The dielectric spectra of 5CB, 5CB/LC1 and 5CB/LC2 liquid crystals at the frequency range of 100 Hz–5 MHz at different external voltages are shown in Fig. 5. At lower frequencies, the real part of the dielectric constant of the liquid crystals does not significantly change with frequency up to a certain frequency and then drastically decreases with increasing frequency.

At lower frequencies, the real part of the dielectric constant increases with applied voltage due to the molecular reorientation. The real part of the dielectric constant is lowest for 5CB/LC2 liquid crystal composite due to lowest dielectric anisotropy property.

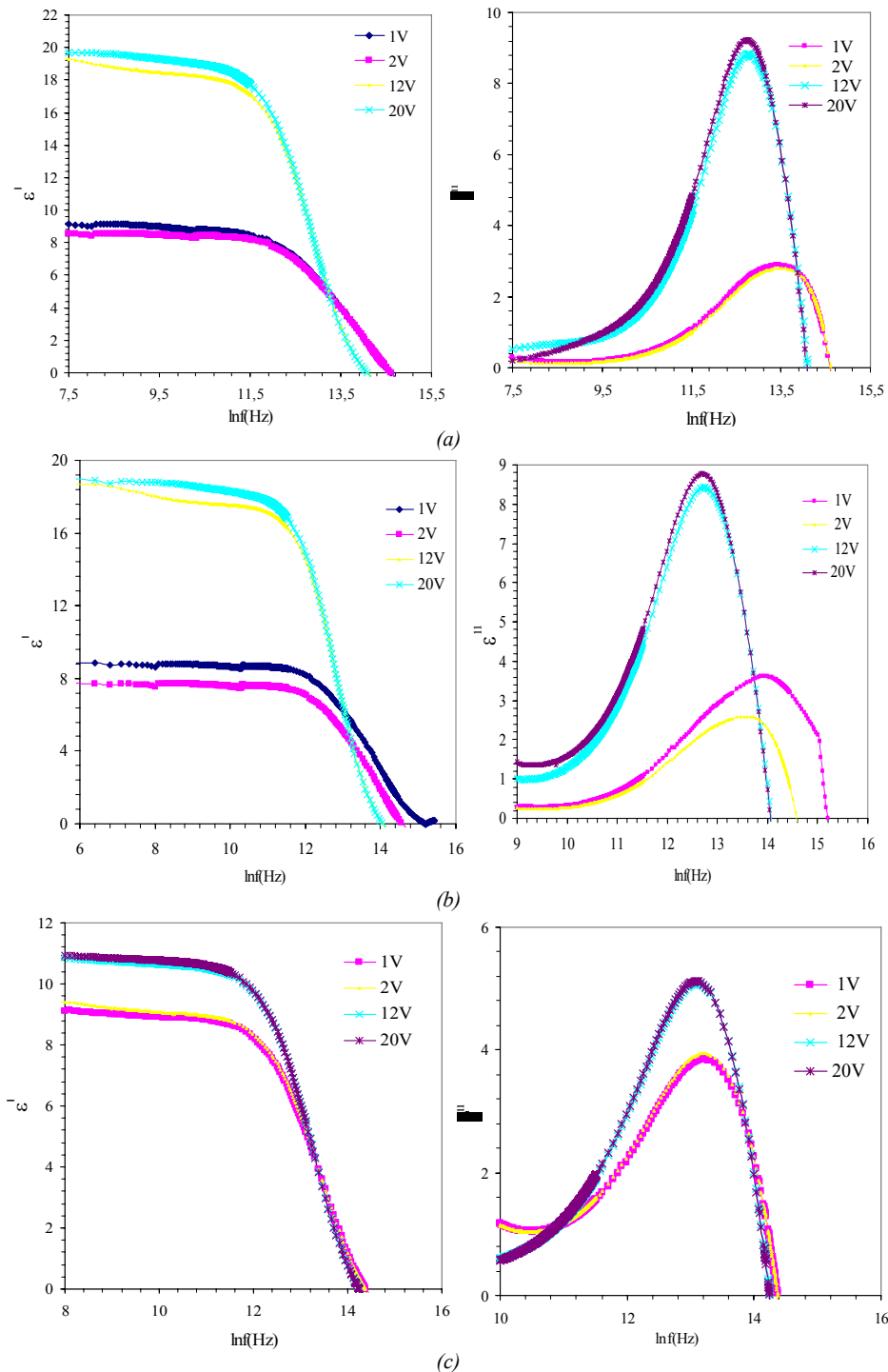


Fig. 5. The real and imaginary dielectric constants of the liquid crystals at different frequencies a) 5CB, b) 5CB/LC1 c) 5CB/LC2.

The imaginary part of the dielectric constant indicates a peak corresponding to dielectric relaxation process. As seen in Fig. 5, the peak position shift to lower frequencies. This can be explained as follows; when the applied electrical field is increased, the dipoles get strongly

aligned, and the mobility of ions is decreased and in turn, at lower frequencies a relaxation peak appears. The relaxation process becomes slower due to the decrease in mobility and hence the relaxation frequency decreases.

The relaxation frequency remains stable up to 12 and 20 V voltages.

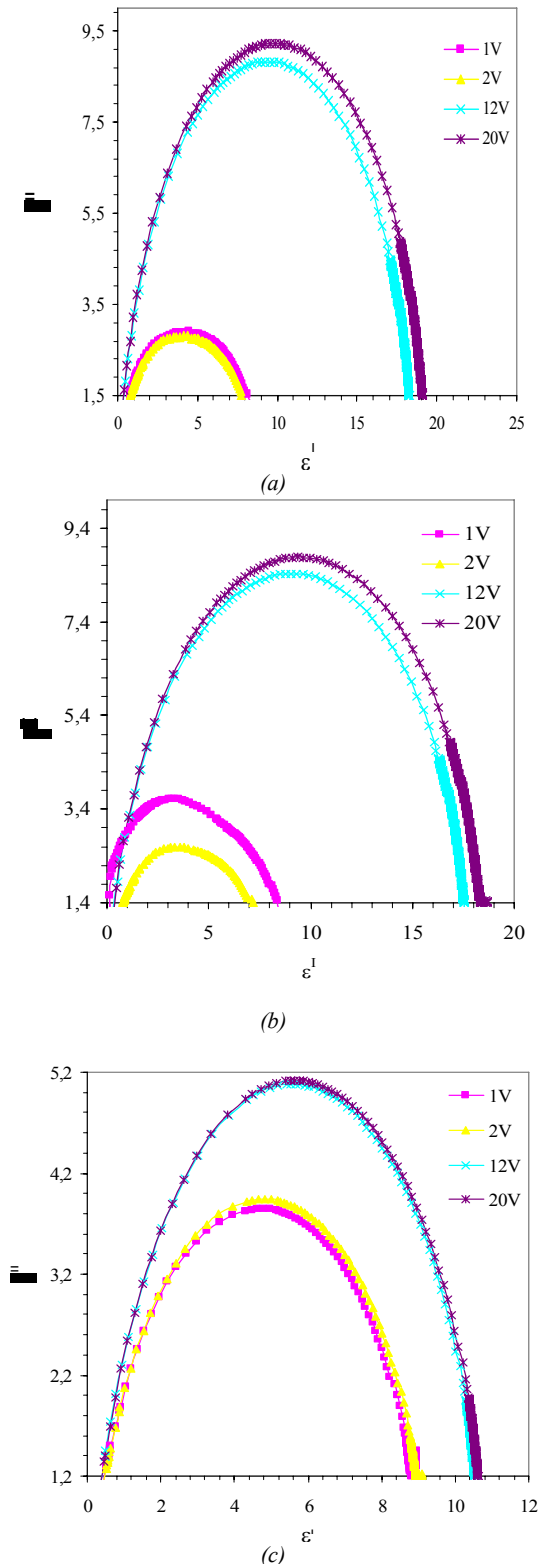


Fig. 6. Cole and Cole plots of the liquid crystals a) 5CB, b) 5CB/LC1, c) 5CB/LC2.

In order to analyze dielectrical relaxation mechanism of the liquid crystals, we plotted Cole-Cole plots, as shown in Fig. 6. Figs. 6 (a-c) show the Cole-Cole plots at different applied voltages. The complex dielectric dispersion curves are described by the Cole-Cole relation [12-14],

$$\varepsilon^*(\omega) = \varepsilon_{\infty} + \frac{\varepsilon_0 - \varepsilon_{\infty}}{1 + (i\omega\tau)^{1-\alpha}} \quad (4)$$

where $\varepsilon^*(\omega)$ is the complex dielectric constant, ε_0 is the limiting low-frequency dielectric constant and ε_{∞} is the limiting high-frequency dielectric constant, τ is the average relaxation time, ω is the average angular frequency, α is the distribution parameter. This equation describes the relaxation time distribution that manifests itself in the shape of the Cole-Cole diagrams [12]. In the pure Debye model ($\alpha=0$), the dipoles are assumed to be non-interacting with each other. The plots indicate semicircles and are passing through the origin. The Cole-Cole plot is a semicircle centered on the ε' -axis. In the opposite case ($\alpha>0$) the semicircles are centered below this axis. The ε_0 and ε''_{\max} values were calculated from the Cole-Cole curves and are given in Table 3. These values change with applied voltage for both the liquid crystals.

Table 3. The ε_0 and ε''_{\max} values were calculated from the Cole-Cole curves.

5CB	1V	2V	12V	20V
ε_0	8,58	8,28	18,49	19,40
ε''_{\max}	2,88	2,79	8,82	9,22
5CB/LC1	1V	2V	12V	20V
ε_0	8.34	7.14	17.49	18.34
ε''_{\max}	3.61	2.59	8.41	8.77
5CB/LC2	1V	2V	12V	20V
ε_0	8.79	8.91	10.51	10.59
ε''_{\max}	3.84	3.94	5.07	5.11

The Cole-Cole plots of molecules align perpendicular to the applied field do not appear as semicircle centered on the ϵ' -axis. This suggests that dielectric relaxation process is the non-Debye type relaxation behavior. The type of the relaxation mechanism of the liquid crystals changes when the molecular reorientation from perpendicular to parallel direction to the applied field.

4. Conclusions

The dielectric anisotropy and dielectric relaxation dynamics in 4-cyano-4'-pentylbiphenyl (5CB) and salicylaldimine compounds 5-octyloxy-2-[(4-hexyloxyphenylimino)methyl]phenol (LC1) and (S)-5-octyloxy-2-[[4-(2-methylbutoxy)phenylimino]methyl]phenol (LC2) composites have been investigated. The salicylaldimine compounds LC1 and LC2 exhibits enantiotropic SmC and SmC* mesophases, respectively. The $\Delta\epsilon$ values of the 5CB liquid crystal are higher than that of 5CB/LC1 and 5CB/LC2 liquid crystal composites and 5CB/LC2 liquid crystal has the lowest $\Delta\epsilon$ value. The Frederiks threshold voltage of the 5CB/LC1 liquid crystal has the highest voltage value with respect to other LC samples. The dielectric relaxation mechanism of the liquid crystals is the non-Debye type relaxation behavior.

References

- [1] R.B. Meyer, L. Liebert, L. Strzelecki, P. Keller, J. Phys. Lett. **36**, L69 (1975).
- [2] J. Czub, S. Urban, A. Würflinger, Liq. Cryst. **33**(1) 85 (2006).
- [3] C. P. Smyth, Molecular Interactions **II**, Wiley, New York, 1980.
- [4] F. Yakuphanoglu, M. Okutan, O. Köysal, S.-R. Keum, Dyes and Pigments, 2006.
- [5] Ç. Yörür, A. Nesrullajev, B. Bilgin-Eran, Molecular Physics **105**, 2961 (2007).
- [6] N. Yılmaz Canlı, A. Nesrullajev, Ö. Yaşa, B. Bilgin-Eran, J. Optoelectron. Adv. Mater. – Symposia **1**(3), 577 (2009).
- [7] A. Nesrullajev, B. Bilgin-Eran, Crystal Research and Technology **43**, 308 (2008).
- [8] B. Bilgin-Eran, A. Nesrullajev, N. Yılmaz Canlı, Materials Chemistry and Physics **111**, 555 (2008).
- [9] Kawamoto H. Proceedings of the IEEE, 90:4 (2002).
- [10] M. Okutan, San S Eren, O. Koysal, Dyes and Pigments **65**, 169 (2005).
- [11] E. Lueder, Liquid crystal displays. England: John Wiley & Sons Ltd, 2001.
- [12] K. S. Cole, R. H. Cole, J. Chem. Phys. **9**, 341 (1969).
- [13] I. Bunget, M. Popescu, Physics of Solid Dielectrics, Elsevier Publishing Company, Amsterdam, 1984.
- [14] A. Chelkowski, Dielectric Physics, Elsevier Publishing Scientific Publishing Company, Amsterdam, 1980.

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