

# Molecular orientation and electrical properties of 4-cyano-4'-n-heptylbiphenyl-salicylaldimine compound composite liquid crystals by dielectric impedance spectroscopy and current-voltage techniques

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The dielectric and current voltage properties of 4-cyano-4'-n-heptylbiphenyl doped LC1 and LC2 salicylaldimine compounds have been investigated. The polarizing microscopy and differential scanning calorimetry results show that the salicylaldimine compounds (LC1, LC2) exhibit liquid crystalline properties. The salicylaldimine compound LC1 exhibits SmC and SmA mesophases, while LC2 exhibits only SmA mesophase. The dielectric anisotropy of the LCs was found to vary from positive type to negative type. The LC1 liquid crystal significantly the dielectrical anisotropy behavior of the 7CB. The dielectrical relaxation mechanism analyzed by the Cole-Cole plots of the liquid crystals is close to Debye type relaxation behavior. The current voltage characteristics indicate that the 7CB and 7CB/LC1 liquid crystals exhibit voltage-controlled differential negative resistance (VCNR) behavior. It is evaluated that the molecular orientation and electrical properties of the 7CB liquid crystal can be controlled by salicylaldimine compounds.

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## 1. Introduction

Liquid crystals exhibit anisotropic property of solids as well as fluidity of isotropic liquid and made up of rod like molecules due their orientational order. 4-cyano-4'-n-heptylbiphenyl (7CB) is one of the best-known liquid crystalline substances. 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. Liquid crystal mixtures with a positive dielectric anisotropy are used for most active matrix displays and the image quality of liquid crystal displays (LCDs) is strongly dependent on the dielectric anisotropy of the LC [1]. Dielectric relaxation spectroscopy has proven to be powerful technique to obtain the valuable information about the molecular properties of nematic liquid crystals. The anisotropic dielectric properties of liquid crystals play an important role in determining the electro-optical response of liquid crystal devices. The relationship between static dielectric permittivity and molecular properties of liquid crystals has long been an objective of dielectric studies [2–4].

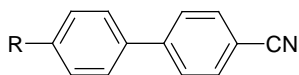
In present study, we have investigated the dielectrical properties of salicylaldimine compounds doped 7CB liquid crystal. In order to explain the dielectric anisotropy and

relaxation mechanism of the prepared liquid crystals, we have used the capacitance-frequency-voltage and Cole-Cole relations. We have focused on the study of the effect of salicylaldimine compounds on current-voltage characteristics of 7CB liquid crystal.

## 2. Experimental

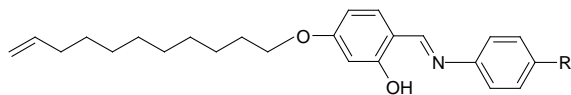
### 2.1 Synthesis of the salicylaldimine compounds (LC1 and LC2)

The salicylaldimine compounds LC1 and LC2 were prepared in usual way [5] by a p-toluensulfonic acid (80 mg) catalyzed condensation of 2-hydroxy-4-(10-undecenyloxy)benzaldehyde (5 mmol) with 4-hexylaniline (6 mmol) and 4-hexyloxyaniline (6 mmol), respectively, in toluene (50 ml) and purified by crystallization from acetone/methanol. The structure of LC1 and LC2 were characterized using various spectroscopic methods (<sup>1</sup>H-, <sup>13</sup>C-NMR and mass). The proposed structures are in full agreement with these spectroscopic data. The spectroscopic data for compounds LC1 and LC2 are given in Ref. [6]. The chemical structure of the compounds LC1 and LC2 are shown in Fig. 1.



**7CB:** R = C<sub>7</sub>H<sub>15</sub>; Cr (30)

N (42.8) Iso



**LC1:** R = C<sub>6</sub>H<sub>13</sub>; Cr (37.3)

SmC (64.5) SmA (89.5) Iso

**LC2,** R = OC<sub>6</sub>H<sub>13</sub>; Cr (60.9)

SmA (118.5) Iso

Fig. 1. The chemical structures and phase transition temperatures (°C) of the liquid crystals 4-cyano-4'-n-heptylbiphenyl (7CB); salicylaldimine compounds (LC1 and LC2).

## 2.2 Dielectrical measurements

The doped samples were prepared by the dispersion of LC1 and LC2 liquid crystals in 7CB in the concentration of about 1% (w/w). The liquid crystal mixtures were mixed by ultrasonic effect. The prepared liquid crystals were named as 7CB/LC1 and 7CB/LC2 and were filled into the cells of 5.4 μm thickness by the capillary action at temperature which is slightly higher than its isotropic

temperature. The cells consist of two indium tin oxide (ITO) coated glass substrates. The dielectrical measurements were performed using a HIOKI 3532 LCR meter at room temperature. The measurements were limited to 5 MHz due to the effect of finite resistance of ITO on coating on glass substrates.

## 3. Results and discussions

### 3.1 Liquid crystalline properties of the salicylaldimines

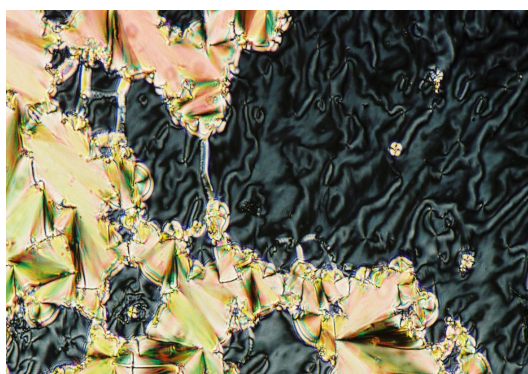
The mesomorphic properties of the salicylaldimine compounds LC1 and LC2 have been studied by polarizing microscopy (PM) technique using a Linkam THMS 600 hot stage and a Linkam TMS 93 temperature control unit in conjunction with a Leitz Laborlux 12 Pol polarizing microscope. The temperatures of phase transitions taking place in the LC1 and LC2 and enthalpies of these transitions were determined by Differential Scanning Calorimeter (DSC). The DSC curves were recorded on a Perkin-Elmer DSC-7, heating and cooling rate: 10 K min<sup>-1</sup>. The salicylaldimine compounds LC1 and LC2 exhibit liquid crystalline properties and show thermotropic enantiotropic mesophase. The transition temperatures, corresponding enthalpy values and mesophase types observed for this compound are given in Table 1.

Table 1. Phase transition temperatures  $T$  (°C) and transition enthalpies  $\Delta H$  (kJ mol<sup>-1</sup>) of LC1 and LC2; Cr: crystalline, SmC: smectic C, SmA: smectic A and Iso: isotropic phase.

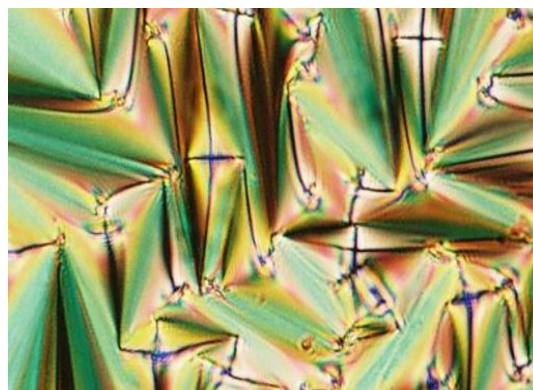
Compound	R	$T$ °C ( $\Delta H$ kJ/mol)
LC1	C <sub>6</sub> H <sub>13</sub>	Cr 37.3 (24.83) SmC 64.5 (1.19) SmA 89.5 (5.48) Iso
LC2	OC <sub>6</sub> H <sub>13</sub>	Cr 60.9 (35.34) SmA 118.5 (5.68) Iso

<sup>a</sup>Perkin-Elmer DSC-7; heating rates 10 K min<sup>-1</sup> for the melting and clearing process.

The compound LC1 showing smectic A and smectic C mesophases whereas the mesophase of the LC2 is only a smectic C. The textures of LC1, LC2 showed in Fig. 2.



(a)



(b)

Fig. 2. Polarized light optical photomicrographs of the (a) LC1 as observed on cooling 52°C; (b) LC2 as observed on cooling at 98°C (magnification x200).

### 3.2 Dielectrical anisotropy properties of the liquid crystals

The dielectric spectra of 7CB/LC1 and 7CB/LC2 liquid crystals at the frequency range of 100 Hz–5 MHz at room temperature without and different external voltages. Fig. 3(a-b) show the plots of the capacitance-voltage.

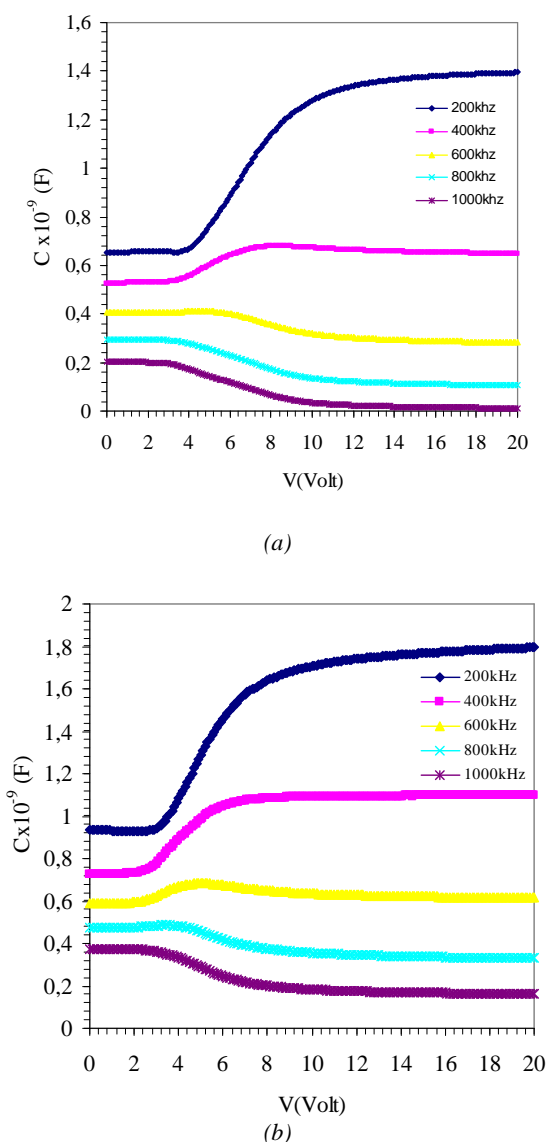


Fig. 3. Plots of capacitance–voltage ( $C$ – $V$ ) of the liquid crystals for  $\Delta\epsilon > 0$  at different frequencies: (a) 7CB/LC1, (b) 7CB/LC2.

As seen in Fig. 3, at lower voltages, the capacitance is almost constant and after a certain voltage, it increases with increasing voltage and reaches a saturation. This increase in the capacitance is an indicative of molecular reorientation in liquid crystal. The capacitance of the liquid crystals decreases with increasing frequency and after a certain frequency value, the capacitance at higher voltages is lower than that of the capacitance at lower voltages. This indicates the presence of negative dielectrical anisotropy. In case of negative dielectrical

anisotropy, liquid crystal molecules align perpendicular to the electric field. The constant values of the capacitance at lower voltages show that LC molecules are in their original orientation. The dielectric anisotropy for the LCs is expressed by the following relationship [7]:

$$\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp} \quad (1)$$

where  $\epsilon_{\parallel}$  is the parallel and  $\epsilon_{\perp}$  is the perpendicular part of the dielectric constant. The dielectric anisotropy values were calculated via  $C$ – $V$  curves and are shown in Fig. 4.

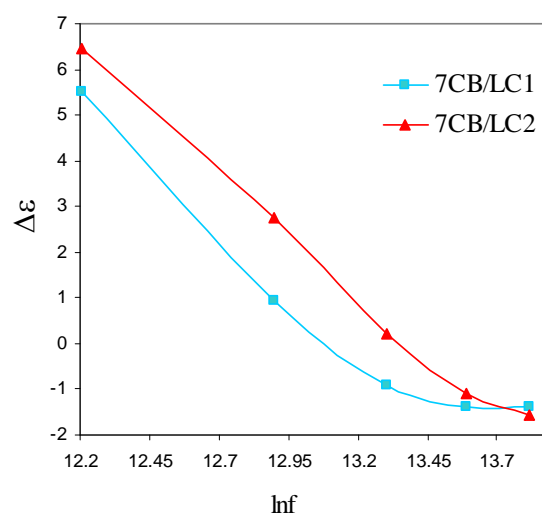


Fig. 4. The dielectric anisotropy dependence on frequency for the 7CB/LC1 and 7CB/LC2 liquid crystals.

The  $\Delta\epsilon$  values of the 7CB/LC1 and 7CB/LC2 liquid crystals are lower than 7CB [7], i.e. dielectric anisotropy values decrease with doping of LC1 and LC2, as LC1 and LC2 molecules make to easy the exchange of carrier charges. The decrease in dielectrical anisotropy may be attributed to the strong dipolar interactions between the LC1 and the 7CB liquid crystal and the change in reorientation of molecules of the 7CB after LC1 addition. This interaction results from the large dipole moment and high polarizability of the 7CB/LC1 molecules.

As seen in Fig. 4, the dielectrical anisotropy changes from positive to negative at a critical frequency value,  $f_c$ . The  $f_c$  values of the 7CB and 7CB/LC1, 7CB/LC2 liquid crystals were determined from the Fig. 4 and were found to be 644.74 and 479.76, 617.41 kHz, respectively. The LC1 dopant significantly changes  $f_c$  value of 7CB, whereas LC2 does not change it. Dielectrical anisotropy arises from not only a dielectric effect but also a current effect of ions in liquid crystal. The decrease in dielectrical anisotropy with LC1 and LC2 contents is attributed to the fact that the change of alignment of LC1 and LC2 molecules as well as 7CB molecules should take place to change the molecular state. The dielectric behavior of the 7CB/LC1 and 7CB/LC2 composites can be accounted for due to the difference in electrical conductivity of the LC1, LC2 liquid crystals and the 7CB liquid crystal.

**3.3 Dielectrical relaxation and current voltage properties of the liquid crystals**

The complex dielectric constant for liquid crystals is defined as [7-8],

$$\epsilon^*(\omega) = \epsilon' + i\epsilon'' \tag{2}$$

where  $\epsilon'$  and  $\epsilon''$  are the real and imaginary part of the dielectric constant, respectively. Figs. 5(a-b) plots of the real and imaginary dielectric constants of the liquid crystals at different voltages. The LC1 and LC2 molecules affect both dielectric losses and the dielectric permittivity of the LC system. As seen in Fig. 4, the dielectric constant of the composite liquid crystals is different from that the 7CB liquid crystal [7]. The change in the dielectric

constant is probably due to molecular reorientation which starts by applied voltage, i.e, the dielectric constant is dependent of external effects due to the anisotropic nature of LC [7]. The increase in the dielectric constant is probably due to molecular reorientation which starts by applied voltage.

Fig. 5 shows curves of the imaginary part of the dielectric constant at various frequencies. A peak in curves is observed and the intensity of the peak decreases with increasing bias voltages. The dielectric loss attains a maximum that increases and shifts to lower frequencies as the applied voltage increases. This maximum corresponds to the relaxation frequency. The relaxation frequency changes with bias voltages. This shows a relaxation mechanism dependent on voltage.

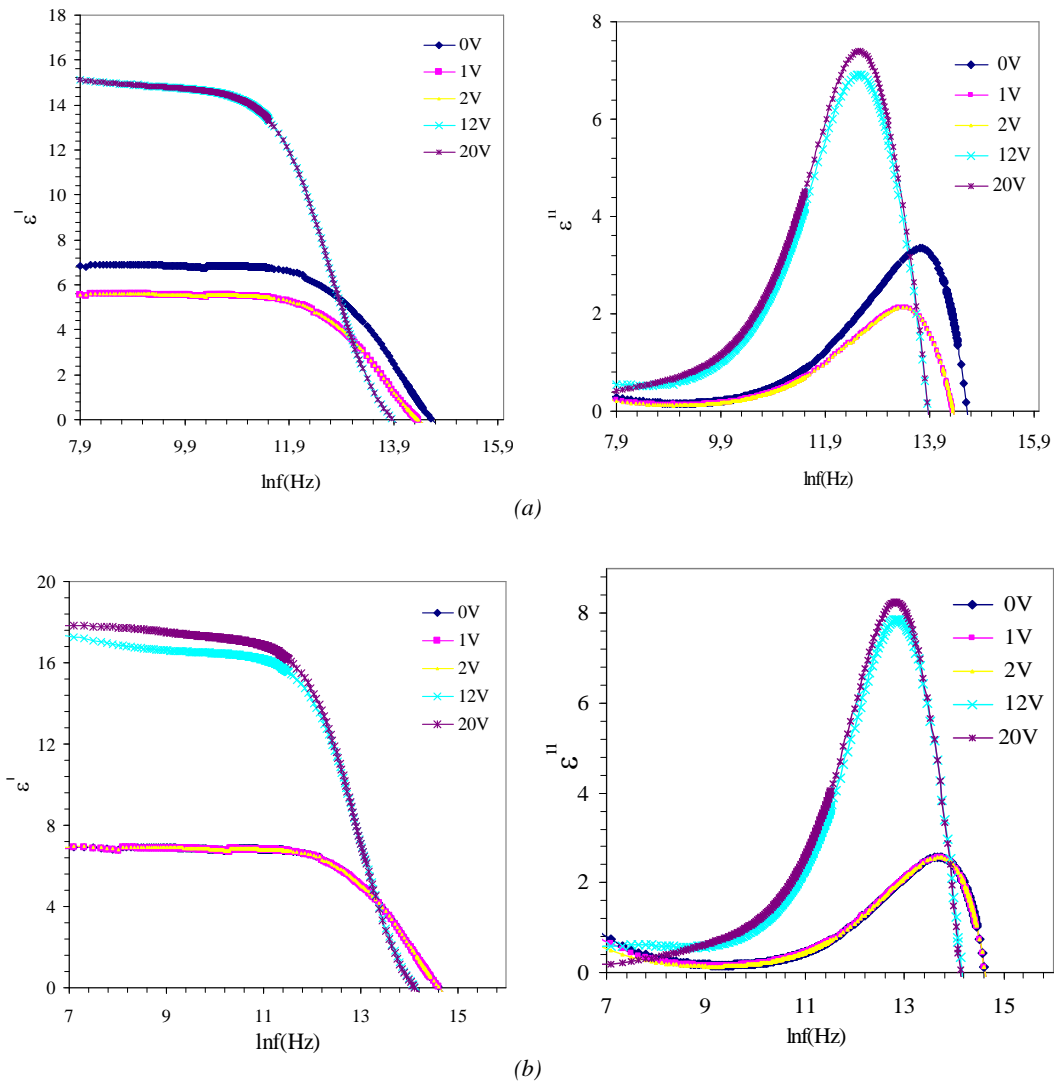


Fig. 5. The real and imaginary dielectric constants of the liquid crystals at different frequencies (a)7CB/LC1, (b) 7CB/LC2.

To analyze the relaxation mechanism of the liquid crystals, we plotted Cole-Cole curves for the LCs, as

shown in Fig. 6 (a-b). The Cole-Cole curves can be analyzed by the following relation [9-10],

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + (i\omega\tau)^{1-\alpha}} \quad (3)$$

where  $\epsilon^*(\omega)$  is the complex dielectric constant,  $\epsilon_0$  is the limiting low-frequency dielectric constant and  $\epsilon_\infty$  the limiting high-frequency dielectric constant,  $\tau$  is the average relaxation time,  $\omega$  is the average angular frequency,  $\alpha$  is the distribution parameter.

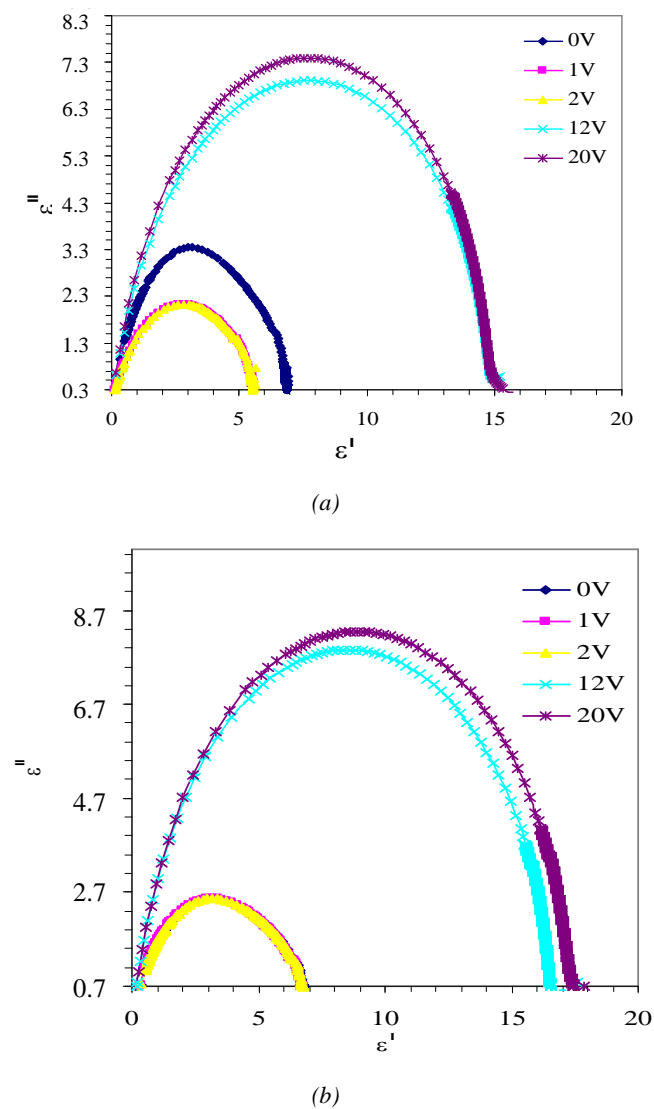


Fig. 6. Cole and Cole plots of the liquid crystals a) 7CB/LC1, b) 7CB/LC2.

It is evaluated that the Cole-Cole plots for LCs are close to Debye type relaxation behavior. This behavior is probably due to the dipolar rotation around the long molecular axis. The diameter of Cole-Cole plots increases with applied voltage. This shows that reorientation of molecules varies with applied voltage. The current-voltage characteristics of the liquid crystals are shown in Fig. 7.

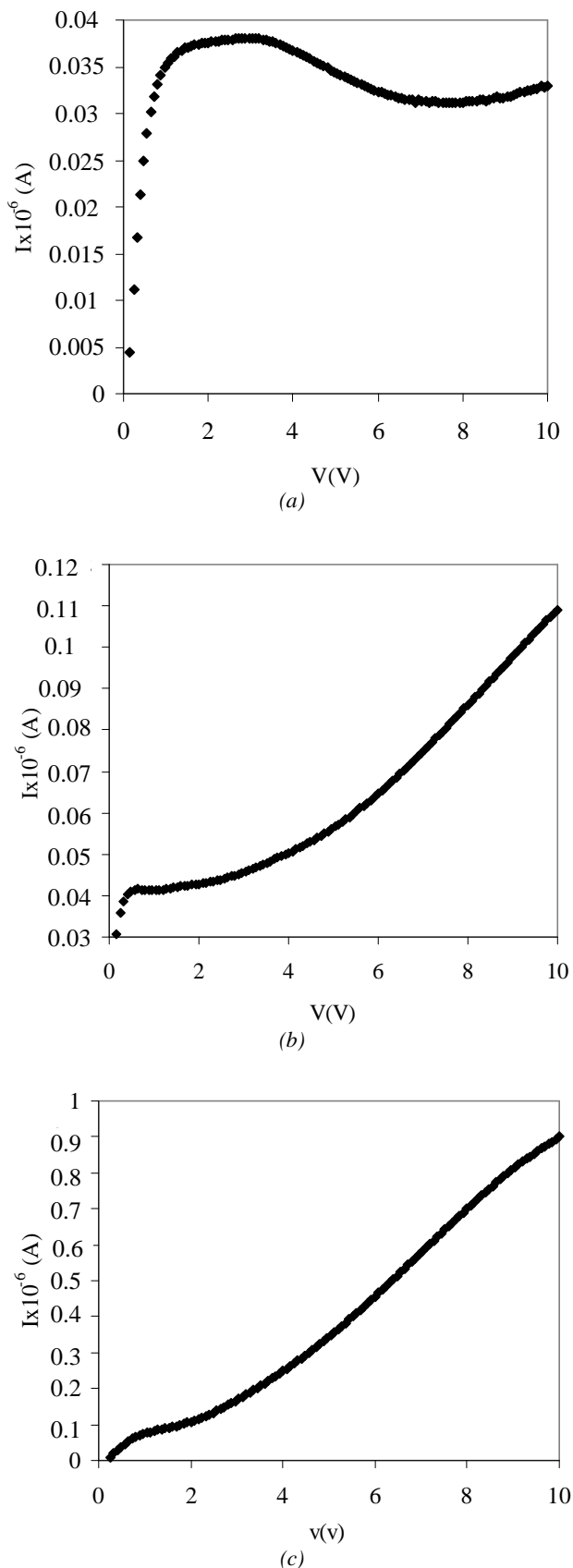


Fig. 7. I-V characteristics of the liquid crystals a) 7CB b) 7CB/LC1 c) 7CB/ LC2.

Table 2. The  $\epsilon_0$  and  $\epsilon_{\max}''$  values of the liquid crystals.

7CB/LC1	1V	2V	12V	20V
$\epsilon_0$	5.51	5.51	15.17	15.17
$\epsilon_{\max}''$	2.13	2.13	6.91	7.39

7CB/LC2	1V	2V	12V	20V
$\epsilon_0$	6.70	6.75	16.50	17.33
$\epsilon_{\max}''$	2.56	2.56	7.85	8.25

For 7CB and 7CB/LC1 liquid crystals, the current increases sharply and a current peak takes place and subsequently the current decreases to minimum but not zero and then the current increases linearly with increasing voltage. The current peak suggests that the 7CB and 7CB/LC1 liquid crystals exhibit voltage-controlled differential negative resistance (VCNR) behavior [11]. But, 7CB/LC2 liquid crystal does not indicate VCNR behavior. It is evaluated that LC1 and LC2 liquid crystals change VCNR behavior of 7CB liquid crystal.

## References

- [1] F. Yakuphanoglu, M. Okutan, O. Köysal, S.-R. Keum, *Dyes and Pigments* **76**, 202 (2008).
- [2] C. P. Smyth, *Molecular Interactions*, vol. II, Wiley, New York, 1980.
- [3] P. Maurel, A. H. Price, *J. Chem. Soc. Farad. II* **69**, 1486 (1973).
- [4] G. M. Janini, A. H. Katrib, *J. Chem. Educ.* **60**, 1087 (1983).
- [5] B. Bilgin-Eran, C. Yörür, C. Tschierske, M. Prehm, U. Baumeister, *J. Mater. Chem.* **17**, 2319 (2007).
- [6] N. Coskun, MSc Thesis, Yıldız Technical University, Department of Chemistry, Istanbul, 2006.
- [7] M. Okutan, F. Yakuphanoglu, O. Köysal, S. E. San, G. A. Oweimreen, *J. of Non-Crystalline Solids* **354**, 3529 (2008).
- [8] S. Matsumoto, I. Kadota, *Liquid Crystals—Fundamentals and Applications Kogyochosa-kai*, Tokyo, Japan, 1991.
- [9] I. Bunget, M. Popescu, *Physics of Solid Dielectrics*, Elsevier Publishing Company, Amsterdam, Oxford, New York, Tokyo, 1984.
- [10] A. Chelkowski, *Dielectric Physics*, Elsevier Publishing Scientific Publishing Company, Amsterdam, Oxford, New York, Warszawa, 1980.
- [11] Sergei AY, Orlov S, Rakulijic GA, *J. Opt. Soc. Am.* **B13**, 513 (1996).

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