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Dielectric properties of N-SmC* liquid crystalline composite

N. YILMAZ CANLI[*], F. YAKUPHANOGLU[a], O. YASA[c], B. BILGIN-ERAN[c]
Yildiz Technical University, Department of Physics, 34210 Istanbul, Turkey
[a]*Firat University, Department of Physics, 23169 Elazığ, Turkey*
[b]*Yildiz Technical University, Department of Chemistry, 34210 Istanbul, Turkey*

The dielectric relaxation and anisotropy properties of 4-cyano-4'-pentylbiphenyl and salicylaldimine compound (**LC1**) liquid crystals have been investigated. The polarizing microscopy and differential scanning calorimetry results show that the chiral salicylaldimine compound (**LC1**) exhibits enantiotropic SmC* mesophases. The dielectric anisotropy of the liquid crystals changes from positive type to negative type. The critical frequency values of dielectrical anisotropy for 4-cyano-4'-pentylbiphenyl and salicylaldimine compound (**LC1**) were found to be 693.84 and 577.61 kHz, respectively. The dielectric anisotropy value of **5CB/LC1** liquid crystal composite is lower than **5CB** liquid crystal. It is evaluated that the **5CB/LC1** composite liquid crystal gives new dielectrical anisotropy and electrical properties.

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Keywords: Liquid crystal, Dielectric anisotropy, Electrical properties

1. Introduction

Composites based on liquid crystals (LCs) have attracted much attention over a number of years because of their unique electro and magneto-optic properties and novel display applications [1]. Dielectric anisotropy is one of the most important physical properties of liquid crystalline compounds, which in essence determines the lower threshold voltages of liquid crystal displays (LCDs) [2]. Liquid crystal mixtures with a positive dielectric anisotropy are used for most active matrix displays and the image quality of liquid crystal displays is strongly dependent on the dielectric anisotropy of the liquid crystal.

There are various works concentrating on the electro-optical characterization of LC [3-6]. The dielectric-spectroscopy technique (DST) has been used by various workers for the study of systems in different phases. This method has been found to be one of the best for the measurement of permittivity and dielectric loss with high accuracy and sensitivity [7, 8]. 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. Nematic liquid crystals have been extensively studied due to their extraordinary properties and their promising applications in recent technologies [9-14]. 4-cyano-4'-pentylbiphenyl (5CB) exhibit nematic mesophase and 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 [15].

This paper reports the dielectric anisotropy properties of mesogenic salicylaldimine compound (LC1) in 5CB nematic liquid crystal. Thus, we have prepared a liquid crystal mixture of 5CB/LC1 to develop its dielectric anisotropy property and dielectric parameters. The aim of this study is to prepare new liquid crystal material and develop its electronic properties.

2. Experimental

2.1 Synthesis of the salicylaldimine compound (LC1)

The salicylaldimine compound (S)-5-hexadecyloxy-2-[{4-(2-methylbuthoxy)-phenylimino}-methyl]phenol (LC1) was prepared in the usual way [16] by a p-toluensulfonic acid (40 mg) catalyzed condensation of 4-hexadecyloxy-2-hydroxybenzaldehyde (2.5 mmol) with (S)-4-(2-methylbutoxy) aniline (3 mmol) in toluene (20 ml). The LC1 purified by crystallization from acetone/methanol. Yield: 0.66 g (63 %) of yellow crystals. The LC1 was characterized by spectroscopic methods. The proposed structures are in full agreement with these spectroscopic data. The spectroscopic data for compound LC1 are given in Ref. [17]. The chemical structure of the LC1 is shown in Fig. 1.

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}).

2.2 Measurements

Measurement cells were made up of two indium tin oxide (ITO) conductive glass plates with planar alignment having ~ 5.2 μm thicknesses. The prepared 5CB and 5CB/LC1 **1% (w/w)** samples were mixed in ultrasonic water bath for 30 minutes. The cells were filled in capillary action with the 5CB and 5CB/LC1 **1% (w/w)** samples. The experimental setup is shown in Fig. 2. The capacitance-voltage measurements were performed by an HIOKI 3532 LCR meter impedance analyzer with high accuracy at room temperature to determine the dielectric constants of the 5CB and 5CB/LC1.

LC1: R = $C_{16}H_{33}$ 5CB: R = C_5H_{11}

Compound	T/°C (ΔH/kJ mol^{-1})
5CB^{a}	Cr 24 N 35 I
LC1^{b}	Cr 69.3 (30.5) SmC* 80.4 (1.4) I

Abbreviations: Cr: crystalline, N: nematic, SmC*: chiral smectic and I: isotropic phase.

[a] E. M. Merck Chemicals, Hawthorne, NY.

[b] Perkin-Elmer DSC-7; heating rates 10 K min^{-1} for the melting and clearing process; enthalpy values are given behind the phase transition temperatures in parentheses.

Fig. 1. The chemical structures and phase transition temperatures of the liquid crystals of 5CB and LC1.

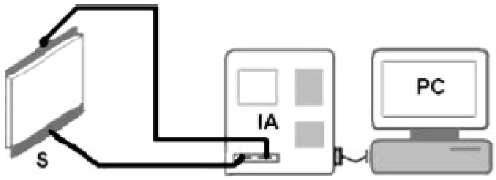


Fig. 2. Experimental setup for electrical measurements: S, sample; IA, impedance analyzer.

Before the dielectrical analysis of liquid crystals, the capacitance and dielectric loss factor of the empty cell were studied in the frequency range 40 Hz to 10 MHz. The dielectric loss for the empty cell was found to exhibit no peaks in this frequency range. This indicates that neither the conductive coating of the cell plates, nor any trace level impurities in the cell are exhibiting any relaxation in this frequency range. This analysis is in agreement with analyzed in Ref [18].

Also, the contribution in the high frequency part of the spectrum due to the resistance of the ITO layer was corrected in described in Ref [19].

3. Results and discussion

3.1 Liquid crystalline properties of the salicylaldimine (LC1)

The mesomorphic properties of the salicylaldimine compound (LC1) were investigated using polarized light optical microscopy and differential scanning calorimetry. The transition temperatures, corresponding enthalpy values and mesophase type observed for the LC1 and 5CB are summarized in Fig. 1.

The salicylaldimine compound (LC1), containing two peripheral alkyl chains (one alkyl chain and one short and branched chiral chain), exhibits liquid crystalline properties and shows thermotropic enantiotropic smectic mesophase. When cooled from its isotropic phase, LC1 displays a fingerprint texture of chiral smectic C*. (see Fig. 3). Chirality of molecules in the SmC* mesophase leads to layered character of confocal formations. Such type of textures was observed also for the SmC* mesophase of usual liquid crystals in Ref [20-21]. The DSC curve of the LC1 confirms the phase transition temperatures detected under microscope (see Fig. 4).

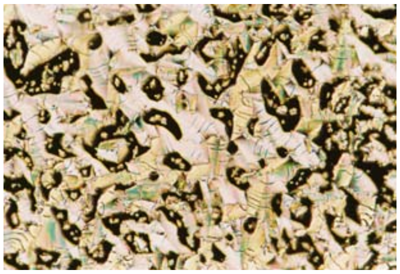
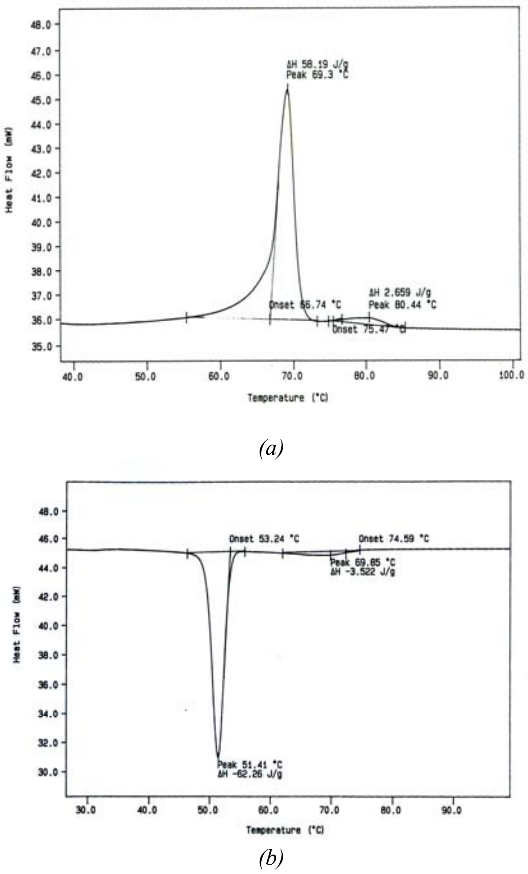


Fig. 3. Polarized light optical photomicrograph of LC1 on cooling at 67 °C.

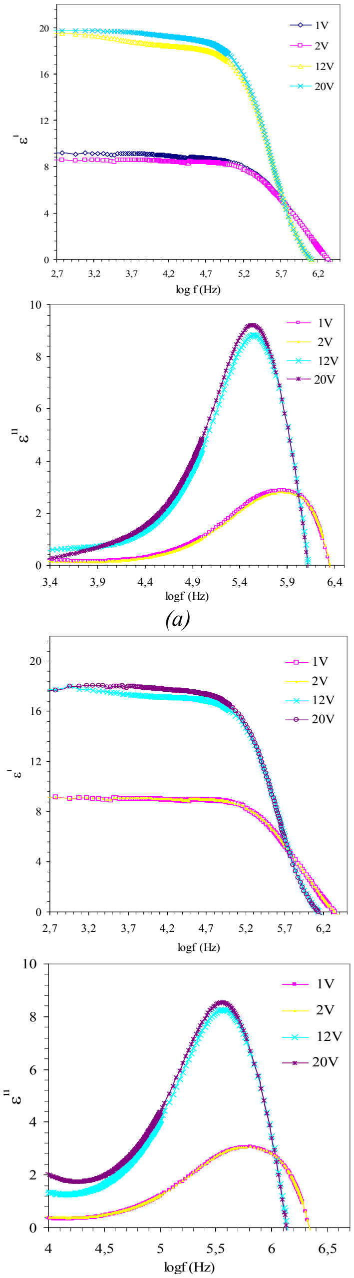


(b)

Fig. 4. DSC curve of LC1 a) during the second heating b) during the second cooling.

3.2 Dielectrical and conductivity properties of the liquid crystals

The dielectric spectra of 5CB and 5CB/LC1 liquid crystals, with different external voltages, are (frequency range of 100 Hz–5 MHz) shown in Fig 5. The real part of the dielectric constant 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 (Fig. 5a-b).

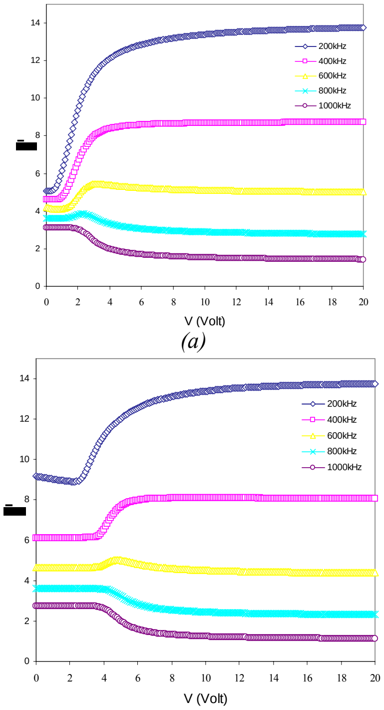


(a)

(b)

Fig. 5. The real and imaginary dielectric constants of the liquid crystals at different voltages (a) 5CB and (b) 5CB/LC1.

The change in the dielectric constant is probably due to the molecular reorientation, which starts by applied voltage, i.e, the dielectric constant is dependent of external effects due to the anisotropic nature of their [22]. The imaginary part of the dielectric constant indicates a relaxation process with a relaxation frequency. The relaxation frequency shifts to lower frequencies due to molecular reorientation. When the applied voltage 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 relaxation frequency decreases. The relaxation frequency remains stable up to 12 and 20 V voltages. It is well known that molecules of 5CB liquid crystal have the dipole moment oriented in parallel to the long axis of the molecule. As seen in relaxation process curves of the liquid crystals, the relaxation process takes almost place in megahertz frequency. In the nematic phase of 5CB liquid crystal, the relaxation process, due to the restricted rotation of molecules was observed in megahertz range, once the applied electric field is parallel to the director of the liquid crystal. Fig. 6 shows real part of the dielectric constant-voltage characteristics of the liquid crystals under various frequencies. As seen in the figures, at a certain frequency value the real part of the dielectric constant ε^1 increases exponentially with increasing applied voltage. Afterwards, ε^1 almost doesn't change with applied voltage. The dielectric constant dependence of the voltage applied has valuable information about reorientation. It is seen in Fig. 6 that when there is no voltage applied, real part of the dielectric constant has a minimum value where molecules are in their original orientation. When the applied voltage is increased, orientation starts and as a result of this, the dielectric constant increases with applied voltage and reaches saturation.



(a)

(b)

Fig. 6. Dependence of real dielectric constant on voltage at different frequencies (a) 5CB and (b) 5CB/LC1.

The real dielectric constant at higher voltages is higher than that of the real dielectric constant at lower voltages. This suggests that the liquid crystals have positive dielectrical anisotropy. In absence of voltage, the real dielectric constant has a minimum value, i.e, where molecules are in their original orientation [23]. Once the voltage applied is increased, the molecular orientation starts and that are why, the real part of the dielectric constant increases with voltage applied. At lower voltages, the real part of the dielectric constant remains up to a certain voltage. This voltage is so-called Frederic's threshold. As seen in Fig. 6, the molecular reorientation in 5CB/LC1 starts at higher voltages, i.e, the threshold voltage of the 5CB/LC1 liquid crystal is higher than that of the 5CB liquid crystal. This suggests that the LC1 molecules have the lower molecular orientation ability.

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 Δε > 0 in which the molecules align parallel to the applied electric field;
- negative or n-type, when Δε < 0, in which the molecules align perpendicular to the applied field [24, 25].

The dielectric anisotropy for the liquid crystals is determined by the following relationship [26].

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

where $\varepsilon_{\parallel}$ is the parallel and $\varepsilon_{\perp}$ is the perpendicular part of the dielectric constant. The dielectric anisotropy values were calculated via C-V characteristics and are shown in Fig. 7.

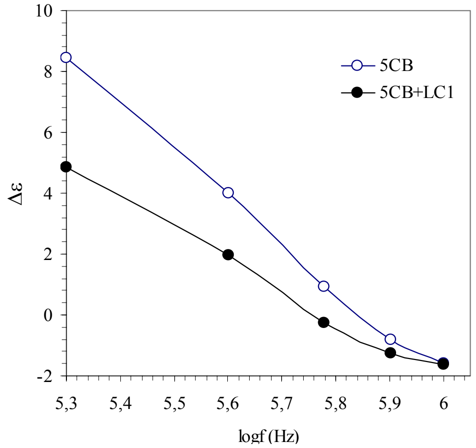


Fig. 7. The dielectric anisotropy dependence on frequency of the 5CB and 5CB/LC1 liquid crystals.

An example graph as to how C⊥ and C|| values are calculated is shown in Fig. 8, in which, at applied voltages lower than Vth, the capacitance measured is C⊥ (since the director is perpendicular to the electric field) which gives ε⊥ (C⊥ =ε0ε⊥A/d) and where A is the cross-sectional area of LC cell, d is the cell gap. At applied voltages much higher than the Frederiks transition (V > 3Vth), the capacitance can be plotted as a function of Vth/V. By linearly fitting the data, the intercept (Vth/V=0) gives the capacitance C|| (i.e., the director is parallel to the electric field) which yields ε|| [27].

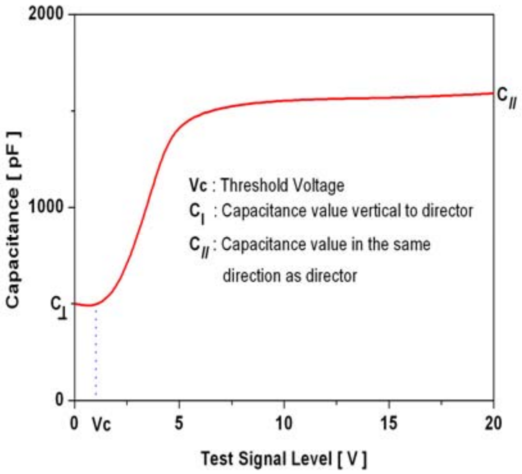


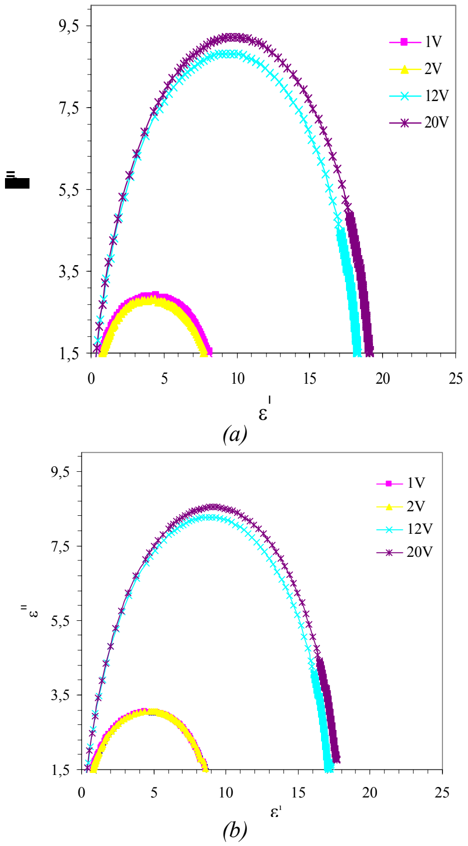
Fig. 8. An example graph as to how C⊥ and C|| values are calculated for LCs.

The Δε values of the 5CB liquid crystal are higher than that of 5CB/LC1. This indicates that the strong interactions occur between the 5CB molecules and LC1. This interaction results from the large dipole moment and high polarizability of the LC1 molecules. The LC1 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 LC1 molecules. As seen in Fig. 7, the dielectrical anisotropy of 5CB and 5CB/LC1 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 complex dielectric constant ε^* for the liquid crystals is expressed as

$$\varepsilon^*(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega) \qquad (2)$$

where ε' and ε'' the real and imaginary parts of the dielectric constant and their spectra are respectively called dispersion and absorption curves. The relaxation process of the liquid crystals is analyzed by Cole-Cole plot. Figs. 9(a-b) show the Cole-Cole plots at different applied voltages.



(a)

(b)

Fig. 9. Cole and Cole plots of the liquid crystals a) 5CB and b) 5CB/LC1.

The complex dielectric dispersion curves are described by the Cole-Cole relation [28-30],

$$\varepsilon^{*}(\omega)=\varepsilon_{\infty}+\frac{\varepsilon_{o}-\varepsilon_{\infty}}{1+(i\omega\tau)^{1-\alpha}} \tag{3}$$

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 [28]. In the pure Debye model (α=0), the dipoles are assumed to be non-interacting with each other. The plots indicate semi-circles and are passing through the origin. The Cole-Cole plot is a semicircle centered on the ε'-axis. In the opposite case (α>0) the semicircles are centered below this axis. The ε_0 and $\varepsilon''_{\max}$ values were calculated from the Cole-Cole curves and are given in Table 1. These values change with applied voltage for both the liquid crystals. The Cole-Cole plots of molecules aligned 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. This behavior is probably due to the dipolar rotation around the long molecular axis. The Cole-Cole plots of molecules align parallel to the applied field appear as semicircle centered on the ε'-axis. This confirms that dielectric process is very close to the Debye type of relaxation. The type of the relaxation mechanism of the liquid crystals changes when the molecular reorientation from perpendicular to parallel to the applied field. The ε_0 value of the 5CB/LC1 liquid crystal is lower than that of 5CB. This suggests that ε_0 values of the relaxation process are associated with the reorientation of molecules. These values increase with increasing voltages.

Table 1. The ε_0 and $\varepsilon''_{\max}$ parameters of the liquid crystals.

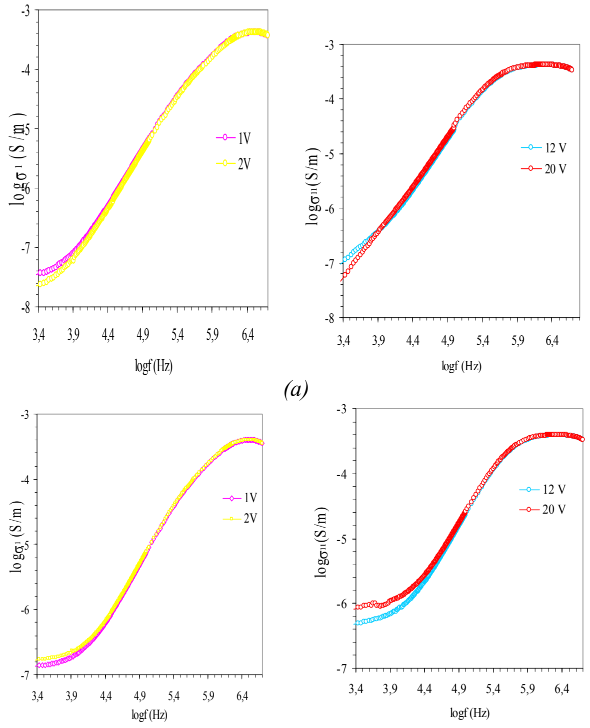
5CB	1V	2V	12V	20V
ε_o	8,58	8,28	18,49	19,40
$\varepsilon''_{\max}$	2,88	2,79	8,82	9,22
5CB/LC1	1V	2V	12V	20V
ε_o	8,18	8,20	16,97	17,61
$\varepsilon''_{\max}$	3,05	3,05	8,26	8,52

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

$$\sigma_{\perp}=A\omega^{S\perp} \tag{4}$$

$$\sigma_{II}=B\omega^{SII} \tag{5}$$

where $\sigma_{||}$ and $\sigma_{\perp}$ are respectively the parallel and perpendicular conductivities, A and B are constants, $s_{||}$ is a constant for parallel conductivity, $s_{\perp}$ is a constant for perpendicular conductivity, ω is the angular frequency. The plots of log $\sigma_{||}$ and log $\sigma_{\perp}$ versus logf of the liquid crystals are shown in Fig. 10. The $\sigma_{\perp}$ plots of the liquid crystal indicate two different regions, which are dependent and independent on frequency. The frequency independent conductivity corresponds to direct current conductivity, while the conductivity dependent on frequency is corresponding to alternating current. The $s_{||}$ and $s_{\perp}$ values for the 5CB and 5CB/LC1 liquid crystals were obtained from the linear region of log $\sigma_{\perp}$ vs. logf plots. The $s_{||}$ and $s_{\perp}$ values of the 5CB and 5CB/LC1 were found to be 1.82, 1.72 and 1.91, 1.81, respectively. The electrical conductivity of the 5CB/LC1 liquid crystal is higher than that of the 5CB liquid crystal. This suggests that the LC1 liquid crystal modifies the electrical conductivity of the 5CB liquid crystal.



(a)

(b)

Fig. 10. Perpendicular and parallel conductivities of the liquid crystals at different frequencies, a) 5CB and b) 5CB/LC1.

4. Conclusions

The dielectric relaxation and anisotropy properties of salicylaldimine compound (LC1) in 4-cyano-4'-pentylbiphenyl (5CB) nematic liquid crystal have been investigated by the dielectric spectroscopy method. The salicylaldimine compound (LC1), containing two peripheral alkyl chains (one alkyl chain and one short and branched chiral chain), exhibits enantiotropic SmC* mesophase. The dielectric anisotropy of the liquid crystal composite changes from positive type to negative type and the critical frequency values of 5CB and 5CB/LC1 liquid crystals are 693.84 and 577.61 kHz, respectively. The liquid crystals indicate a dielectrical relaxation process.

Acknowledgements

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*Corresponding author: nimetcanli@yahoo.com