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ABSTRACT
The electrical and dielectric properties of the nematic liquid crystal (E63) and Nickel Phthalocyanine (NiPc) doped E63 composite have been investigated by dielectric spectroscopy under 0–0.4 T magnetic field. It has been observed that NiPc doping and external magnetic field, *B* decrease threshold voltage. Moreover, conductivity of the composite has an increasing tendency with magnetic field. Furthermore, a significant decrease in relaxation frequency with *B* has been interpreted as the simplification of molecular orientation. Hence, NiPc doping enhances the magnetic sensitivity of E63 and increases molecular orientation ability and conductivity.

KEYWORDS
Liquid crystal; Nickel phthalocyanine; dielectric properties; magnetic sensitivity; molecular orientation

1. Introduction

Liquid crystals share properties of both crystalline and liquid materials [1]. In general, while liquids are characterized by isotropic macroscopic properties and fluidity, crystals are characterized by long-range positional order, which leads to anisotropic macroscopic properties. Liquid crystals (LCs) have an increasing attention of the scientific community due to their advanced electro-optic applications [2–7]. Their response to external electrical and magnetic fields has a crucial importance for display applications. The LC molecules can be easily oriented by application of external forces originated from electric or magnetic field. Moreover, the oriented direction of LC molecules can be re-oriented by changing the external electric or magnetic field direction. As a result of these self-assembling abilities and responsiveness of the orientation direction with external forces, LCs have afforded macroscopically aligned states in many materials. In particular, conjugated polymers [8–11], phorpyrine derivatives [12, 13], fullerenes [14,15] and nanographenes [16–20], which are difficult to organize and align because of extensive van der Waals interactions, are efficiently organized by using LCs.

As is known, while LCs respond quickly to an external electric field due to their large dielectric anisotropy [21–27], they are weakly sensitive to the external magnetic field [28–30]. Essentially, the behavior of LCs under magnetic field is very similar to what happens for an electric field. As application of electric field causes a polarization or electric dipole moment, magnetic field produces a magnetization or magnetic dipole moment in an LC that results the orientation of LC molecules.

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To enhance the magnetic field sensitivity of liquid crystals, magnetic dopants such as magnetic nano particles have been utilized [29]. From this point of view, Nickel Phthalocyanine (NiPc) has been selected as a magnetic doping compound in this work. The dielectric and electrical properties of 1% (w/w) (NiPc) doped nematic LC composite have been studied under 0–0.4 T magnetic field. It has been shown that developing of magnetic sensitivity of nematic LC on electrical and dielectric properties has been achieved by doping 1% (w/w) NiPc. In this context, high molecular orientation ability and the increase in conductivity has been obtained for the nematic LC composite under magnetic field.

2. Experimental

The nematic LC coded as E63 is the mixture of four nematogens (51% K15, 25% K21, 16% M24 and 8% T15) and it has been purchased by Merck. As a doping material Nickel (II) phthalocyanine, $C_{32}H_{16}N_8Ni$, (NiPc) have also been obtained from Sigma Aldrich. The chemical structures of E63 nematic host LC and NiPc have been shown in Fig. 1.

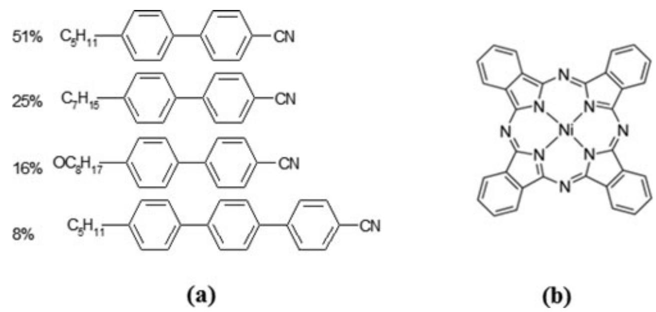

Figure 1. Molecular structure of (a) E63 nematic host and (b) Nickel (II) phthalocyanine.

Two LC sandwich cells with thickness of 9.8 µm have been prepared for $C-V$ measurements. The planar LC cells have been purchased from Instec Colorado Inc. The cells have been filled with pure E63 and E63+(1%)NiPc by capillary action at isotropic phase. The experimental set-up for dielectric measurements under magnetic field has been given in Fig. 2.

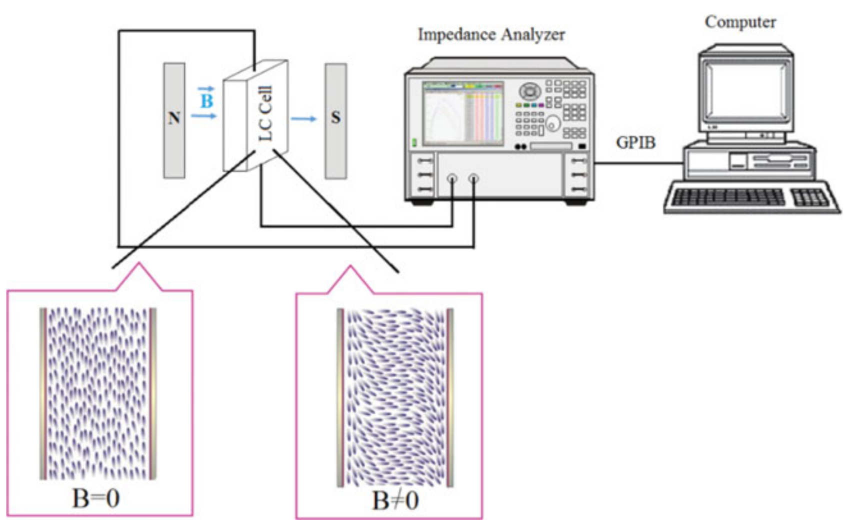

Figure 2. Experimental set-up for dielectric measurements and the orientation of dipoles in LC cell due to applied magnetic field, B.

The variations of capacitance with applied voltage of pure E63 and E63+(1%)NiPc have been performed by HP 4194A Impedance Analyzer within the frequency range of 100 Hz–10 MHz at room temperature.

3. Results and discussions

3.1. The effect of magnetic field on DC bias-dependent dielectric parameters

The variation of the real part of dielectric constant (ε') with voltage characteristics of pure nematic LC E63 and E63+(1%)NiPc at different spot frequencies (100 Hz, 1 kHz, 10 kHz, 100 kHz, 1 MHz, 10 MHz) under magnetic fields varying from 0 to 0.4 T have been given in Figs. 3 and 4, respectively.

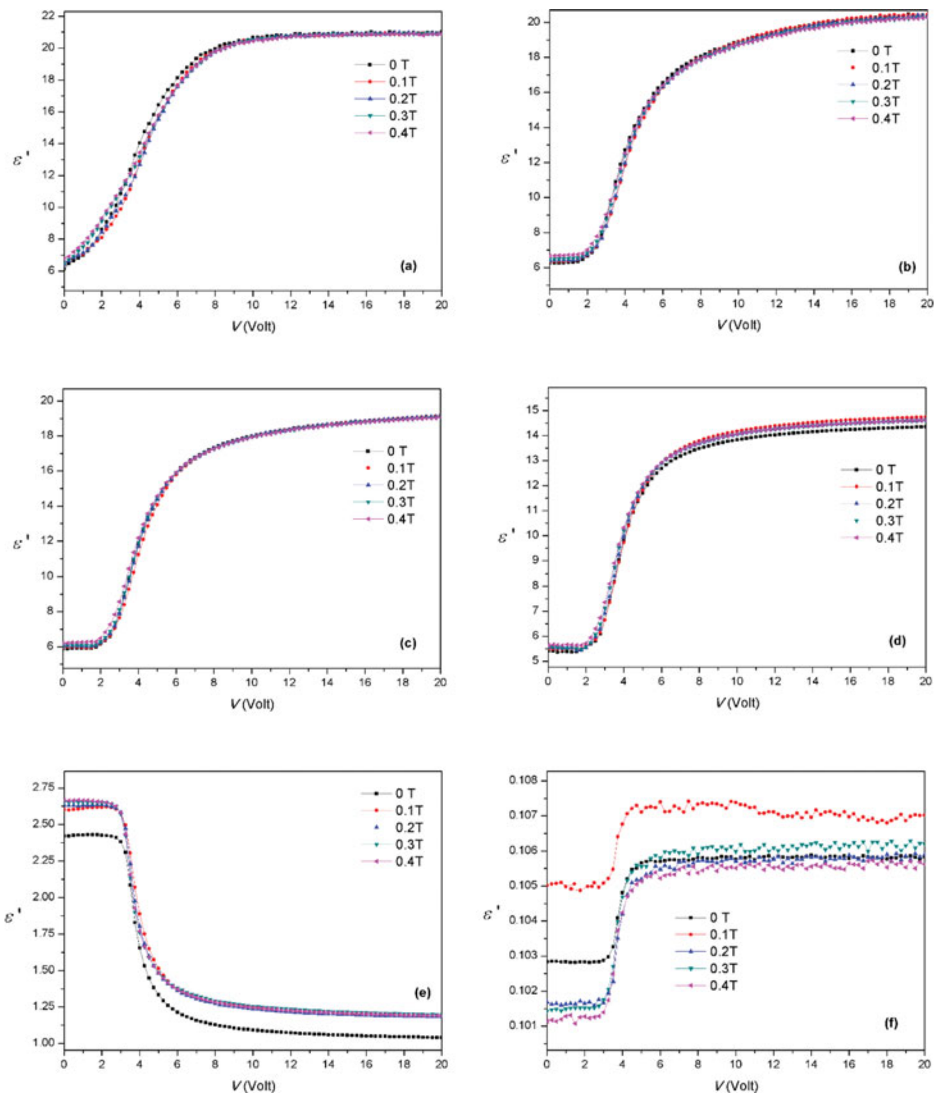

Figure 3. Threshold voltage versus applied frequency under zero and 0.4 T magnetic fields of E63 pure nematic LC and E63+(1%)NiPc composite.

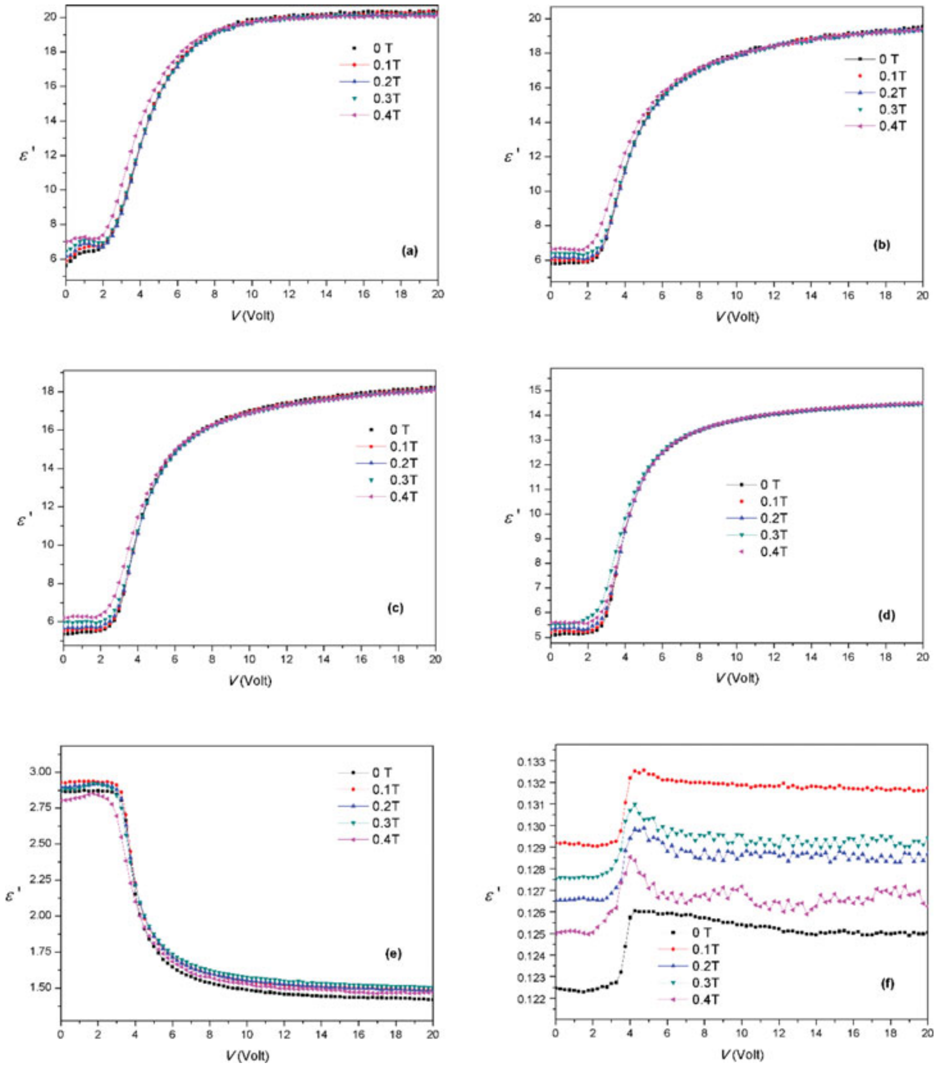

Figure 4. The influence of magnetic field on the real part component of dielectric constant versus dc bias curves of E63+(1%)NiPc at (a) 100 Hz, (b) 1 kHz, (c) 10 kHz, (d) 100 kHz, (e) 1 MHz, and (f) 10 MHz frequencies.

At lower voltages, the real parts of dielectric constant of both LCs are almost constant and after a certain voltage, i.e., threshold voltage, V_{th}, they increase drastically and reaches saturation due to molecular reorientation of the liquid crystals (see Figs. 3 and 4(b–d) and (f)). This behavior is valid for the frequency interval of 1 kHz–10 MHz except for 1 MHz. For 1 MHz, the real component of dielectric constant is almost constant to V_{th}, and then it decreases and finally reaches saturation. In this respect, it has been deduced that the orientations of molecules change their direction at the critical frequency of 1 MHz. The variations of V_{th} with applied frequency under zero and 0.4 T magnetic fields have been given in Fig. 5. When applied magnetic field is zero, it has been determined that while NiPc doping lowers V_{th} values at low frequencies, V_{th} increases with NiPc doping between 200 kHz and 10 MHz high-frequency region. If the external magnetic field of 0.4 T is applied to the LC cells, NiPc doping decreases the V_{th} values with respect to pure E63 at all frequencies. Moreover, it has been deduced that both NiPc doping and the application of magnetic field have a remarkable decreasing effect on V_{th} value. Since the decrease in threshold voltage means that the change of the orientation of LC molecules starts with lower voltage, this is very important for display applications. On the other hand, it has been revealed that the minimum value ofε', which corresponds to original orientation of the molecules, has been affected by the magnetic field magnitude. As the magnetic field increases, the minimum value of ε' increases for both LCs within the frequency interval of 100 Hz–1 MHz.

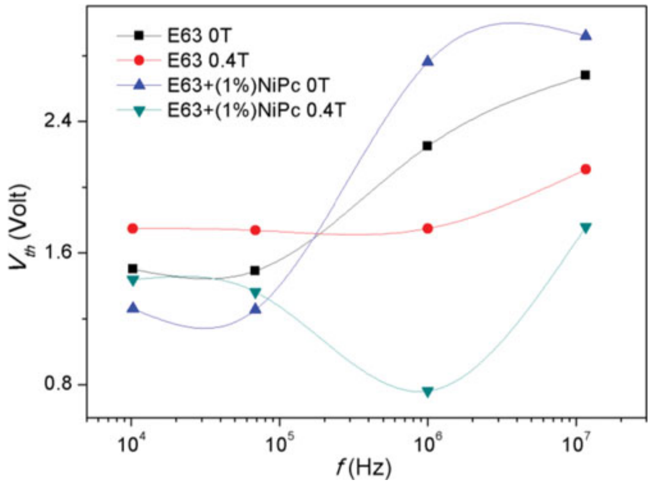

Figure 5. Threshold voltage versus applied frequency under zero and 0.4 T magnetic fields of E63 pure nematic LC and E63+(1%)NiPc composite.

According to Figs. 3 and 4, the parallel and perpendicular dielectric constants ($\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$) of E63 nematic LC and E63+(1%)NiPc composite have also been determined for the selected spot frequencies under different magnetic field magnitudes (see Table 1a and 1b). According to data given in Table 1a and 1b, the dielectric anisotropy,$\Delta\varepsilon$, has been calculated by

$$\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp} \tag{1}$$

Table 1a. Frequency and magnetic field dependence of dielectric parameters of E63.

	$B = 0$ T		$B = 0.1$ T		$B = 0.2$ T		$B = 0.3$ T		$B = 0.4$ T	
Frequency (Hz)	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$
1×10^2	21.016	6.127	20.892	6.442	20.904	6.430	20.895	6.519	20.885	6.783
1×10^3	20.423	6.255	20.433	6.350	20.306	6.411	20.296	6.490	20.270	6.675
1×10^4	19.127	5.875	19.118	5.984	19.111	6.048	19.099	6.073	19.060	6.194
1×10^5	14.350	5.408	14.732	5.500	14.618	5.564	14.608	5.583	14.611	5.484
1×10^6	1.038	2.420	1.188	2.599	1.182	2.631	1.197	2.653	1.188	2.666
1×10^7	0.106	0.103	0.107	0.105	0.106	0.102	0.106	0.101	0.105	0.101

Table 1b. Frequency and magnetic field dependence of dielectric parameters of E63+(1%)NiPc.

	$B = 0$ T		$B = 0.1$ T		$B = 0.2$ T		$B = 0.3$ T		$B = 0.4$ T	
Frequency (Hz)	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$
1×10^2	20.309	5.618	20.267	5.879	20.172	6.162	20.118	6.462	20.124	6.997
1×10^3	19.551	5.818	19.344	6.025	19.303	6.146	19.261	6.389	19.414	6.643
1×10^4	18.223	5.363	18.178	5.522	18.149	5.659	18.092	5.949	18.064	6.197
1×10^5	14.452	5.076	14.503	5.175	14.487	5.344	14.452	5.513	14.497	5.608
1×10^6	1.417	2.869	1.484	2.927	1.484	2.927	1.484	2.895	1.503	2.876
1×10^7	0.125	0.122	0.132	0.129	0.129	0.126	0.129	0.127	0.126	0.125

The frequency dependences of dielectric anisotropy of pure E63 LC and E63+(1%)NiPc composite have been shown in Figs. 6(a) and (b), respectively. According to Fig. 6, the sign of the dielectric anisotropy changes from positive to negative at the critical frequency of 629 kHz and 619 kHz for E63 and E63+(1%)NiPc composite, respectively. From this point of view, it has been deduced that NiPc doping enhances the dipole effect of the molecules at lower frequencies relative to pure E63. Moreover, it has been determined that the critical frequency is sensitive to NiPc doping even if the doping concentration is 1% (w/w) and the magnetic field does not change the value of $f_{critical}$.

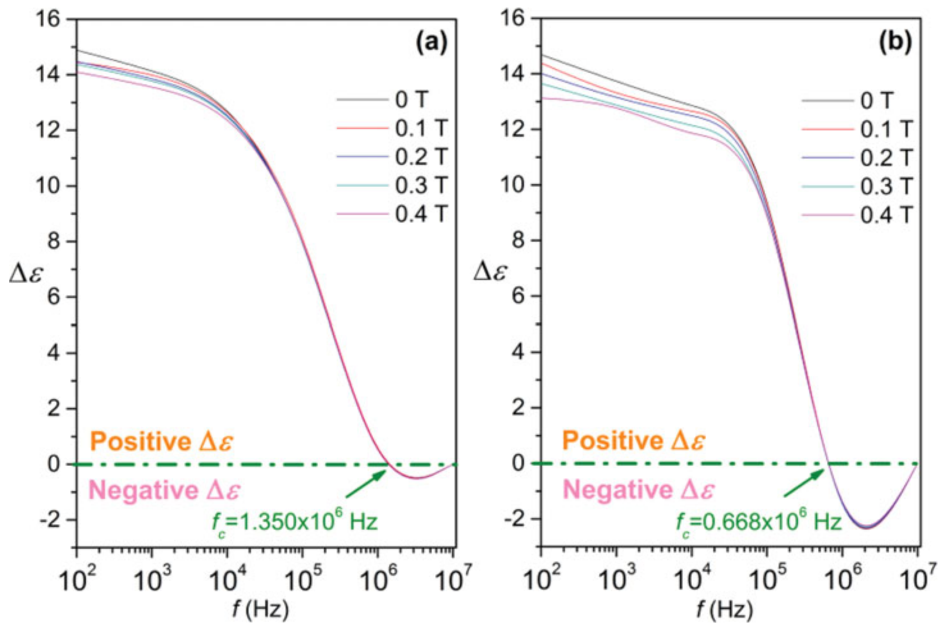

Figure 6. The frequency dependence of dielectric anisotropy under different external magnetic fields for (a) E63 and (b) E63+(1%)NiPc composite.

On the other hand, the effect of magnetic field on $\Delta\varepsilon$ has been observed at the low frequencies up to 20 kHz and 80 kHz for pure E63 and E63+(1%)NiPc. Furthermore, it has been observed that the maximum value of $\Delta\varepsilon$ decreases as the magnitude of magnetic field is increased from 0 to 0.4 T. When the magnetic field is applied, NiPc doping enhances magnetic sensitivity of E63 and strengthens dipole effect on molecular orientation. Hence, NiPc doping directly decreases the magnitude of dielectric anisotropy.

3.2. The effect of magnetic field on frequency-dependent dielectric parameters

The frequency dependences of the real and imaginary part of pure E63 and E63+(1%)NiPc under zero and 0.4 T magnetic field have been given in Fig. 7(a) and (b), respectively. The real component of dielectric constant versus frequency curves have been fitted by Origin Lab 8.5. The equation of fitting dispersion curve has been represented by Eq. (2):

$$\varepsilon'(\omega) = \left[\varepsilon'_{high\ freq.} + (\varepsilon'_{low\ freq.} - \varepsilon'_{high\ freq.})\frac{1 + (\omega\tau)^{1-\alpha}\sin\frac{1}{2}\alpha\pi}{1 + 2(\omega\tau)^{1-\alpha}\sin\frac{1}{2}\alpha\pi + (\omega\tau)^{2(1-\alpha)}}\right], \quad (2)$$

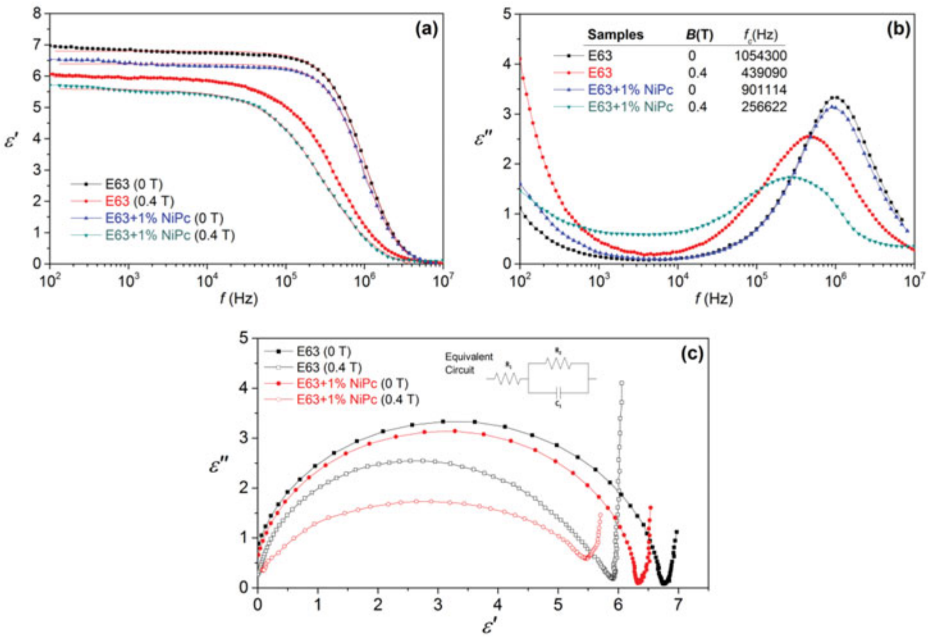

Figure 7. (a) The real and (b) imaginary component of dielectric constant, (c) Cole-Cole plot of E63 and E63+(1%)NiPc.

where α and τ are absorption coefficient and relaxation time. In general, absorption coefficient parameter, α changes from zero to one ($0 < \alpha \leq 1$). If α equals to zero, it corresponds to standard Debye type relation. The non-Debye type occurs when the value of absorption coefficient varies between $0 < \alpha < 1$ region [31]. The relaxation times and absorption coefficients for pure E63 and the composite under various magnetic fields have also been given in Fig. 7(a). Since the absorption coefficient values of E63 and the E63+(1%) NiPc at zero magnetic field are very close to zero with 99.9% accuracy, it has been determined that they show nearly-Debye type relaxation. On the other hand, application of 0.4 T increases the absorption coefficient values of E63 and the E63+(1%) NiPc. Hence, it has been deduced that the relaxation type of these materials changes from nearly-Debye to non-Debye type. Moreover, the dielectric strength, $\Delta\varepsilon_s$, and the related low- and high-frequency dielectric constants have been listed in Table 2.

Table 2. Dielectric parameters from the real part of the dielectric constant with fit equation.

	E63 (0 T)		E63+(1%)NiPc	
Parameter	(0 T)	(0.4 T)	(0 T)	(0.4 T)
$\varepsilon'_{low freq.}$	6.97	6.02	6.53	5.70
$\varepsilon'_{high freq.}$	0.02	0.01	0.13	0.10
$\Delta\varepsilon_s$	6.95	6.01	6.40	5.60
R^2	0.99897	0.99953	0.99852	0.99933
α	0.0485	0.1917	0.0341	0.2209
τ (s)	9.751×10^{-7}	2.290×10^{-6}	1.046×10^{-6}	3.247×10^{-6}

It has been observed that the dielectric strength decreases with both NiPc doping and application of magnetic field. The remarkable decrease in $\Delta\varepsilon_s$ has been recorded for the 1% NiPc doped nematic LC composite at 0.4 T. From this point of view, it has been understood that application of magnetic field makes the alignment of molecules easier and decreases the power required. Hence, high molecular orientation ability has been achieved for NiPc doped E63 composite under magnetic field.

According to the variation of imaginary component with frequency curves, the relaxation frequencies have been determined. It has been revealed that relaxation frequency shifts to low frequencies with both NiPc doping and the applied magnetic field. The considerable decrease in relaxation frequency has also been observed for the 1% NiPc doped nematic LC at 0.4 T. From this point of view, the significant decrease in relaxation frequency with magnetic field for 1% NiPc doped nematic LC can be attributed to an evidence that the application of external magnetic field makes molecules' orientation easier.

In order to investigate the dielectric relaxation mechanisms of E63 and NiPc doped LC under different magnitude of magnetic field have also been investigated by Cole-Cole graphics, at which the real component of dielectric constant, $\varepsilon'$is plotted against the imaginary component of dielectric constant, ε'' for each frequency (see Fig. 7(c)). As is seen from Fig. 7(c), since the magnetic field deforms the shape of semi-circles, the change of relaxation mechanism from nearly-Debye to non-Debye type by magnetic field has been confirmed. This result is in agreement with the increase in absorption coefficients given in Fig. 7(a). As shown in Fig. 7(c), all curves exhibit a single semi-circle and a straight line. Regardless of magnetic field, the equivalent circuits of the pure LC and the composite have been determined as a series resistance (R_1), which is connected by parallel resistance and capacitance (R_2, C_1) (see the inset of Fig. 7(c)). However, it has been clearly observed that application of magnetic field on NiPc doped E63 decreases both the value of serial resistance, R_1 and the energy loss. Hence, this property of E63+(1%NiPc) under magnetic field makes the composite as an ideal device for optoelectronic applications.

3.3. The effect of magnetic field on alternative current (ac) conductivity

In this section, we have focused on the effect of magnetic field on ac conductivity of the LCs. Ac conductivity, σ_{ac}, has been calculated by

$$\sigma_{ac} = \varepsilon_0 \omega \varepsilon'', \tag{3}$$

where $\varepsilon_0$is the electric permittivity of free space, ω is angular frequency and ε'' is the imaginary component of dielectric constant. According to Jonscher's "Universal dielectric response," conductivity power law obeys $\sigma = \sigma_0 + A\omega^s$ relation, where σ_0 is the dc component and $\sigma_{ac} = A\omega^s$ is the ac component [32]. Depending on the value of s parameter, the conductivity mechanism can be classified by different power laws in scientific literature (see Table 3).

In order to determine the magnetic field dependency of conductivity mechanism, $\ln \sigma_{ac}$versus $\ln \omega$ graphics have been drawn under zero and 0.4 T for E63 and E63+(1%)NiPc in Figs. 8(a) and (b), respectively. The frequency exponent, s, have been calculated from the

Table 3. The conductivity mechanisms depending on the s parameter.

Conductivity model	Frequency exponent	Ref.
DC Conductivity	$s \approx 0$	[33]
Correlated Barrier Hoping (CBH)	$s \approx 0.5$	[34]
Quantum Mechanical Tunneling (QMT)	$0.7 \leq s < 1$	[35]
Nearly Constant Loss (NCL)	$s = 1$	[33, 36-41]
Super Linear Power Law (SLPL)	$s > 1$	[33, 36-41]
Extended Pair Approximation (EPA)	$s \approx 2$	[41]

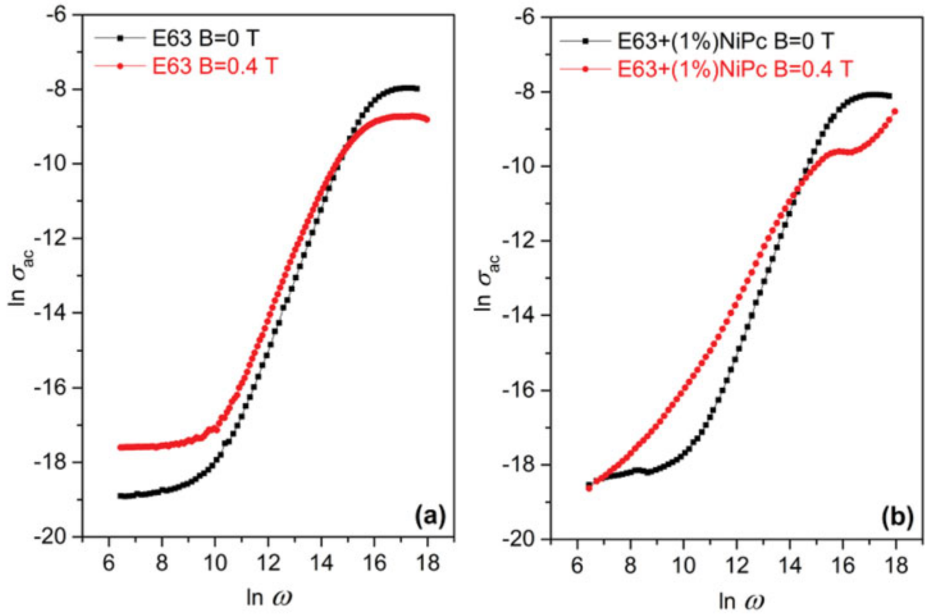

Figure 8. The ln σ_{ac} versus ln ω curves of (a) E63 and (b) E63+(1%)NiPc under zero and 0.4 T magnetic fields.

slopes of these curves for the low-, intermediate- and high-frequency regions (see Table 4). The curves have been divided into three regions, called as the low (100 Hz–8 kHz), intermediate (8 kHz–8 MHz) and high (8 MHz–15 MHz) frequency domains.

According to the values of frequency exponent varying from 0.09 to 1.76 (Table 4), different types of conductivity mechanisms have been determined for the LCs. It has been determined that the conductivity mechanisms of E63 ($B = 0$ T), E63 ($B = 0.4$ T) and E63+(1%)NiPc ($B = 0$ T) obey nearly DC conductivity, super linear power law and nearly DC conductivity for the low-, intermediate- and high-frequency regions, respectively.

It has been observed that the conductivity mechanism does not change with NiPc doping at zero magnetic field. On the other hand, the low- and high-frequency conductivity mechanisms of NiPc doped E63 at 0.4 T have been determined as SLPL and QMT, respectively. From this point of view, it has been revealed that the conductivity mechanism can be changed by the application of magnetic field for only NiPc doped composite. Referring to the remarkable change in conductivity mechanism of E63 +(1%)NiPc from nearly DC to QMT by application of magnetic field at high-frequency region, the effect of magnetic field on conductivity at zero dc bias has also been studied for E63 and E63+(1%)NiPc at 10 MHz. It has been clearly

Table 4. The conductivity mechanism and the related *s* parameters of E63 and its NiPc doped composite at zero and 0.4 T magnetic field.

Sample	$s_{lowfreq.}$	$s_{int.freq.}$	$s_{highfreq.}$
E63 (0 T)	0.120[a]	1.760[b]	0.070[a]
E63 (0.4 T)	0.090[a]	1.676[b]	0.042[a]
E63+(1%)NiPc (0 T)	0.129[a]	1.760[b]	0.070[a]
E63+(1%) NiPc (0.4 T)	1.133[b]	1.133[b]	0.903[c]

[a]Nearly DC.
[b]SLPL.
[c]QMT.

seen that the conductivity of both E63 and E63+(1%)NiPc has a tendency of increase with the change of magnetic field magnitude from zero to 0.4 T (see Fig. 8(b)).

4. Conclusions

In this work, the pure nematic liquid crystal (E63) and 1%(w/w) NiPc doped E63 have been investigated by means of their dielectric and electrical properties under the magnetic fields changing from 0 T to 0.4 T. A remarkable decrease in threshold voltage, V_{th}, has been observed on NiPc doped E63 composite under magnetic field. Since the decrease in threshold voltage corresponds to the fact that the change of the orientation of LC molecules starts at lower voltage, it has been revealed that this composite has a promising potential for electro-optic applications. Moreover, it has been deduced that the relaxation type of these materials changes from nearly-Debye to non-Debye type by applying magnetic field.

The sensitivity of conductivity mechanism to magnetic field has also been investigated. By application of magnetic field, a significant change in conductivity mechanism from Nearly DC to QMT at high frequency has been found for NiPc doped LC. In addition, it has been clearly seen that the conductivity of the composite has a tendency of increase with the change of magnetic field magnitude from zero to 0.4 T.

Ultimately, it has been determined that the dielectric strength, $\Delta\varepsilon_s$, decreases with both NiPc doping and application of magnetic field. From this point of view, since V_{th} and $\Delta\varepsilon_s$decrease with the applied magnetic field, E63+(1%)NiPc composite may become a suitable material with having desirable molecular alignment and requires less power for electro-optic applications. The increase of the magnetic sensitivity of the nematic LC by doping NiPc presented by this work has a crucial importance, which can potentially broaden the applications area and may offer an opportunity to develop next generation electro and magneto-optic devices.

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