Impedance and dielectric spectroscopy study of graphene-doped liquid crystal E7

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Abstract. The change in electrical conductivity and dielectric response of liquid crystal (LC) E7 by doping with graphene nanoparticles was experimentally studied by complex electrical impedance and dielectric spectroscopy over the frequency range from 0.1 Hz to 1 MHz of the applied electric field. In the measured graphene/E7 nanocomposite films (7 µm-thick, with planar orientation), graphene nanoflakes were dispersed in the nematic E7 at the concentration of 10⁻³ wt.%. Graphene nanodopants lead to a change of both electrical transport and dielectric permittivity of the LC E7 which should render improved electro-optic response of the considered room-temperature nanocomposite nematic films.

1. Introduction
Nanodoping with small amount of graphene is currently trending nanotechnology to largely improve the properties of liquid crystals LC (LCs), in particular their electrical and electro-optic responses. As found quite recently, graphene nanoparticles can considerably depress the ion transport [1-3] and reduce the ionic shielding and related ion-induced side effects in the practical LC devices, e.g., LC displays [4-6]. Such negative effects occur due to free ion carriers present in the LCs [7]. Although the initial density of mobile ions in the nematic LCs is relatively low, the ion-charge effects can strongly influence the performance of electro-optical (EO) devices based on nematic LCs [8,9]. In the study presented here, we deal with thin (7 µm) planar films of nematic LC E7 doped with 10⁻³ wt.% graphene nanoparticles. In order to assess the effect from this small amount of graphene doping, we compared the electrical and dielectric response of such nanocomposite nematic films with that of the same LC E7 but undoped. The study is in the area of physics/material nanoscience and nanotechnology, and is closely related to practical applications of nematic nanomaterials.

2. Experimental
The LC mixture E7, composed of 4-cyano-4′-n-pentyl-biphenyl (5CB), 4-cyano-4′-n-heptyl-biphenyl (7CB), 4-cyano-4′-n-octyloxy-biphenyl (8OCB), and 4-cyano-4″-n-pentyl-p-terphenyl (5CT), has been widely used in LC devices due to its large birefringence (~ 0.2 in the visible) and wide temperature range of the nematic phase (from −10 °C to 58 °C). E7 has relatively large positive dielectric
anisotropy, $\Delta \varepsilon_\parallel = 19$ and $\Delta \varepsilon_\perp = 5.2$ at 20 °C and 1 kHz [10]. The graphene nanoparticles used in the present study (nanoflakes with an average thickness of 12 nm) were in the form of nanopowder – a commercial product from Graphene Supermarket Inc. Subsequently, they were ball milled. The graphene nanoflakes was added at the concentration of $10^{-3}$ wt.% to the nematic LC E7 (from Merck). To obtain a homogeneous dispersion, graphene-E7 mixture was tip-sonicated for 30 min at 4000 rpm by DW-SLD20-1200 (Dowell Ultrasonic Technology). Then this mixture was heated above 60 °C to reach isotropic phase of the LC and was capillary filled into glass cells with a gap of $7 \pm 0.5 \mu m$. The inner surfaces of the glass plates of the cells have transparent conductive layers of indium-tin oxide (ITO) (to serve as electrodes), being further overcoated with polyimide alignment layers, parallel-rubbed to achieve a planar orientation of the films. As reference cells, identical empty cells were filled with undoped LC E7.

Complex electrical impedances of the films were measured by a potentiostat/galvanostat (SP–200, Biologic) in the frequency range 0.1 Hz – 1 MHz of the external alternating-current (AC) electric field. The electrically active area (the contact area, the area of ITO) of the samples were $A = 1 \text{ cm}^2$, as imposed from the ITO electrodes of the cells. Sinusoidal voltage of $10 \text{ mV}_{\text{RMS}}$ was applied to the ITO electrodes. At such voltage, the examined LC films keep their initial planar orientations. The temperature of the films was maintained by Mettler FP82 hot stage having an accuracy of $\pm 0.1^\circ\text{C}$. The complex impedance spectra were recorded at 5 °C intervals within the range from 15 °C to 60 °C.

3. Results and discussion

By the technique of complex electrical impedance spectroscopy, both real ($Z_r$) and imaginary ($Z_i$) parts of the complex electrical impedance ($Z^*$) were simultaneously measured as a function of the frequency ($f$) of the AC electric field applied on the sample. The Nyquist plots ($Z_i$ versus $Z_r$) for the studied samples demonstrated semi-circular arcs (figure 1a). The deep valleys in these plots are associated with the bulk resistance ($R_b$) of the samples. The $R_b$ values can be associated to the projections of the valleys on the abscissa ($Z_r$ axis) [11,12]. As seen from figure 1(a), $R_b$ of our thin planar films with graphene-doped E7 is approximately twice higher than $R_b$ of such films with pure E7 and this applies to any temperature in the range 15 – 60 °C (figure 1b).

Figure 1. The complex Nyquist plots for planar films of graphene/E7 nanocomposite and undoped E7, measured upon identical experimental conditions, but at various temperatures; (b) The same as in (a) but in logarithmic scale
The corresponding values of the ionic conductivity (\(\sigma\)) of the samples (in direction that is perpendicular to the nematic director) were calculated by \(\sigma = \frac{d}{R_b A}\), where \(d\) and \(A\) represent the film thickness and electrically-active area of the samples, respectively. This bulk conductivity is relevant to the low-frequency region \((f < 10^2 \text{ Hz})\) where the dielectric behavior is attributable to the space-charge polarization. Hence, the lower \(\sigma\) resulting from the addition of graphene nanoparticles to the ion-rich nematic host E7 implies that they effectively capture mobile ions and reduce the space-charge polarization.

Indeed, the reducing of the ionic conductivity of the nematic LC E7 due to the presence of graphene nanoparticles can be explained by ion trapping effect, well known for nematic LCs doped by relatively small amount of graphene nanoparticles [5]. Basically, the LCs are weakly conducting dielectrics. Their ionic conduction comes from impurities in these materials (uncontrollable contamination during their synthesis). The impurity ion concentration in cyanobiphenilic E7 is relatively low and corresponds to electrical conductivity \(\sim 10^{-8} - 10^{-7} \text{ S/m}\) [13]. However, a charge injection from the cell electrodes may induce migration of free ions from the electrodes into the bulk of the LC medium. The presence of alignment layers and planar boundary conditions should increase both the concentration and the mobility of the free ions in the bulk of the nematic LCs in upon electric field. In the case of the nematic LC E7, this fact is well established, e.g. in the frequency range 0.5 Hz – 200 kHz [14]. As known, the high density of mobile ions in the nematic LCs leads to several negative effects that restrict their EO applications [6,8,9,15-17]. In this context, it should be noted that an improvement of EO, optical and non-linear optical responses has been reported for a number of nematic LCs doped with graphene and graphene derivatives [1,18-21]. Most probably this happens owing to ion trapping due to interaction (\(\pi-\pi\) electron stacking and interfacial interactions) between graphene nanodopants and nematic LC molecules [5,22]. We have to point out that the result for the depression of the ion-charge effects observed here for the considered graphene/E7 nanocomposite is consistent with the scientific reports published previously.

Figure 2. Variation of ionic conductivity (\(\sigma\)) of E7 and graphene/E7 samples vs temperature.

Figure 2 shows the temperature dependence of the ionic conductivities of E7 and graphene/E7 samples. The \(\sigma\) values for both E7 and graphene/E7 increase by elevating temperature (figure 2a) that is reasonable. Further, the plots for both materials demonstrated a linear relation between the logarithmic conductivity (\(\log(\sigma)\)) and inverse temperature (figure 2b), i.e., their temperature behaviours follow the Arrhenius relation \(\sigma = \sigma_0 \exp(-E_a/kT)\), where \(T\), \(k\), \(E_a\) and \(\sigma_0\) are the absolute temperature, the Boltzmann constant, activation energy and pre-exponential factor, respectively. The linear slopes \((s)\) in figure 2(b) suggest a hopping mechanism of ion conduction (hopping of charge carriers between localized states). Determined from linear fits to the data in figure 2(b) according to the Arrhenius equation, the linear slope is related to the values of \(E_a\) by \(E_a = -s \times R\), where \(R = 8.314 \text{ J.mol}^{-1}.\text{K}^{-1}\) is the universal gas constant. Within the uncertainty limits by the measurements, \(E_a\) values calculated in this way for both graphene/E7 and undoped E7 are nearly equal, hence a very little change in the threshold energy for the ions to hop from one site to another takes place due to doping with graphene.
nanoparticles. This can be attributed to negligible structural changes in the nematic LC E7 that are relevant to and influence the ion transport, e.g., eventual change in viscosity that could have impact on the diffusivity of the mobile ions. The lack of such structural modifications corroborates the ion-trapping mechanism as a main reason for lowering of the ionic conductivity of E7 by graphene doping.

In fact, a clear difference between the graphene/E7 nanocomposite and the undoped E7 was also present in their dielectric spectra (figure 3). The real ($\varepsilon'$) and imaginary ($\varepsilon''$) components of the complex dielectric permittivity were calculated from the measured frequency spectra $Z_r(f)$ and $Z_i(f)$ by means of the well known relations [12]:

$$\varepsilon'(f) = -\frac{Z_i d}{2\pi f \varepsilon_0 A (Z_r^2 + Z_i^2)}$$ \hspace{1cm} (1)$$

and

$$\varepsilon''(f) = \frac{Z_r d}{2\pi f \varepsilon_0 A (Z_r^2 + Z_i^2)}$$ \hspace{1cm} (2)$$

where $\varepsilon_0 = 8.85 \times 10^{-12} \text{ F.m}^{-1}$ is the permittivity of free space. $\varepsilon'$ has the same significance as that of the ordinary dielectric constant of the material. It is a measure of the energy stored in the material during each cycle, to be returned to the electric field at the end of the cycle. The high values of $\varepsilon'$ in the low-frequency region ($f < 10^2$ Hz) can be attributed to a build-up of space charge near electrode/LC interface, which partially blocks the charge transport. With increasing $f$, $\varepsilon'$ decreases up to a nearly constant value, because at such frequencies the ions will hardly able to follow the periodic reversal of the electric field. Significantly, graphene-doped E7 exhibits a lower value of dielectric constant $\varepsilon'$ than the undoped E7. This difference is most pronounced in the low-frequency region, in our case from 1 Hz to 100 Hz. As known, in this range the dielectric behavior is attributable to the space-charge polarization, i.e. the addition of graphene nanoparticles to the ion-rich nematic host E7 effectively leads to capturing of mobile ions and reducing of the space-charge polarization. The decrease in the dielectric constant represents a fractional decrease in charge density due to the addition of graphene nanoparticles in the LC E7, resulting in a lower ion conductivity.

Using the frequency spectrum of $\varepsilon''$, one can calculate the dielectric loss tangent, $\tan \delta = \varepsilon'' / \varepsilon'$ [11], and the real part of the AC conductivity $\sigma_{AC} = 2\pi f \varepsilon_0 \varepsilon''$ [23]. Figure 4 shows the corresponding frequency-dependent characteristics. Regarding $\tan \delta$, the effect from graphene nanodopants was evident in the frequency range 1 Hz – 10 kHz (figure 4a). In the half of this range ($f < 10^2$ Hz), the dielectric loss is enhanced by graphene nanodopants, and in the other part is reduced. The shift of the frequency dependence of $\tan \delta$ by doping with graphene suggests that the relaxation frequency of the graphene-doped E7 is different (slightly lower) from that of pure E7 sample, i.e. the graphene
nanodopants do affect at detectable level the molecular dynamics of the nematic LC molecules. As a ratio of dielectric loss factor to the dielectric constant, the loss tangent is a measure of the ratio of the electrical energy lost to the energy stored in a periodic field. The shift of the frequency dependence of $\tan\delta$ towards the lower frequencies by doping with graphene nanoparticles may be a sign that the nanodopants effectively suppress the space-charge polarization and ion-charge effects.

![Figure 4](image_url)

**Figure 4.** Frequency spectra of dielectric loss tangent (a) and the real part of the AC conductivity (b) for pure E7 (open circles) and graphene/E7 nanocomposite (colored with red), at 26°C.

The frequency-dependent behaviour of $\sigma_{AC}$ (in our case, measured perpendicular to the nematic LC director) is shown in figure 4(b). It is apparent that $\sigma_{AC}$ increases with $f$, but a nearly frequency-independent plateau at intermediate frequency region takes place. The increasing conductivity behaviour is relevant to the electrode polarization effects, while saturation-like behaviour results from the failure of movement of ions. As seen from figure 4(b), in the frequency range 10 Hz – 10 kHz graphene/E7 nematic nanocomposite displays a lower $\sigma_{AC}$ than that of the undoped nematic LC E7. Both reduced AC conductivity and dielectric loses in the above mentioned frequency range can be connected with the immobilization of the ions in the presence of graphene. In particular, these effects are well pronounced by graphene-doped ferroelectric LCs [5, 20,24,25].

4. Conclusion

Our study shows that the electrical and dielectric behaviours of planarly-aligned relatively thin films of nematic LC (E7 in the present case) are influenced by its doping with graphene nanoflakes, even at very low concentration of $10^{-3}$ wt.%. Essentially, the results obtained here confirm the concept that the doping with graphene nanoparticles reduces the ion diffusivity, and thereby, lowers the room-temperature electrical conductivity of the doped nematic LCs. This applies to the ionic conductivity (relevant to the low frequencies) (and direct-current conductivity), as well as to AC conductivity in certain frequency range (in our case, 10 Hz – 10 kHz). Slight amounts of graphene nanodopants reduce the concentration of impurity and injected ions and their diffusivity, thus depressing the unwanted ion-charge effects in the nematic LCs. The ion immobilization effect through graphene nanoparticles is well pronounced. As such, it will be useful in view of practical applications of nematic nanocomposites produced from graphene-doped nematic LCs (e.g., as EO materials in high-quality LC display technology). Providing an efficient reducing of the negative side effects, the purification by graphene nanodopants is of paramount importance for the functionality of nematic LCs EO devices and for applicability of nematic LCs in organic electronics. Further, the considered important modification is useful for development of new advanced and multifunctional nanocomposite nematic materials working at ambient temperatures, as well as over a wide temperature range of the nematic phase.
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