Investigation of dielectric anisotropy and birefringence of binary liquid crystal mixtures

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ABSTRACT

Absorbance, capacitance, conductance, dielectric anisotropy and birefringence properties and splay elastic coefficient of 4'-Hexyl-4-biphenylcarbonitrile (6CB) and its mixture with 4'-Octyl-4-biphenylcarbonitrile (8CB) were investigated. The absorbance was studied using the UV-visible spectrophotometry. Capacitance, conduction and dielectric measurements for 6CB and its mixture were performed in 0-1000 kHz frequency range at the room temperature. Capacitance-voltage and capacitance-frequency changes were investigated for the mixture. Threshold voltage was determined as 2.1 V. It was seen that the capacitance suddenly damped at this voltage. Capacitance is large at lower frequencies and small at higher frequencies than 100 kHz. The conductance-voltage change was obtained for the mixture. The conduction suddenly rose at the threshold voltage. The conduction is small at lower frequencies and large at higher frequencies. Dielectric, birefringence index and splay elastic constant were investigated for 6CB/8CB mixture. The measured values of the mixture are bigger than 6CB values up to the certain frequency.

Keywords: Electric properties, Elasticity, Optical properties, Liquid crystals

İkili sıvı kristal karışımların dielektrik anizotropi ve çift kırıcılığının araştırılması

ÖZ

4'-Hexyl-4-biphenylcarbonitrile (6CB) ve 4'-Octyl-4-biphenylcarbonitrile (8CB) ile karışımının emilim, sığa, iletkenlik, dielektrik anizotropi ve çift kırınım özellikleri ve splay elektrik katsayısı incelendi. Emilim, görünür bölge ultraviyole spektrofotometre kullanılarak incelendi. 6CB ve karışımı için sığa, iletkenlik ve dielektrik ölçümleri oda sıcaklığında 0-1000 kHz frekans aralığında gerçekleştirildi. Karışım için sığa-voltaj ve sığa-frekans değişimleri araştırıldı. Eşik voltajı 2.10 V olarak belirlendi. Bu eşik voltajında sığanın aniden azaldığı görüldü. Sığa düşük frekanslarda büyük ve 100 kHz'den büyük frekanslarda küçüktür. Karışım için iletkenlik-voltaj değişimi elde edildi. İletkenlik, eşik voltajında aniden yükseldi. İletkenlik düşük frekanslarda küçük daha yüksek frekanslarda büyüktür. 6CB/8CB karışımı için dielektrik, çift kırınım indeksi ve splay elastikiyet katsayısı incelendi. Karışımın ölçülen değerleri belli bir frekansın üzerinde 6CB değerlerinden daha büyüktür.

Anahtar Kelimeler: Elektrik özellikler, elastikiyet, optiksel özellikler, sıvı kristaller

1. INTRODUCTION

The state of matter whose physical properties are between those of a crystalline solid and an isotropic liquid is named liquid crystal (LC). The LC is obtained in two different ways as heat or solvent. According to the used processes, these LCs are called thermotropic or liyotropic LCs. LCs is utilized for the display systems of laptop, television, computers and other devices with display systems increasing in size. Development of LC materials and their physical properties play the most important role for their application in liquid crystal display (LCD) devices. The performance of LC materials in LCDs depends seriously on the temperature dependence of the dielectric, capacitance, conductivity, optical and elastic constants of the materials. There is no known a single mesogen containing all of the properties needed for displays. Such a material can be obtained only by preparing a mixture of mesogens which collectively have the desired properties.[1-8] For instance, two eutectic nematic mixture LCs, E7 and E8, of cyanobiphenyls and terphenyls have been developed with positive and high dielectric anisotropy.[9]

The absorption spectra of LCs have been studied by using UV-vis spectrophotometer.[10,11] The LCs and their composites have paid attention continuously because they have their unique electro-optic and magneto-optic properties and novel display application.[12,13] 4'-Hexyl-4-biphenylcarbonitrile LC (6CB) is one of the liquid crystalline substances which is known best. This matter has high dipole moment and stability for the application of nematic phase.[14] In the dielectric studies of LCs, it is benefited generally from relationships between their static dielectric permittivity and molecular properties for

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Özğan

a long time.[15,16] It is known that the static dielectric measurement is a successful technique for characterization of molecular anisotropy and intermolecular ordering in nematic LCs. Nowadays, an LC mixture which has a positive dielectric anisotropy is utilized in most active matrix display. As the physical and optical properties of LCs can be developed by mixing of different organic materials, thus new crystalline materials with high clearing temperature, large dielectric anisotropy and low viscosity can be prepared.[17] Dielectric and optical properties[18-21], permittivity and conductivity[22] and Freedericksz transition[23] of 6CB and 4'-Octyl-4-biphenylcarbonitrile LC (8CB) have been investigated. The 6CB and 8CB nematic LCs are used at display technology. These LCs have low phase transition temperatures and superior physical properties at room temperature. Conductance and dielectric anisotropy properties of 4'-Hexyl-4-biphenylcarbonitrile and 4'-octyloxy-4-biphenylcarbonitrile LCs and their composite have been studied in our previous paper.[24]

Phase transitions of 6CB and 8CB LC mixtures have been studied by differential scanning calorimeter (DSC). The results of DSC clearly point to the existence of four phase transitions in the 6CB/8CB LC mixtures. The phase diagrams of the mixtures have been obtained from DSC and theoretical calculations. The experimental and theoretical phase diagrams are approximately similar to each other. The phase transition temperatures of the 6CB/8CB LC mixtures rise with the heating rate between 2 and 10ºC/min. The activation energies have been determined for the phase transitions of 50% 6CB and 50% 8CB LC mixtures.[25]

Herein, we aimed to investigate phase transition temperatures for different concentrations of 6CB/8CB LC mixtures, by obtaining their theoretical and experimental phase diagrams. Eutectic concentrations are found as 45% 6CB and 55% 8CB in Ref.25. It is understood from the phase transition diagram that the range of the LC is the greatest value at the eutectic concentration.

In this study, therefore, a LC mixture of 50% 6CB and 50% 8CB was investigated in terms of their absorbance, capacitance, conductance, dielectric, birefringence index and splay elastic constant values. The absorbances of 6CB and 8CB LCs were determined using UV-Vis spectrophotometer. The capacitance-voltage change in different frequencies and the capacitance-frequency change in different voltages were investigated for 6CB/8CB LC mixture at room temperature. The conductance-voltage change in different frequencies was obtained for 6CB/8CB LC mixture. The variation of dielectric, birefringence index and splay elastic constant K_{11} with frequency were investigated for 6CB/8CB LC mixture, and the results were compared with 6CB LC values.

2. EXPERIMENTAL

The 4'-hexyl-4-biphenylcarbonitrile and 4-octyl–4'-cyanobiphenyl LC materials were received from Sigma–Aldrich. The chemical structures and formulas of 6CB and 8CB nematic LCs used are given in Table 1. Because 6CB is a little viscous liquid and 8CB is solid powder at room temperature, the solutions of the mixtures in the concentration range 1.7×10^{-5} and 4.1×10^{-5} M were prepared by dissolving in chloroform after weighed the needed amounts. Uniform samples of 6CB and 8CB LCs were prepared using magnetic stirrer. Absorption measurements were performed in real time between 200 and 350 nm wavelengths using an UV-vis spectrophotometer, Perkin-Elmer Lambda 45. For absorption measurements, the quartz cuvette of 1 cm was used. The capacitance-voltage and conductance-voltage values of both pure 6CB LC and the mixture of 6CB and 8CB LC at the same ratio were measured at room temperature by using a KEITHLEY 4200-SCS (Semiconductor characterization system). Before the construction of the cells, glass substrates coated with indium tin oxide (ITO) were spin coated with a polyimide layer about 100 nm thick. Measurement cell was made of two glass slides separate by Mylar sheets having 14.1 μm thicknesses. The mixture of 6CB and 8CB LCs was mixed in bandeling sonorex and heiddolp type reaxtop for 10 minutes, respectively. The LC cells were filled by insulin hypo with the prepared samples on hot plate at 50ºC.
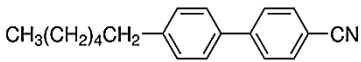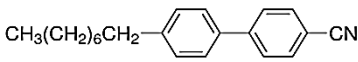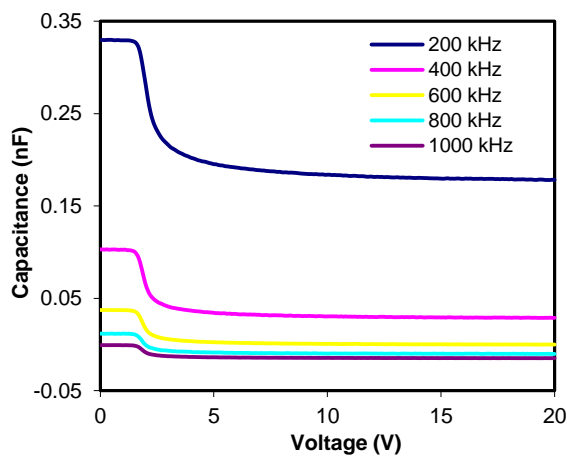
3. RESULTS AND DISCUSSION

The absorption spectra of 6CB and 8CB LCs in chloroform solutions is shown in Figure 1. The spectra of 8CB and 6CB LC have maximum absorption wavelengths at 253 nm and 283 nm at room temperature, respectively.

Figure 2 shows the change of capacitance depending on voltage for 6CB/8CB LC mixture at different frequencies at room temperature. The capacitance indicates a threshold voltage, and the capacitance values is dropped suddenly and molecular reorientation is occurred above a threshold voltage. The capacitance values are bigger at lower voltages than the threshold voltage, and it is smaller at higher voltages than the threshold voltage. The threshold voltage is about 2.1 V. This voltage is named as Freedericksz threshold voltage. Freedericksz threshold voltage is a key parameter in the electro-optic application of LCs.[26]

The interaction between a LC and an electric field is dependent on the magnitude of the dielectric permittivity measured parallel $\in_{\parallel}$ and perpendicular $\in_{\perp}$ to the director and to the difference between them, the dielectric anisotropy $\Delta\in$. When the LC is placed in an electric field, the electric field to LC molecules induces a torque. So, the orientation of the molecules changes and the dielectric anisotropy emerges. The dielectric constants

Table 1. Chemical structures of the 6CB and 8CB LCs

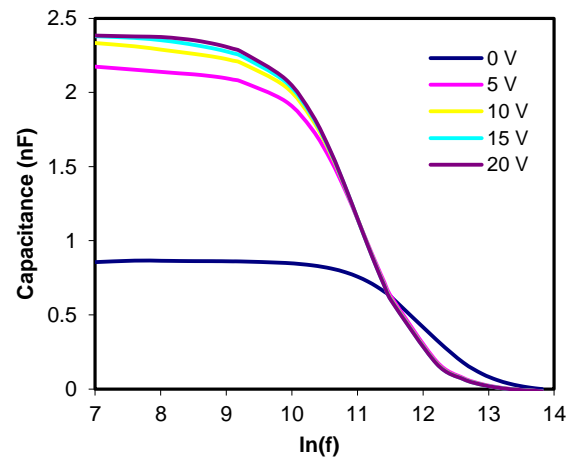|	6CB	8CB
Linear Formula	$CH_3(CH_2)_5C_6H_4C_6H_4CN$	$CH_3(CH_2)_7C_6H_4C_6H_4CN$
Chemical Structure	$CH_3(CH_2)_4CH_2$—⬡—⬡—CN	$CH_3(CH_2)_6CH_2$—⬡—⬡—CN
Molecular Weight (g mol^{-1})	263.39	291.44
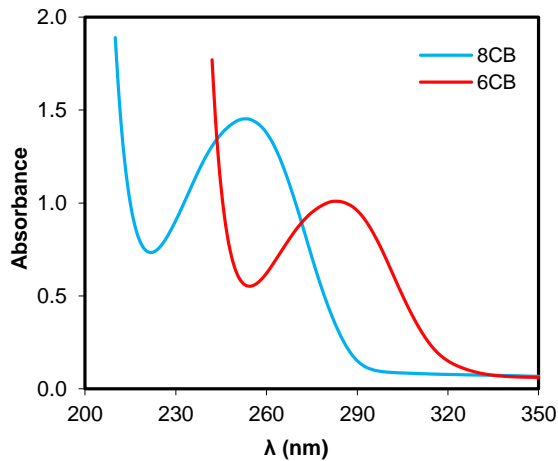
Figure 1. Absorption spectrum of 6CB and 8CB LCs.

the final value of $C_\perp$. The dielectric constant components, the parallel $\epsilon_\parallel$ and the perpendicular $\epsilon_\perp$ to the plane, and the dielectric anisotropy are expressed in Equations (1a-c).

$$\epsilon_\parallel = \frac{C_\parallel}{C_o} \tag{1a}$$

$$(1a) \quad \epsilon_\perp = \frac{C_\perp}{C_o} \tag{1b}$$

$$\Delta\epsilon = C_\parallel - C_\perp \tag{1c}$$

Where, C_o is the capacitance when the cell is empty. The capacitance-frequency changes of 6CB/8CB LC mixture were obtained for different voltages (see Figure 3). The capacitance is fixed as at low frequency but it decreases with increasing frequency. The capacitance is small at low voltages and is big at high voltages up to a certain frequency, and after 100 kHz this processes is vice versa.

Figure 2. Plots of capacitance-voltage of the 6CB/8CB LC mixture at the different frequencies.

Figure 3. Plots of capacitance-frequency of the 6CB/8CB LC mixture at the different voltages.

depend on temperature and frequency of applied electrical field on LC material. Up to nematic-isotropic phase transitions temperature, clearing point temperature, there are two components of dielectric constant as there are two components of dielectric constant as parallel $\epsilon_\parallel$ and perpendicular $\epsilon_\perp$ to the director and dielectric anisotropy. Above this temperature, there is only one dielectric constant ($\epsilon_\parallel = \epsilon_\perp$) and no dielectric anisotropy ($\Delta\epsilon = 0$).

As the capacitance values decrease with increasing frequency, they decrease from the initial value of $C_{//}$ to

The electrical conductivity of 6CB/8CB LC mixture is obtained as a function of voltage at different frequencies (see Figure 4). The conductance is small at lower voltages than the threshold voltage, $V_{th} = 2.1$ V, it suddenly rises at the threshold voltage and it is big at higher voltages than the threshold voltage. The conductance is small at lower voltages than the threshold voltage, $V_{th} = 2.1$ V, it suddenly rises at the threshold voltage and it is big at higher voltages than the threshold voltage. What is more, conductance change at the threshold voltage is bigger at the low frequencies than the higher frequencies.

The variations of dielectric constant components and dielectric anisotropy with frequency for 6CB/8CB LC mixture are shown in Figure 5. The parallel and perpendicular components of dielectric constant and dielectric anisotropy have little changes at lower frequencies than 100 kHz, but they decrease with increasing frequency.
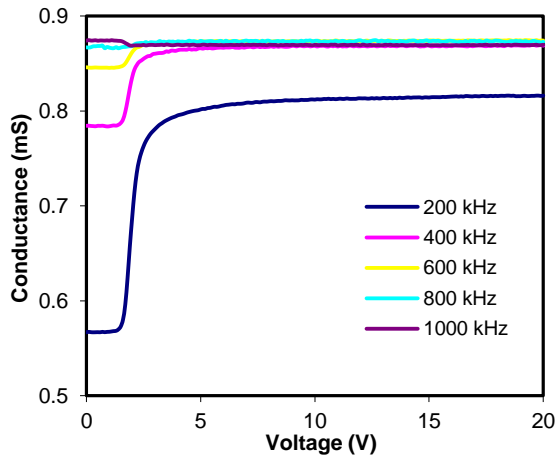
The variation of birefringence and parallel and perpendicular components of birefringence index with frequency are given for 6CB/8CB LC mixture (see Figure 6). The birefringence and its components are almost constant toward a frequency of 100 kHz, and then they decrease with increasing frequency.

Figure 4. Plots of conductance-voltage of the 6CB/8CB LC mixture at the different frequencies.

Figure 6. The birefringence index dependence on frequency for 6CB/8CB LC mixture.

The birefringence is negative over the frequency of 100 kHz. Most nematic LC have positive birefringence ($\Delta n > 0$), meaning that the parallel components of birefringence index is bigger than the perpendicular components of birefringence index. After the frequency of 100 kHz, the components of birefringence index are vice versa, and the birefringence index is negative. Birefringence is responsible for the appearance of interference colors in LCDs operating with plane-polarized light. This is meaning of different velocity on every dimensions of light ray which have traveled through the medium. The birefringence depends on light wavelength and temperature. Above the clearing point temperature of nematic LC, nematic-isotropic liquid phase transition temperature, the material is the isotropic liquid, and there is no birefringence ($n_{\parallel} = n_{\perp}$).
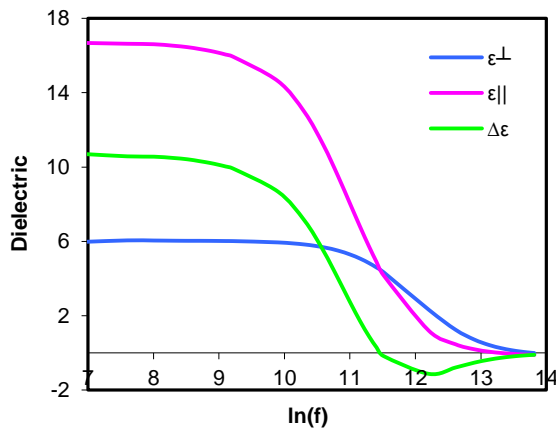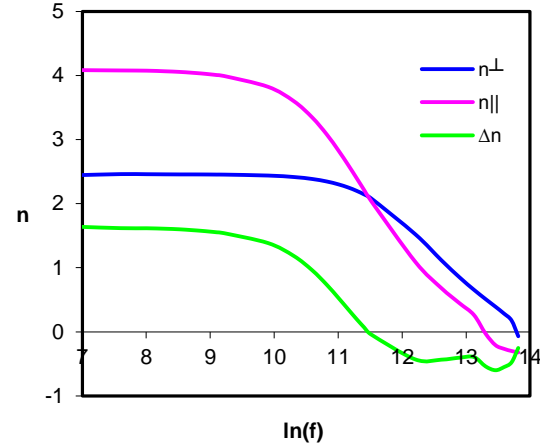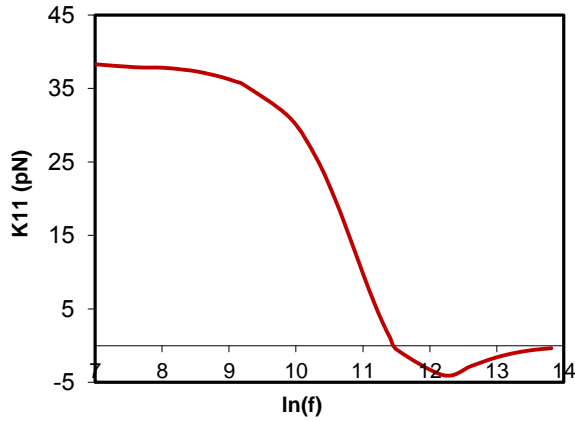

Figure 5. The dielectric anisotropy dependence on frequency for 6CB/8CB LC mixture.

The parallel component of dielectric is bigger than the perpendicular components of dielectric that is, dielectric anisotropy is positive up to a certain frequency (i.e.100 kHz) but after passing 100 kHz, dielectric anisotropy is negative.

The parallel and perpendicular components of birefringence index and birefringence can be written as a function of dielectric constant in Equations (2a-c).[6]

$$n_{\parallel}^2 = \epsilon_{\parallel} \tag{2a}$$

$$n_{\perp}^2 = \epsilon_{\perp} \tag{2b}$$

$$\Delta n = n_{\parallel} - n_{\perp} \tag{2c}$$

Freedericksz threshold voltage for LC samples can be expressed as in Eq. (3).[27]

$$V_{th} = \pi \left(\frac{K_{11}}{\epsilon_0 \, \Delta\epsilon} \right)^{1/2} \tag{3}$$

Where, ϵ_0 is dielectric constant of the vacuum, the K_{11} is the splay elastic coefficient, and $\Delta\epsilon$ is the dielectric anisotropy. When a distorting force affects to a LC phase as an electrical force or to an interface with a solid surface, the three elastic constants such as K11, K22, and K33 which are called splay, twist, and bend emerge, respectively. The elastic constants are molecular parameters, and they explain the restoring forces on a molecule in a LC phase in response to an external force

that distorts the medium from its lowest energy configuration. At the same time, the elastic constants are reaction to external electrical and magnetic forces applied to the material. Reorientation of LC molecules and LCD devices' response time obviously depend on these elastic constants.

Figure 7. The splay elastic coefficient dependence on frequency for 6CB/8CB LC mixture.
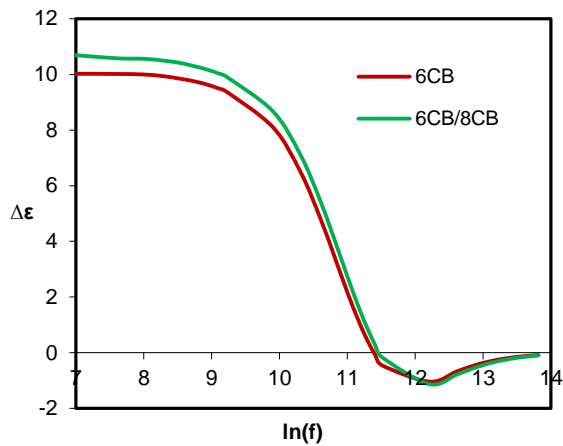

Figure 8. The dielectric anisotropy dependence on frequency for 6CB LC and 6CB/8CB LC mixture.

The splay K_{11} values were estimated by Eq. (3). The K_{11} values obtained for 6CB/8CB LC mixture as a function of frequency are shown in Figure 7. The splay elastic coefficient K_{11} decreases with increasing frequency, and they are negative at bigger frequencies than 100 kHz.

The relationship between dielectric anisotropy and frequency of 6CB LC and 6CB/8CB LC mixture is shown in Figure 8. The dielectric anisotropy of the mixture is bigger than 6CB LCs values up to 100 kHz frequency. The change of birefringence with frequency for 6CB and 6CB/8CB LCs is shown in Figure 9. The birefringence of mixture is bigger than 6CB LC values up to 100 kHz frequency like the dielectric anisotropy. The splay elastic coefficient K_{11} with frequency for 6CB

LC and 6CB/8CB LC mixture is shown in Figure 10. The splay elastic coefficient of mixture is bigger than 6CB LC values up to 100 kHz frequency.
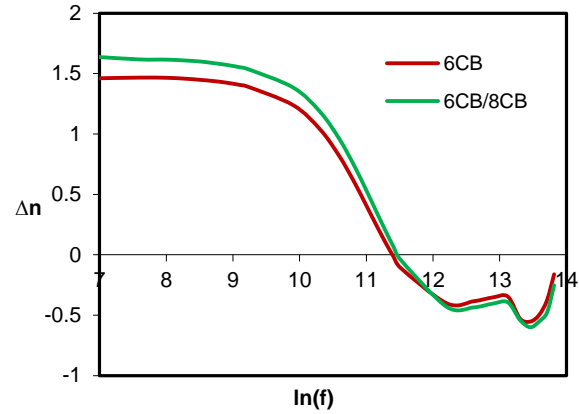
Figure 9. The birefringence index dependence on frequency for 6CB LC and 6CB/8CBLC mixture.
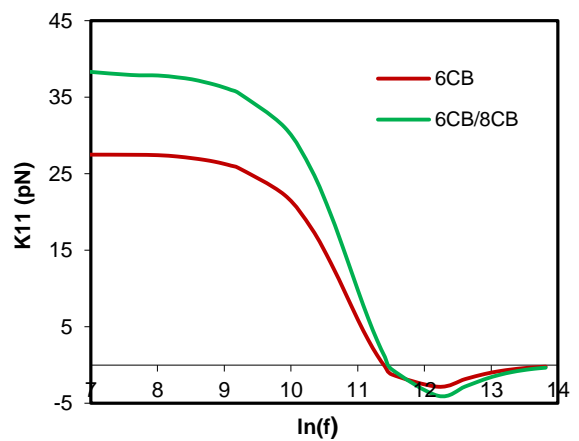
Figure 10. The splay elastic coefficient dependence on frequency for 6CB LC and 6CB/8CB LC mixture.

4. CONCLUSIONS

The absorbencies of 6CB and 8CB LCs were measured using UV-vis spectrophotometer. The mixture of 6CB (50%) and 8CB (50%) LC was prepared, and the capacitance-voltage, capacitance-frequency and conductance-voltage plots for 6CB/8CB LC mixture were investigated at the different frequencies. The dielectric anisotropy, birefringence, parallel and perpendicular components of dielectric and splay elastic coefficient were obtained as a function of frequency. Threshold voltage was found as 2.1 V for 6CB/8CB LC mixture. The dielectric anisotropy of LC mixture is positive at lower frequencies and it is negative at higher frequencies than 100 kHz. The dielectric anisotropy,

birefringence and splay elastic coefficient of 6CB LC and 6CB/8CB LC mixture were compared. The dielectric anisotropy, birefringence and splay elastic coefficient values of 6CB/8CB LC mixture are bigger than those of 6CB LC up to a certain frequency value of 100 kHz. The dielectric anisotropy of 6CB/8CB LC is bigger than that of 6CB LC values up to 100 kHz frequency. The birefringence value of 6CB/8CB LC is bigger than that of 6CB LC up to 100 kHz frequency like the dielectric anisotropy. Similarly, the splay elastic coefficient values of 6CB/8CB LC mixture are bigger than that of 6CB LC.

Conflict of interest

I declare that there is no a conflict of interest with any person, institute or company, etc.

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