



Nanoparticle-Induced Ionic Effects in Liquid Crystal Devices [†]

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Abstract: The applications of liquid crystals continue to expand. They include conventional and advanced liquid crystal displays, electrically controlled lenses, tunable optical elements such as filters, light shutters, waveplates, and spatial light modulators, smart windows and sensors, and reconfigurable antennas and microwave devices, to name a few. As a rule, liquid crystal devices are controlled by applying an external electric field. This field reorients liquid crystals in a desirable way, thus leading to the tunability of their physical properties. The electric-field-induced reorientation of liquid crystals can be affected by ions typically present in molecular liquid crystals. In the case of liquid crystal displays, ions in liquid crystals can lead to image sticking, a reduced voltage holding ratio, and altered electro-optical performance. Therefore, the development of efficient ways to better control ions in liquid crystal devices is of utmost importance to existing and future liquid crystal technologies. In this paper, we discuss how nanomaterials can affect the electrical properties of molecular liquid crystals. In general, nanomaterials in molecular liquid crystals can behave as ion-capturing objects or act as a source of ions. Ion-capturing nanomaterials in molecular liquid crystals can enhance their electrical resistivity. On the other hand, ion-releasing nanoparticles can lead to the opposite effect. By considering the competition between two nanoparticle-induced ionic processes, namely the ion capturing and ion releasing effects, the electrical resistivity of liquid crystals can be controlled in a desirable way.

Keywords: liquid crystal device; molecular liquid crystals; ions; nanoparticles; electrical resistivity



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1. Introduction

Molecular liquid crystals are at the heart of modern display and non-display applications [1–4]. As a rule, liquid crystal devices are driven by electric fields. The applied electric field controls the orientation of liquid crystals, thus enabling the tunability of liquid crystal devices. One important requirement determining the suitability of liquid crystal materials for a chosen application includes relatively high values of their electrical resistivity ($\rho > 10^{10} \Omega\text{m}$) [5,6]. Therefore, the development of new ways to design high-resistivity liquid crystals is highly desirable. A general approach to producing such materials relies on chemical design and synthesis methods [7]. Recent advances in nanoscience and nanotechnology resulted in the development of an alternative way to increase the electrical resistivity of molecular liquid crystals by doping them with nanomaterials [8–10]. Under certain conditions, nanomaterials dispersed in molecular liquid crystals can trap mobile ions, effectively immobilizing them and leading to higher values of the electrical resistivity [11,12]. In principle, this rather general approach, if properly implemented, can convert low-resistivity liquid crystals into high-resistivity liquid crystals. However, an uncontrolled ionic contamination of nanoparticles can make this method invalid. Indeed, as was discussed in several papers, nanomaterials contaminated with ions, instead of increasing the electrical resistivity, can lead to its decrease [11,12]. As a result, it is important to analyze

major physical factors affecting the electrical resistivity of molecular liquid crystals doped with nanoparticles.

In this paper, we discuss the dependence of the electrical resistivity ρ of molecular liquid crystals on the concentration of nanodopants, their size, and their ability to capture mobile ions. In addition, we show how ionic contamination of nanoparticles can affect the values of ρ .

2. Model

Consider molecular liquid crystals containing monovalent ions. Once nanoparticles are dispersed in molecular liquid crystals, interactions between them and ions affect the ion density n according to Equation (1):

$$\frac{dn}{dt} = -k_{NP}^a n n_{NP} A_{NP} \sigma_S^{NP} (1 - \Theta_{NP}) + k_{NP}^d n_{NP} \sigma_S^{NP} A_{NP} \Theta_{NP} \quad (1)$$

where the first term describes the ion-capturing effect quantified by a constant k_{NP}^a (mobile ions are captured by nanoparticles), and the second term accounts for the ion release process characterized by a parameter k_{NP}^d . We assume a spherical nanoparticle of a surface area A_{NP} . n_{NP} is the volume concentration of nanoparticles, σ_S^{NP} is the surface density of surface sites on a surface of nanoparticle, and Θ_{NP} is the fractional surface coverage of a nanoparticle [13].

The conservation of the total number of ions is represented by Equation (2):

$$n_0 + n_{NP} A_{NP} \sigma_S^{NP} \nu_{NP} = n + n_{NP} A_{NP} \sigma_S^{NP} \Theta_{NP} \quad (2)$$

where n_0 represents the initial concentration of mobile ions in molecular liquid crystals (prior to mixing them with nanoparticles), and ν_{NP} is the contamination factor accounting for the possibility of ionic contamination of nanoparticles [13].

By solving Equations (1) and (2), the concentration of mobile ions in liquid crystals doped with nanoparticles can be found. The presence of mobile ions in molecular liquid crystals results in their electrical resistivity ρ expressed by Equation (3):

$$\rho = \frac{1}{q\mu n} \quad (3)$$

where μ is the effective ion mobility, and $q = |e| = 1.6 \times 10^{-19} \text{C}$.

3. Results and Discussion

The electrical resistivity of molecular liquid crystals doped with nanoparticles can be computed using Equations (1)–(3) and assuming steady state. The goal of the present paper is to show the effect of the size of nanodopants and their weight concentration on the electrical resistivity of molecular liquid crystals. The values of the relevant physical parameters are listed in Table 1.

Table 1. Parameters used to produce solid curves shown in Figures 1–4.

Physical Parameter	Value
n_0	$1.0 \times 10^{20} \text{ m}^{-3}$ (Figures 1–4)
R_{NP}	2.5; 5; 10; 25; 50 nm (Figures 1–4)
σ_S^{NP}	$1.0 \times 10^{18} \text{ m}^{-2}$ (Figures 1–4)
$K_{NP} = k_{NP}^a / k_{NP}^d$	$1.0 \times 10^{-24} \text{ m}^3$ (Figure 1)
$K_{NP} = k_{NP}^a / k_{NP}^d$	$1.0 \times 10^{-23} \text{ m}^3$ (Figure 2)
$K_{NP} = k_{NP}^a / k_{NP}^d$	$1.0 \times 10^{-22} \text{ m}^3$ (Figures 3 and 4)
ν_{NP}	0 (Figures 1–3) 10^{-5} ; 10^{-4} ; 10^{-3} ; 10^{-2} (Figure 4)
μ	$4.0 \times 10^{-10} \text{ m}^2/\text{Vs}$ (Figures 1–4)

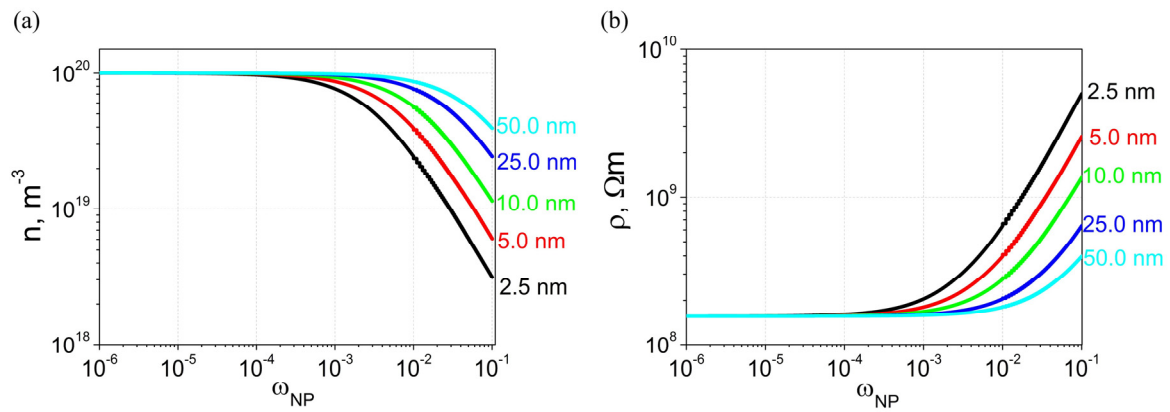


Figure 1. (a) The dependence of the concentration of mobile ions n on the weight concentration of nanoparticles ω_{NP} . (b) The electrical resistivity of molecular liquid crystals as a function of the weight concentration of nanoparticles. $K_{NP} = 10^{-24} \text{ m}^3$.

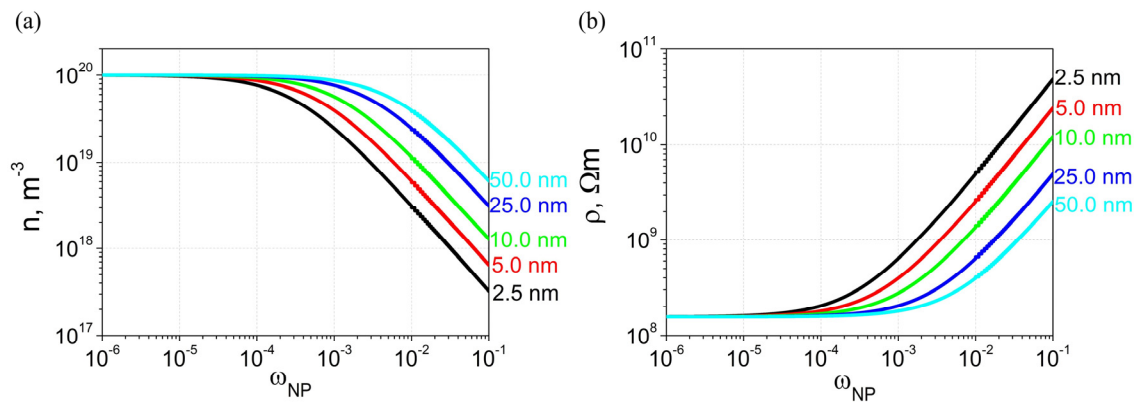


Figure 2. (a) The dependence of the concentration of mobile ions n on the weight concentration of nanoparticles ω_{NP} . (b) The electrical resistivity of molecular liquid crystals as a function of the weight concentration of nanoparticles. $K_{NP} = 10^{-23} \text{ m}^3$.

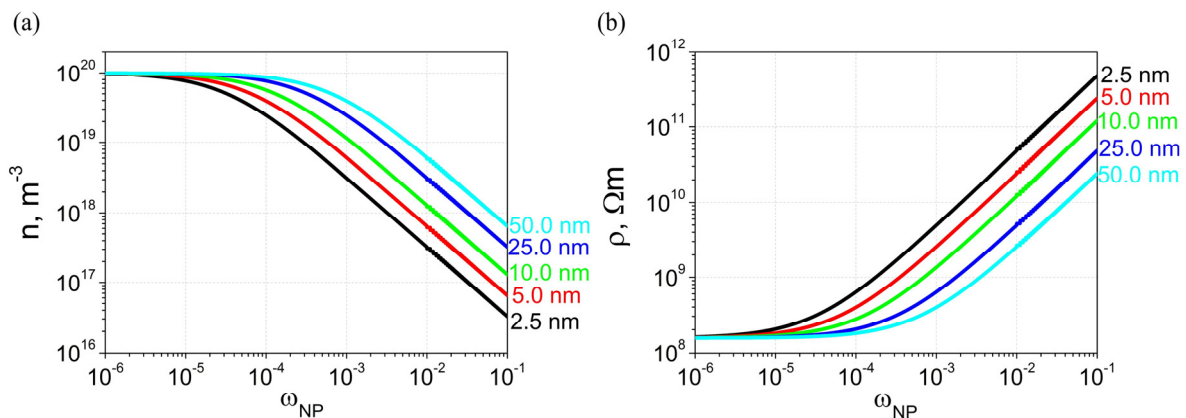


Figure 3. (a) The dependence of the concentration of mobile ions n on the weight concentration of nanoparticles ω_{NP} . (b) The electrical resistivity of molecular liquid crystals as a function of the weight concentration of nanoparticles. $K_{NP} = 10^{-22} \text{ m}^3$.

To account for different types of nanoparticles, such as ferroelectric, titanium dioxide, and carbon-based nanoparticles, we varied the value of parameter K_{NP} , which quantifies the ability of nanodopants to capture mobile ions (Table 1). The values of this parameter can vary within several orders of magnitude ($10^{-25} - 10^{-20} \text{ m}^3$) depending on the type of

nanomaterials, as discussed in greater detail in reviews [11,12]. In our paper, the chosen values of K_{NP} (10^{-24} m^3 ; 10^{-23} m^3 ; 10^{-22} m^3) overlap with the reported values for a variety of nanomaterials [11,12]. The concentration of nanoparticles ω_{NP} defined as the weight of the nanoparticles divided by the weight of a mixture (nanoparticles and liquid crystals) varies within a $10^{-6} - 10^{-1}$ range. The analyzed range ($10^{-6} - 10^{-1}$) indicates that the concentration of nanoparticles can vary from $10^{-4} \%$ up to 10% by weight.

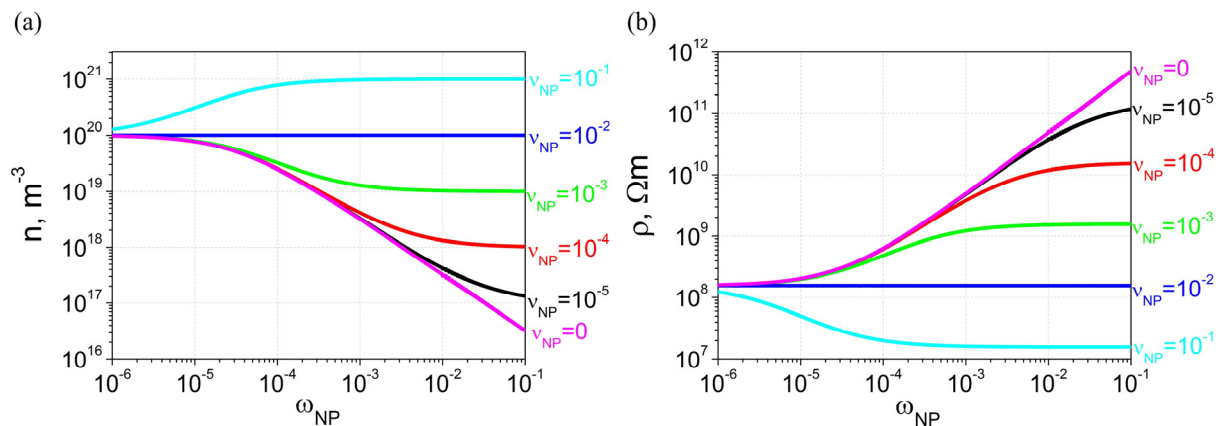


Figure 4. (a) The dependence of the concentration of mobile ions n on the weight concentration of nanoparticles ω_{NP} . (b) The electrical resistivity of molecular liquid crystals as a function of the weight concentration of nanoparticles. The radius of nanoparticles is 2.5 nm and $K_{NP} = 10^{-22} \text{ m}^3$.

Consider an ideal case of 100% pure nanoparticles (it corresponds to a contamination factor $v_{NP} = 0$). Once nanoparticles have been added to a liquid crystal host, they will capture some fraction of mobile ions, leading to a decrease in the volume concentration of free ions, as shown in Figure 1a. This decrease in the concentration of mobile ions results in a higher value of electrical resistivity, as shown in Figure 1b. According to Figure 1, larger concentrations of nanoparticles result in greater values of electrical resistivity of molecular liquid crystals. This effect becomes more pronounced if smaller nanoparticles are used (Figure 1b). For example, by reducing the radius of nanoparticles from 50 nm to 2.5 nm, the electrical resistivity can be enhanced by more than one order of magnitude (Figure 1b).

Figure 1 clearly shows that the electrical resistivity of molecular liquid crystals can be controlled by changing the size of nanoparticles (their radius R_{NP} varies from 2.5 nm to 50 nm) and by varying their weight concentration ω_{NP} . It should be noted that high concentrations of nanoparticles ($\omega_{NP} > 0.01$) can lead to aggregation phenomena and a percolation effect. In general, the aggregation and percolation effects can even change the type of major charge carriers [14–16]. In principle, this complication can be avoided in the following way. If higher concentrations of nanoparticles are used with the goal of enhancing the resistivity of liquid crystals via the ion-capturing effect, once ions are captured by nanodopants, they (nanoparticles with trapped ions) can be separated from a liquid crystal host using either an ultracentrifuge method [17], a harvesting technique (if nanoparticles are ferroelectric [18]) or a magnetic field (if nanoparticles are magnetic [19]). Because of this, in the present paper, we focus on ionic conductivity only.

Another important factor is the ability of nanoparticles to capture ions quantified by the parameter $K_{NP} = k_{NP}^a/k_{NP}^d$. In general, the value of this empirical parameter depends on the type of nanomaterials, the nature of ions, and the dielectric constant of liquid crystals [11–13]. Greater values of K_{NP} will result in higher values of the electrical resistivity, as evidenced from Figure 2 ($K_{NP} = 10^{-23} \text{ m}^3$) and Figure 3 ($K_{NP} = 10^{-22} \text{ m}^3$).

Figures 2 and 3 show the ion density as a function of the weight concentration of nanoparticles ω_{NP} (Figures 2a and 3a), and the dependence of the electrical resistivity ρ on ω_{NP} (Figures 2b and 3b).

Figure 3 indicates that the use of smaller nanoparticles with a larger value of the parameter K_{NP} can result in more than three orders of magnitude enhancement in the electrical resistivity of molecular liquid crystals.

An uncontrolled ionic contamination of nanomaterials can significantly affect the change in the electrical resistivity of molecular liquid crystals. Figure 4 shows a significant effect of the ionic contamination of nanoparticles on the ion density (Figure 4a) and on the electrical resistivity (Figure 4b).

Even minor levels of ionic contamination of nanoparticles can lead to a reduction in the values of electrical resistivity of molecular liquid crystals (Figure 4b). Moreover, higher levels of ionic contamination of nanoparticles ($v_{NP} > 10^{-2}$) can even reverse the sign of the effect, resulting in a decrease in the electrical resistivity (Figure 4).

4. Conclusions

The presented results (Figures 1–4) clearly indicate that the electrical resistivity of molecular liquid crystals can be enhanced by mixing them with nanoparticles. This effect can become very strong if smaller nanodopants are used. For example, Figure 3 shows a more than three-order-of-magnitude enhancement of the electrical resistivity of molecular liquid crystals doped with 5 nm-diameter nanoparticles. In principle, by using nanoparticles that effectively capture ions, it is possible to convert low-resistivity liquid crystals into high-resistivity liquid crystals. The performed analysis is in good agreement with recently reported experimental results [20] and offers additional insights into the dependence of the electrical resistivity of molecular liquid crystals on the size of nanoparticles and their ion-capturing properties.

It should be noted that the process of converting low-resistivity liquid crystals into high-resistivity liquid crystals is very sensitive to the ionic contamination of nanoparticles as evidenced from curves shown in Figure 4. Depending on the interplay between material parameters characterizing the tested system (they are listed in Table 1), ionic contamination of nanomaterials can result in several regimes corresponding to an increase in the electrical resistivity ρ , no change in ρ , and decrease in the values of ρ (Figure 4b).

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