

Review

## Nano-Objects and Ions in Liquid Crystals: Ion Trapping Effect and Related Phenomena

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**Abstract:** The presence of ions in liquid crystals is one of the grand challenges that hinder the application of liquid crystals in various devices, which include advanced 3-D and flexible displays, tunable lenses, *etc.* Not only do they compromise the overall performance of liquid crystal devices, ions are also responsible for slow response, image sticking, and image flickering, as well as many other negative effects. Even highly purified liquid crystal materials can get contaminated during the manufacturing process. Moreover, liquid crystals can degrade over time and generate ions. All of these factors raise the bar for their quality control, and increase the manufacturing cost of liquid crystal products. A decade of dedicated research has paved the way to the solution of the issues mentioned above through merging liquid crystals and nanotechnology. Nano-objects (guests) that are embedded in the liquid crystals (hosts) can trap ions, which decreases the ion concentration and electrical conductivity, and improves the electro-optical response of the host. In this paper, we (i) review recently published works reporting the effects of nanoscale dopants on the electrical properties of liquid crystals; and (ii) identify the most promising inorganic and organic nanomaterials suitable to capture ions in liquid crystals.

**Keywords:** nano-objects; nanoparticles; ions; liquid crystals; electrical conductivity; ion trapping; purification

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## 1. Introduction

Liquid crystals have become an important facet of modern technologies. Their numerous applications include displays and E-books, tunable filters and lenses for applied optics and biomedicine (hyper spectral imaging, ophthalmology), polarization control devices (tunable wave-plates, retarders, rotators, polarization generators), and components in optical processing systems (spatial light modulators and optical light valves). They are also used in adaptive optics, lasers, holography, optical communications (beam steering devices and optical waveguides), microwave technologies (tunable delay lines, phase shifters, antennas), and countless other areas [1–7]. Typically, commercial devices based on molecular liquid crystals are driven by an electric field. Liquid crystals used in such devices should exhibit high electrical resistivity (or low electrical conductivity) of the order of  $10^{10}$ – $10^{12}$   $\Omega\cdot\text{m}$  (or  $10^{-10}$ – $10^{-12}$  S/m) [2]. However, ions are always present in liquid crystals [2,8]. Their negative impact on the overall performance of liquid crystal devices was reported in many publications [9–18]. For example, ions in liquid crystals can cause slow response, image sticking, image flickering, the reduction of the voltage holding ratio, and color staining and non-uniformity of the image, to name a few. As a result, an ionic contamination of the liquid crystals is very undesirable and should be minimized.

Although the existing liquid crystals can be considered “pure enough” for many applications used nowadays, the problem of the *uncontrolled* ionic contamination during the manufacturing process is still among the grand challenges the liquid crystal industry continues to face. Recent studies revealed that after the completion of the liquid crystal display (LCD) cell manufacturing process, the resistivity of liquid crystals can decrease by more than two orders of magnitude because of uncontrolled contamination [19].

Considering the large impact of this problem and the wide-spread use of liquid crystal devices in our daily life, the development of new concepts for the purification of liquid crystals is of utmost importance to the modern, technology-driven society. In this manuscript, we will review how nanotechnology can contribute to the solution for the difficulties stemming from liquid crystal contamination. We will focus on *molecular* liquid crystals characterized by ionic conductivity; liquid crystals exhibiting *electronic* conductivity are beyond the scope of this manuscript, and we refer interested readers to the available literature [20–22] for more details. In addition, we would like to mention materials called *ionic liquid crystals* [23,24]. They exhibit high ionic electrical conductivity, and are promising for numerous non-display applications [25,26].

The main body of this manuscript is composed of two sections. Each section is divided into several subsections. The first section of the review provides a general description of ions in liquid crystals and issues associated with ionic contamination. This section is followed by an experimental example of liquid crystals driven by an electric field. The second section contains five subsections. Classical methods of liquid crystal purification are briefly outlined in the first subsection, which is followed by the practical example of high resistivity liquid crystals. The rest of the second section reviews effects of different nanoparticles (carbon-based, metallic, dielectric, semiconductor, ferroelectric, and conducting polymers) on the electrical conductivity of liquid crystals, and aims to identify the most promising candidates for their purification. Nanoparticles made of such materials and then dispersed in liquid crystals can trap mobile ions, thus decreasing their concentration and providing a *permanent*

purification of liquid crystals. The remaining challenges and future courses of action are summarized in the Section 4.

## 2. Ions in Liquid Crystals and Methods of Liquid Crystal Purification

### 2.1. Issues Associated with Ions in Liquid Crystals from Electro-Optical Perspectives

#### 2.1.1. Ions in Liquid Crystals

Ions are inherently present in molecular liquid crystals and are the origin of their finite electrical conductivity [2,8–19].

The electrical conductivity of thermotropic liquid crystals can vary depending on the type of the materials ( $10^{-7}$ – $10^{-13}$  S/m). For example, classical liquid crystals based on cyanobiphenyls such as 5CB, E7 exhibit an electrical conductivity of the order of  $10^{-7}$ – $10^{-8}$  S/m [8,27]. The electrical conductivity of TL-series liquid crystals (a mixture of cyclohexane-fluorinated biphenyls and fluorinated terphenyls) is of the order of  $10^{-10}$  S/m [28].

Ions in liquid crystals can originate from different sources. The most important are ionic dissociations of the residual impurities [2,29], ionic contamination during the manufacturing process (the alignment layers, the glue, and the filling process are the sources of the contaminations) [19,30], charge injection, charge transfer and electrochemical reactions in the electrodes and/or in the bulk of the liquid crystal cell [2,31–35], and aging (chemical decomposition and self-dissociation of liquid crystals) [2,11]. The simultaneous presence of more than one of the processes mentioned above is a very common thing and should be considered by experimentalists [2,36,37].

The electrical conductivity  $\sigma$  is proportional to the charge of ions  $q$ , their concentration  $n$ , and their mobility  $\mu$  [2]. Assuming that the electrical conductivity is caused by monovalent ions ( $q = e$ , the charge of an electron), the following equation can be written ( $\mu_+$  ( $\mu_-$ ) is the mobility of the positive (negative) ion):

$$\sigma = e(\mu_+ + \mu_-)n \quad (1)$$

The electrical conductivity, the ion mobility, and the concentration of ions are the basic parameters needed to describe an ion transport in liquid crystals *quantitatively*. Their values can be found experimentally by using the methods of dielectric spectroscopy [38–41] and transient current measurements [42–46], which can also be supplemented with electro-optical measurements [47,48]. The concentration of ions in liquid crystals can vary from  $10^{16}$  to  $10^{22}$   $\text{m}^{-3}$  depending on the purity and type of liquid crystals [2]. The mobility of ions is of the order of  $10^{-9}$ – $10^{-10}$   $\text{m}^2 / \text{V} \times \text{s}$ . Table 1 shows examples of the electrical parameters of the most widely studied liquid crystals, 5CB (4-Cyano-4'-pentylbiphenyl) and E7 (a quaternary mixture of cyanobiphenyls), measured at room temperature. (Note: the anisotropy of liquid crystals results in the anisotropy of the electrical conductivity; as a result, the electrical conductivity  $\sigma_{||}$  (or the mobility  $\mu_{||}$ ) measured along the director is different than those values ( $\sigma_{\perp}$ ,  $\mu_{\perp}$ ) measured in a perpendicular direction).

**Table 1.** Electrical parameters of some liquid crystals.

Liquid Crystals	5CB [8]	E7 [27]
Ion mobility, $m^2 / V \times s$	$\mu_{  } = 3.16 \times 10^{-10}$ $\mu_{\perp} = 1.92 \times 10^{-10}$	$\mu_{  } = 2.8 \times 10^{-10}$ $\mu_{\perp} = 1.1 \times 10^{-10}$
Ion concentration, $m^{-3}$	$n = 1.85 \times 10^{20}$	$n = 1.42 \times 10^{21}$
Electrical conductivity, S/m	$\sigma_{  } = 0.9 \times 10^{-8}$ $\sigma_{\perp} = 0.6 \times 10^{-8}$	$\sigma_{  } = 5.7 \times 10^{-8}$ $\sigma_{\perp} = 2.6 \times 10^{-8}$

### 2.1.2. Practical Example: Electro-Optics of Liquid Crystals Driven by DC Field

When an electric field is applied across the liquid crystal cell, positive ions move in the direction of the negative electrode, and negative ions drift toward the positive electrode (an electric field-induced space charge separation). Charges accumulated near electrodes become the source of the electric field  $\mathbf{E}_{ions}$ . This field acts against the applied electric field  $\mathbf{E}$ , resulting in the decrease of the total electric field  $\mathbf{E}_{ions} + \mathbf{E}$  (the charge screening effect), and the alteration of the electro-optical response of the liquid crystal cell.

A practical example of the charge screening effect is shown in Figure 1. A DC electric field is applied across a liquid crystal cell with planar boundary conditions. The cell is placed between two crossed polarizers (the angle between the director and the polarizer's axis is  $45^\circ$ ), and the light passing through the cell is detected by a photo-diode. The applied DC electric field reorients liquid crystal E7 from the planar state toward the homeotropic state (S-effect). As a result, the effective birefringence  $\Delta n$  of liquid crystals changes, leading to the changes in the optical phase shift  $\Delta\Phi$ . The experimentally measured physical quantity is the intensity of the transmitted light  $I(t)$ , which is related to  $\Delta\Phi$  according to the Expression (2) [2]:

$$I(t) = I_0 \left( \sin \left( \frac{\Delta\Phi(t)}{2} \right) \right)^2 \quad (2)$$

where  $I_0$  is the intensity of the incident light, and the electrically induced  $\Delta\Phi$  is expressed by Equation (3):

$$\Delta\Phi = \frac{2\pi}{\lambda} d\Delta n \quad (3)$$

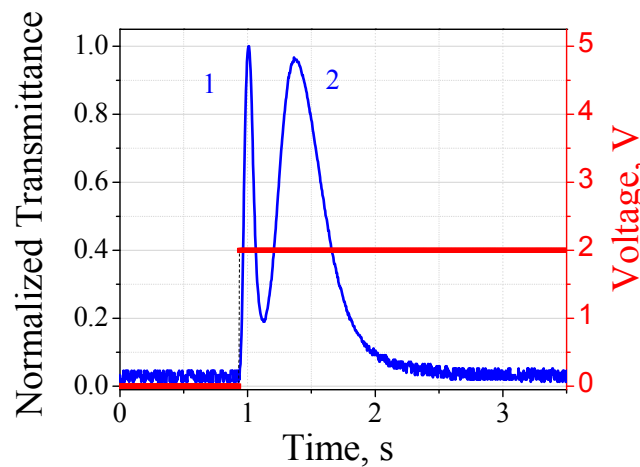
( $\lambda$  is the wavelength of the light, and  $\Delta n$  is the effective optical birefringence of liquid crystals). Thus, by measuring  $I(t)$  we can deduce  $\Delta\Phi$  and  $\Delta n$ .

The electro-optical response shown in Figure 1 exhibits two peaks; the first peak (labeled as "1") is relatively fast (less than a fraction of a second), and the second one (marked as "2") is relatively slow (around one second). Peak 1 shown in Figure 1 corresponds to the reorientation of the liquid crystal from a planar orientation toward a homeotropic. The time  $t_{ON}$  needed to complete this reorientation can be estimated by applying the expression Equation (4):

$$t_{ON} = \frac{\gamma d^2}{\varepsilon_0 |\Delta\varepsilon| U^2 - \pi^2 K_{ii}} \quad (4)$$

For the considered cell geometry (S-effect) and liquid crystals (E7) under study ( $d = 20 \mu\text{m}$ ;  $U = 2\text{V}$ ;  $\gamma = 0.25 \text{ Pa} \times \text{s}$ ;  $K_{ii} = 11.7 \text{ pN}$ ;  $\Delta\epsilon \approx 14$  [49,50]) the Equation (4) yields  $t_{ON} \approx 0.26 \text{ s}$ , which is in good agreement with the experimental data. At the same time, the ions present in the liquid crystal move toward the substrates under the action of the DC electric field. These ions generate the screening field  $\mathbf{E}_{ions}$ , which is opposite to the external field  $\mathbf{E}$ . As a result, the combined electric field  $\mathbf{E}_{ions} + \mathbf{E}$  decreases over time, and the liquid crystal reorient back toward the initial planar state. This process is reflected by Peak 2, shown in Figure 1. The time  $t_{ions}$  needed to develop the screening electric field can be estimated when considering an ion drifting with the velocity  $v$  through the distance  $d$  (the gap between two electrodes):

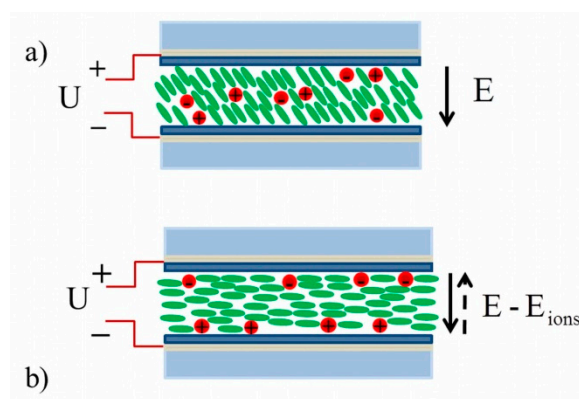
$$t_{ions} \approx \frac{d}{v} = \frac{d^2}{\mu U} \quad (5)$$



**Figure 1.** The electro-optical response of a liquid crystal cell filled with nematic liquid crystal E7 (planar boundary conditions). (Drawn after Ref. [51]).

By applying the expression Equation (5) and using the data shown in Table 1 ( $\mu \approx \frac{\mu_{||} + 2\mu_{\perp}}{3} = 1.7 \times 10^{-10} \text{ m}^2 / \text{V} \times \text{s}$ ) we can find  $t_{ions} \approx 1.2 \text{ s}$ . The experimental data agrees well with this estimation. Figure 2 provides a schematic representation of the discussed processes. The Figure 2a shows the reorientation of the liquid crystals under the action of the applied electric field, and the screening effect is shown in Figure 2b.

In the considered example, the screening electric field compensates for the applied electric field in less than 2 s, resulting in the substantial alteration of the liquid crystal performance. An extensive discussion of the ion-related phenomena in liquid crystals are beyond the scope of this paper, and readers are referred to the original publications [9–22,27–48,52–80] and references therein] for more details.



**Figure 2.** (a) Schematic representation of the liquid crystal reorientation under the action of a DC electric field; (b) Applied electric field  $E$  is screened by the field  $E_{\text{ions}}$  of the space-separated ions in the liquid crystal. (Drawn after Ref. [51]).

## 2.2. The Purification of Liquid Crystals: Classical and Emerging Methods

The abovementioned example is a good illustration of the negative impact of ions on the electro-optical performance of liquid crystals. Had the concentration of ions in the liquid crystals been negligibly small, these effects would never happen. Therefore, the importance of the purification of liquid crystals is impossible to overstate.

### 2.2.1. Classical Methods of Liquid Crystal Purification

According to the existing literature, inorganic ions ( $Na^+$ ,  $NH_4^+$ ,  $K^+$ ,  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Zn^{2+}$ ,  $Al^{3+}$ ,  $F^-$ ,  $Cl^-$ ,  $NO_2^-$ ,  $NO_3^-$ ,  $Br^-$ ,  $SO_4^{2-}$ ) are major contributors to the electrical conductivity of liquid crystals [8,19]. This conclusion was also supported by the experimentally observed correlation between the measured conductivity of liquid crystals and the concentration of free inorganic ions, in line with the expression Equation (1) [8]. It should be noted that some liquid crystals can become chemically unstable, and the probability of this process is higher under harsh conditions such as elevated temperatures, high electric fields, and an exposure to the strong UV light [2,11,81,82]. All these factors create additional sources of ions of organic origin [82]. However, recent advances in the chemical synthesis of novel liquid crystal materials exhibiting improved chemical stability reduced the probability of such events significantly [83–86].

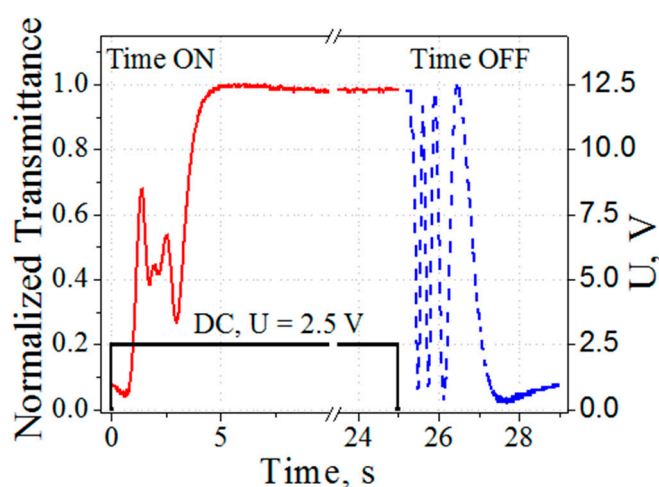
Liquid crystals can get contaminated with ionic impurities during the process of chemical synthesis. The level of this contamination can be reduced by working with highly purified reagents at the stage of chemical synthesis, and by using classical methods such as multiple recrystallization, extraction, vacuum distillation, vacuum sublimation, zone refining, chromatography, ion exchange and other chemical techniques [82,87,88]. Physical-chemical methods used to purify liquid crystals can be applied multiple times to reach a certain level of the chemical purity. The chemical purity of synthesized liquid crystal materials can be checked with the help of high performance liquid chromatography (HPLC), nuclear magnetic resonance (NMR) and electronic paramagnetic resonance (EPR), and differential scanning calorimetry (DSC), to name a few [82,89–91]. However, if not specifically tailored, these methods do not provide information on the ionic content of liquid crystals [82]. Analysis of ionic impurities in liquid

crystals can be done by means of ion chromatography [8,92]. The content of metal ions in liquid crystals can also be analyzed by using high resolution inductively coupled plasma mass spectroscopy [19]. Combined with the electrical conductivity measurements, all above-mentioned methods provide enough information regarding the purity of liquid crystals.

If the level of ionic impurities in liquid crystals is higher than needed, it can be reduced by applying the method of *electrodialysis* [93,94]. The electrodes (the typical distance between electrodes is 6–10 mm) of the liquid crystal cell are covered with semipermeable membranes; the anode's membrane is selectively permeable to negatively charged impurities, and the cathode's membrane is permeable to positive ions only. For example, the electric field ( $\sim 500$  V/cm) applied across the cell for 2 h can decrease the electrical conductivity by more than two orders of magnitude [93]. It should be noted that some ions cannot be removed by using this technique [94].

### 2.2.2. Practical Example: Electro-Optics of Highly Purified Liquid Crystals Driven by a DC Field

By applying the proper chemical design along with the methods of chemical synthesis and post-synthetic techniques, many improved liquid crystal materials were successfully produced and tested in numerous applications [2,28,83–86]. The high resistivity liquid crystals are characterized by extremely low levels of ionic impurities. As a result, such materials are much more reliable than their contaminated counterparts considered in the Section 2.1.2. Ion related effects are hardly observed in the high resistivity liquid crystals (assuming they are not accidentally contaminated). For example, the charge screening effect, which is easily detectable in liquid crystal E7, (Figure 1) is practically not observable in the case of the high resistivity liquid crystal TL205 (a mixture of cyclohexane-fluorinated biphenyls and fluorinated terphenyls) (Figure 3, the experimental set up of which is the same as in Figure 1). A DC electric field applied across the liquid crystal cell reorients the liquid crystal molecules (the reorientation region is shown as “Time ON” in Figure 3). After the reorientation process is completed, the reached level of the transmittance of the liquid crystal cell does not change (the electric field is still applied across the cell). When the electric field is turned off, the liquid crystal molecules reorient back to their initial planar state (Figure 3, the region “time OFF”).



**Figure 3.** Electro-optical response of liquid crystals TL205. Reproduced by courtesy of Y. Garbovskiy.

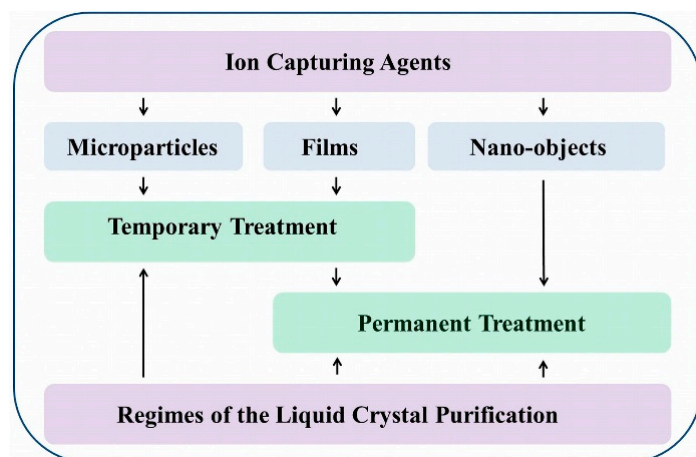
The same experiment conducted with two different liquid crystals yields quite different results (compare Figures 1 and 3). This experimental fact highlights once more the importance of controlling the level of ionic impurities in liquid crystals.

### 2.2.3. Emerging Methods of the Liquid Crystals Purification by Means of Ion Capturing Agents

The methods of the liquid crystal purification mentioned above are either expensive or time and labor consuming. In addition, the possibility of the uncontrolled post-synthetic contamination of liquid crystals always exists. Even highly purified liquid crystals can get contaminated at the stage of device fabrication or during its daily use [19,30]. In some cases, the contamination can increase the electrical conductivity of liquid crystals by more than two orders of magnitude [19]. As a result, the specially designed high resistivity liquid crystals do not exhibit ultra-low electrical conductivity anymore, and all problems associated with ions in liquid crystals arise and alter the performance of the liquid crystal device in very undesirable way. Therefore, there is a need for new ways to purify liquid crystals, which includes the development of a method for *permanent purification* of liquid crystals.

Recently, some alternative approaches of liquid crystal purification were suggested [95–101]. The underlying idea is to treat liquid crystals with ion-capturing agents. An ion capturing agent traps ions in liquid crystals, thus reducing the concentration of mobile ions. A quite broad range of materials was suggested as the ion-capturing agent: porous particles [95–97], oxide nanoparticles [98], ion capturing films [102–104], and metal-organic frameworks [99–101].

Consider the ion-capturing agents fabricated in the form of films, microparticles, and nanoparticles. Such ion capturing agents can be used for both temporal and permanent purification of liquid crystals, as shown schematically in Figure 4.



**Figure 4.** Regimes of the liquid crystal purification by means of ion capturing agents.

Microparticles made of ion capturing materials can be mixed with contaminated liquid crystals, and, after the ion trapping process is completed, filtered out. Since micro-particles distort the alignment of liquid crystals, creating defects and leading to strong light scattering, they are good only for the temporary treatment of liquid crystals, and cannot be considered as candidates for permanent purification (Figure 4). On the other hand, nano-objects such as nanoparticles can be dispersed in a liquid crystal host homogeneously, without the distortion of the surrounding liquid crystal molecules. Such nanoparticles



dispersed in liquid crystals can trap ions generated during the device use, thus providing permanent purification for the liquid crystals. At the same time, the use of nanoparticles is not the best option for the temporary treatment of liquid crystals because it is not easy to filter them out. Ion capturing films can be utilized in both regimes of the liquid crystal purification (Figure 4). However, the film used for the permanent treatment of liquid crystals should be able to serve as an alignment layer, and also either be transparent or exhibit excellent reflection properties in the visible diapason. These requirements limit the number of available materials to produce such films. In contrast, nanoparticles can be made of practically any materials, and are easily embedded in liquid crystals. Since the well-developed surface (in other words, the high surface to volume ratio) and strong enough attractive interactions between the surface of the purifying agents and the ion are the two major factors affecting the trapping efficiency, nanoparticles known for their extremely high surface to volume ratio are promising candidates for the development of the ion capturing agents. Recent progress in the design of nanomaterials and their successful incorporation in liquid crystals [105–117] provides the foundation for considering nano-objects embedded in liquid crystals as ion capturing agents. We will discuss the property of nanoparticles to trap ions in the next section of this manuscript.

### 3. Effect of Nanomaterials on the Electrical Properties of Liquid Crystals

The intriguing properties of nanoparticles in liquid crystals are being actively studied in many laboratories around the globe, and we refer readers to review manuscripts available on this subject for more details [105–117]. In this section, we will analyze the existing literature from the perspective of the ion capturing phenomenon. To accomplish this task, we will discuss the effects of nano-objects made of different materials (carbon-based, metal, dielectric, semiconductor, ferroelectric, organic) on the electrical conductivity of liquid crystals.

#### 3.1. Carbon-Based Nano-Objects in Liquid Crystals

Effects of various carbon-based nanomaterials (fullerenes, graphene, carbon nanotubes, diamond nanoparticles, and carbon dots) on electrical properties of liquid crystals have been reported in numerous papers [105,116,118–153]. Table 2 provides a short summary of the reported effects. As can be seen, both decrease [118,119,121–127,143–152] and increase [105,120,128–142,150–153] in the electrical conductivity of liquid crystals doped with carbon-based nanomaterials were reported.

In the case of ferroelectric liquid crystals (FLC) doped with fullerenes  $C_{60}$ , 0.5 wt. % of  $C_{60}$  mixed with FLC reduced the concentration of ions in FLC from  $2.6 \times 10^{21} m^{-3}$  to  $5.3 \times 10^{20} m^{-3}$  [118].

The effects of carbon-based nanoparticles (fullerene and carbon nanotubes) on the reduction of the screening effect in nematic liquid crystals (NLC) were reported in [119,143]. In the presence of ions, the reduction of the DC voltage  $U$  applied across the symmetric liquid crystal cell caused by the screening effect can be expressed as Equation (6) [119]:

$$U_{LC} = U - \frac{2qn(d_{LC})^2 d_{AL} \epsilon_{AL}}{\epsilon_0 (2d_{AL} \epsilon_{AL} \epsilon_{LC} + \epsilon_{AL}^2 d_{LC})} \quad (6)$$

where  $U$  is the DC voltage applied across the liquid crystal cell;  $U_{LC}$  is the effective voltage applied across the liquid crystal layer,  $q$  is the elementary charge;  $n$  is the concentration of ions;  $\epsilon_0$  is the

electric constant;  $d_{LC}$  and  $\varepsilon_{LC}$  are the thickness and the dielectric constant of liquid crystals;  $d_{AL}$  and  $\varepsilon_{AL}$  are the thickness and the dielectric constant of the alignment layers, respectively. The Equation (6) simplifies for cells without alignment layers to the easily derivable expression Equation (7):

$$U_{LC} = U - \frac{qnd_{LC}^2}{\varepsilon_0\varepsilon_{LC}} \quad (7)$$

Results reported in [119] suggest reducing the concentration of mobile ions in liquid crystals through ion capturing by means of carbon-based nanomaterials (fullerenes and carbon nanotubes, ~0.02 wt. %).

The authors of [143] tried to quantify the effect of the ion capturing reported in [119] by introducing the ion trapping coefficient  $k$ . This coefficient can be defined by writing the concentration  $n$  of the mobile ions in liquid crystals doped with carbon nanomaterials in the form of the expression Equation (8):

$$n = (1 - k)n_0 \quad (8)$$

where  $n_0$  is the concentration of the mobile ions in plain (non-doped) liquid crystals. If  $k = 1$ , then according to Equation (8),  $n = 0 \text{ m}^{-3}$ , and all ions are trapped. For the ion trapping nano-materials the following requirement  $0 < k \leq 1$  always holds true. What is interesting, the coefficient  $k$  can also be applied to materials causing an ionic contamination of liquid crystals. In this case, the ion trapping coefficient  $k$  is negative,  $k < 0$  and, according to Equation (8), the doping of liquid crystals with such materials leads to the increase in the concentration of ions.

**Table 2.** Effect of carbon-based nanomaterials on the electrical properties of liquid crystals.

Carbon-Based Nanomaterials	Liquid Crystals *	Results	Ref.
<i>Fullerenes</i>	FLC	Decrease in ion concentration	[118]
	NLC	Ion trapping	[119,141]
	NLC	Increase in the conductivity	[120]
<i>Graphene</i>	FLC	Reduced AC conductivity and dielectric losses	[121–123]
	NLC	Decrease in ion concentration	[124,125]
	CLC	Decrease in ion concentration	[126]
<i>Carbon Nanotubes</i>	NLC	Increase in the conductivity	[105,127–137]
	PDLC	Increase in the conductivity	[138]
	CLC	Increase in the conductivity	[139]
	FLC	Increase in the conductivity	[140–142]
	NLC	Ion trapping	[126,143–145]
	FLC	Decrease in the conductivity/dielectric losses	[146–149]
<i>Diamond Nanoparticles</i>	NLC	Both decrease and increase in the conductivity	[150–152]
<i>Carbon Dots</i>	FLC	Increase in the conductivity	[153]

\* FLC—ferroelectric liquid crystals; NLC—nematic liquid crystals; CLC—cholesteric liquid crystals; PDLC—polymer dispersed liquid crystals.

In [143], the concentration of carbon nanomaterials in the nematic liquid crystal E7 was set to 0.05 wt. %, and the reported values of the ion trapping coefficient were 0.1 (fullerenes), 0.315

(carbon nano-fibers), 0.24 (carbon nano-coils), 0.3–0.343 (multi-wall carbon nanotubes), and 0.18 (single wall carbon nanotubes).

The authors of [119] mentioned that the use of thicker cells ( $\sim 25 \mu\text{m}$ ) instead of thinner cells ( $\sim 5 \mu\text{m}$ ) facilitates the sample degradation through the aggregation of nanomaterials dispersed in liquid crystals. Thicker cells ( $\sim 25 \mu\text{m}$ ) and higher concentrations of the modified fullerenes (0.1–3 wt. %) in the nematic liquid crystal E25M (cyanobiphenyls/terphenyl mixture) were explored in [120]. It was found that liquid crystals doped with modified fullerenes exhibit higher electrical conductivity than their non-doped counterparts; and the experimental data can be satisfactorily described by the simple power law Equation (9) [120]:

$$\sigma \propto C^m \quad (9)$$

Where  $m = 0.3 \pm 0.04$  (planar alignment), and  $m = 0.46 \pm 0.04$  (homeotropic alignment). All studied samples exhibited a high degree of aggregation with the percolation threshold at 2.0–2.5 wt. % [120].

The electrical properties of liquid crystals doped with graphene were reported in [121–126]. According to [121], graphene sheets, implemented in the design of ferroelectric liquid crystal cell as alignment layers, reduce the electrical conductivity by a factor of  $\sim 10$ . This reduction in the conductivity was associated with the charge annihilation process; ionic impurities combine with the surface charge of the graphene, thus annihilating each other [121]. Graphene flakes, mixed with ferroelectric liquid crystal MX40636 ( $\sim 0.04$  wt. %), reduced the concentration of mobile ions by a factor of 4 [122]. The authors of [122] proposed that the electrostatic field of the graphene sheets (the diameter of the graphene flakes was within the range from 0.5 to 3  $\mu\text{m}$ ) was responsible for the ion capturing and the observed decrease in the concentration of ion. Nano-flakes made of the reduced graphene oxide and mixed with ferroelectric liquid crystals ( $\sim 0.5$  wt. %) led to a noticeable decrease in the imaginary part of the dielectric permittivity of FLCs [123]. It was suggested that this decrease is caused by the ion compensation/neutralization [123].

The effect of graphene nanoplatelets on the concentration of ions  $n$  in liquid crystal 8OCB (n-octyl cyano biphenyl) was reported in [124]. It was found that the 0.5 wt.% dopant content led to the reduction of  $n$  from  $2.5 \times 10^{18} \text{ m}^{-3}$  to  $1.7 \times 10^{18} \text{ m}^{-3}$ , by 30% [124]. The two-fold reduction in the concentration of mobile ions was also demonstrated in [125] for liquid crystal 5CB doped with graphene ( $\sim 0.005$  wt. %). An approximately 32% reduction in the concentration of ions (from  $2.53 \times 10^{19} \text{ m}^{-3}$  to  $1.72 \times 10^{19} \text{ m}^{-3}$ ) was reported in [126] for cholesteric liquid crystals (CLC) doped with graphene nanoplatelets (0.5 wt. %). The ion trapping by graphene nanomaterial was suggested to explain experimental results reported in [125,126].

The electrical properties of liquid crystals doped with carbon nanotubes (CNT) were explored in numerous papers [105,116,127–149]. The majority of these manuscripts [105,116,117,128–142] report the enhancement of the electrical conductivity  $\sigma$  of liquid crystals doped with carbon nanotubes. The increase in  $\sigma$  is associated with the percolation phenomenon and high intrinsic electrical conductivity of carbon nanotubes: a sharp transition from the ionic conductivity to the dominating charge hopping conductivity occurs at a certain concentration called the percolation concentration [105,116]. The measured electrical conductivity obeys the scaling Equation (10) [105,116]:

$$\sigma \propto (C - C_p)^f \quad (10)$$

where  $C_p$  is the percolation concentration, and  $t$  is the transport exponent (or transport index). Typically, the percolation concentration is of the order of 0.001–0.1 wt. %, and the transport exponent  $t = 0.5 - 0.6$ .

The percolation phenomena hinder/mask the ion trapping effects in liquid crystals doped with carbon nanotubes. Nevertheless, there are some papers reporting the suppression of ion-related effects in liquid crystals [119,127,143–149]. The ion trapping coefficient Equation (8) of carbon nanotubes was found to be 0.18–0.34 depending on the type of the CNT [143]. Computations reported in [127] pointed to the possibility of the existence of the permanent dipole moment in the CNT. This dipole moment can facilitate the ion capturing in the super-fluorinated LC mixtures doped with carbon nanotubes (0.0005–0.001 wt. %) [127–129]. The reduction of the charge concentration (from  $0.40 \text{ C/m}^3$  to  $0.27 \text{ C/m}^3$ ) and the diffusion constant (from  $2.21 \times 10^{-10} \text{ m}^2/\text{s}$  to  $1.47 \times 10^{-10} \text{ m}^2/\text{s}$ ) in the nematic liquid crystal E7 doped with carbon nanotubes (0.05 wt. %) was reported in [144]. This observation suggests that carbon nanotubes can absorb the ionic impurity and hinder the ion transport in liquid crystals [144]. Comparative studies of the high resistivity (CYLC-01) and low resistivity (E7) nematic liquid crystals doped with carbon nanotubes (0.05 wt. %) were performed in [145]. Carbon nanotubes did not change the electrical properties of the high resistivity liquid crystal CYLC-01, but reduced the concentration of ions in the low resistivity liquid crystal E7 (the voltage holding ratio was improved from 48% to 61%) [145].

Copper oxide decorated carbon nanotubes (0.5 wt. %)/ferroelectric liquid crystal (commercial name: KCFLC 7S) composites were studied in [146]. In such systems, the reduced concentration of ions (deduced from the observed ~1.5-fold decrease in the dielectric loss factor and the simultaneous 1.75-fold increase in the measured resistance of the sample) was attributed to the ion trapping by the copper oxide decorated carbon nanotubes [146]. Improvements in the electro-optical performance of ferroelectric liquid crystals (commercial name: LAHS7) doped with carbon nanotubes (0.01 wt. %) were also attributed to the trapping of ions through the carbon nanotubes [147].

Electrical properties of nematic liquid crystals (E7 of different purity and MLC6609 (commercially available liquid crystal mixture exhibiting negative dielectric anisotropy)) doped with diamond nanoparticles (0–4 wt. %) were reported in [151,152]. It was found that diamond nanoparticles (DNPs) decrease the electrical conductivity  $\sigma$  of low-resistivity liquid crystals such as E7. At the same time, DNPs increase  $\sigma$  of the high resistivity liquid crystals (MLC6609 or purified E7) [151,152]. The concentration dependence of the electrical conductivity is very nonlinear, pointing to the manifestation of some percolation processes [152]. The observed results were explained by considering different ratios of the ion adsorption / ion desorption at the nanoparticle's surface: the desorption of ions from the surface of DNPs with the ion transfer along the surface of interconnected particles leads to the increase in the electrical conductivity, while the adsorption of ions at the nanoparticle's surface accounts for the decrease in electrical conductivity [151,152].

### 3.2. Metal Nanoparticles in Liquid Crystals

Metal nanoparticles are widely used as dopants to modify/change/alter the physical properties of liquid crystals [106–108,110,113,115]. Table 3 provides a short summary of their effects on the electrical

properties of liquid crystals [154–172]. The majority of published papers report an increase in the electrical conductivity of liquid crystals doped with metal nanoparticles [156–158,160–167,169,171]. In some cases, (columnar liquid crystals doped with gold nanoparticles with the concentration of the order of 1 wt. %) such an increase can be as high as six orders of magnitude [160–164]. This increase in the conductivity is attributed to the formation of chains of gold nanoparticles [162,164]. The high electrical conductivity of nematic liquid crystal—gold nanoparticle nano-composites can be enhanced even more by mixing them with dielectric aerosil particles [165]. The formation of chains and networks of metal nanoparticles in liquid crystal nano-composites points to the involvement of the percolation processes. Indeed, the concentration dependence of the electrical conductivity of the nematic liquid crystal PCPBB doped with gold nanoparticles was well described by the percolation scaling law Equation (10) with  $t = 0.63 \pm 0.03$  [157].

**Table 3.** Effect of metal nanoparticles on the electrical properties of liquid crystals.

Metal Nanoparticles	Liquid Crystals *	Results	Ref.
<i>Gold</i>	FLC	Reduced AC conductivity and the charge transfer	[154,155]
	NLC	Two orders increase in the conductivity	[156–158]
	CLC	Capture and release of ions	[159]
	CoLC	Five-six orders increase in the conductivity	[160–164]
<i>Gold and Aerosil</i>	NLC	Enhancement of the electrical conductivity	[165]
<i>Palladium</i>	NLC	Increased dielectric losses	[166]
<i>Silver</i>	NLC	Increased anisotropy of the conductivity	[167]
	FLC	Ion trapping	[168]
<i>Copper</i>	CoLC	Enhancement of the electrical conductivity	[169]
<i>Nickel</i>	NLC	Ion trapping	[170]
	FLC	Increase in the conductivity	[171]
<i>Titanium</i>	NLC	Ion trapping	[172]

\* FLC—ferroelectric liquid crystals; NLC—nematic liquid crystals; CLC—cholesteric liquid crystals; CoLC—columnar liquid crystals.

The ion capturing through functionalized metal nanoparticles dispersed in liquid crystals was reported in [154,159,168,170,172]. Ferroelectric liquid crystal LAHS 9 doped with decanethiol/dodecanethiol capped silver nanoparticles (0.1 wt. %) exhibited an increase in the resistivity as compared to the pristine FLC [168]. According to [168], the decanethiol/dodecanethiol organic layer around the silver nanoparticle's surface can capture positive and negative ions, leading to the reduction of the conductivity. The ion capturing effect was also discussed in [154]. Functionalized gold nanorods decorated with siloxane based nematogenic ligands and ionic surfactant cetyltrimethylammonium bromide (CTAB) dispersed in ferroelectric liquid crystal decreased the AC electrical conductivity of FLC from  $2.6 \times 10^{-9} S/m$  to  $2.2 \times 10^{-9} S/m$  (0.25 wt. %), and to  $1.9 \times 10^{-9} S/m$  (0.5 wt. %) [154].

The decrease in the electrical conductivity (from  $9.95 \times 10^{-10} S/m$  to  $3.77 \times 10^{-10} S/m$ ) of the cholesteric liquid crystal BL094 doped with 0.5 wt. % gold nanoparticles, stabilized by means of the electrostatic capping made of citrate ions, was reported in [159]. This decrease in the electrical conductivity was measured by applying 100 mV across the 8  $\mu m$  thick cell, and the adsorption of ionic

impurities at the nanoparticle's surface was proposed to explain the observed result. Further increase in the applied voltage (up to 20–40 V) led to the increase in the electrical conductivity [159]. These two results were obtained by using two different experimental methods (an impedance spectroscopy at low electric fields, and the cyclic voltammetry at high electric fields), and a certain degree of caution is needed to interpret them [159]. To explain the increase in the electrical conductivity  $\sigma$  under the action of high electric fields, it was proposed that (i) gold nanoparticles capped with citrate ions could follow the applied electric field increasing  $\sigma$ , and (ii) a fraction of citrate ions could be stripped off thus leading to the increase in the concentration of ions [159].

The reduction of the residual DC voltage through incorporation of Ni nanoparticles in the nematic liquid crystal (1–3 wt. %) was discussed in [170]. According to [170], Ni nanoparticles mixed with NLC eliminated the hysteresis of the capacitance- voltage (C-V) dependence by capturing ions. The enhancement of electro-optical properties of the nematic liquid crystal MJ001929 doped with pure (non-functionalized) titanium nanoparticles (0.1–2.0 wt. %) was reported in [172]. The adsorption of ionic impurities at the surface of titanium nanoparticles was suggested as a possible mechanism accounting for the observed reduction of the threshold voltage and faster switching time [172].

### 3.3. Dielectric and Semiconductor Nanoparticles in Liquid Crystals

Electrical properties of liquid crystals doped with metal oxide nanoparticles were reported in many papers summarized in Table 4 [173–190].

**Table 4.** Effect of nanoparticles made of metal oxides on the electrical properties of liquid crystals.

Nanoparticles	Liquid Crystals *	Results	Ref.
<i>ZnO</i> , <i>TiO<sub>2</sub></i> , <i>Al<sub>2</sub>O<sub>3</sub></i> , <i>ZrO<sub>2</sub></i> , <i>Y<sub>2</sub>O<sub>3</sub></i> , <i>Co<sub>3</sub>O<sub>4</sub></i>	NLC	Reduced ion current and improved voltage holding ratio, decrease in ion concentration	[173–184]
<i>TiO<sub>2</sub></i> , <i>Al<sub>2</sub>O<sub>3</sub></i> , <i>ZrO<sub>2</sub></i> , <i>MgO</i>	FLC	Decrease in the conductivity	[185–188]
<i>ZnO</i>	CoLC	Increase in the conductivity	[189]
<i>SiO<sub>2</sub></i>	NLC	Voltage-assisted ion reduction	[190]

\* NLC—nematic liquid crystals; FLC—ferroelectric liquid crystals; CoLC—columnar liquid crystals.

Transient currents, the concentration of ions, and electro-optical response of nematic liquid crystal MJ9915 doped with insulating nanoparticles made of *TiO<sub>2</sub>*, *ZnO*, and *Si<sub>3</sub>N<sub>4</sub>* (0.02–0.06 wt. %) were explored in [173,174]. The concentration of ions in liquid crystals was reduced by more than two-fold thus suppressing the undesired field-screening effect. This decrease in the concentration of ions was attributed to the ion trapping by insulating nanoparticles polarized under the action of the external electric field [173,174]. Similar results were obtained for the same nematic liquid crystal doped with diamond nanoparticles [150,175]. The effect of the anatase *TiO<sub>2</sub>* nanoparticles (0.05–1 wt. %) on the voltage holding ratio, the concentration of ions, and the diffusion constant of the nematic liquid crystal E44 at different temperatures was investigated in [178]. The concentration of ions  $n$ , the diffusion constant  $D$ , and the electrical conductivity  $\sigma$  were reduced. For example, at room temperature and at the concentration of nanoparticles 0.5 wt%,  $n$  changed from  $3.0 \times 10^{19} \text{ m}^{-3}$  to  $1.7 \times 10^{19} \text{ m}^{-3}$ ,  $D$  decreased from  $2.1 \times 10^{-11} \text{ m}^2 / \text{s}$  to  $1.2 \times 10^{-11} \text{ m}^2 / \text{s}$ , and  $\sigma$  dropped from  $4 \times 10^{-9} \text{ S} / \text{m}$  to

$1.3 \times 10^{-9} S/m$  resulting in the increase of the voltage holding ratio from 66% to 78% [178]. Further increase in the concentration of nanoparticles did not lead to the decrease in  $n$ ,  $D$ , and  $\sigma$  because of the aggregation [178]. The adsorption of mobile ions by nanoparticles along with the ability of nanoparticles to hinder the ion transport in liquid crystals were proposed as major factors accounting for the observed results [178].

The adsorption of ions at the nanoparticle's surface depends on the total surface area of nanoparticles dispersed in liquid crystals. This dependence was experimentally explored in [176].  $TiO_2$  nanoparticles of different sizes (5, 10, and 30–40 nm) were dispersed in nematic liquid crystals E7 at the same concentration of 0.1 wt. %. The transient currents, the current—voltage, and the transmittance—voltage characteristic of these colloids led to the following conclusions: (i) the surface charge and induced dipole moment of  $TiO_2$  nanoparticles could physically trap ions at their surfaces through electrostatic interactions; (ii) the number of the trapped ions increases with the increase of the total surface area of nanoparticles; (iii) at the same weight concentration, smaller nanoparticles have greater surface area and capture higher number of ions [176].

The concept of ion trapping was used to explain improvements in the electro-optical performance of nematic liquid crystals (NLC) doped with  $ZrO_2$  nanoparticles (0.5–1.5 wt. %) [179], NLC MJ001929 doped with  $Y_2O_3$  nanoparticles (2 wt. %) [180], and NLC MAT-05-881 doped with  $Co_3O_4$  nanoparticles (up to 5 wt. %) [181].

There are some examples of very tricky behavior of liquid crystals doped with dielectric nanoparticles. For example, the electrical conductivity of the nematic liquid crystal 5CB doped with  $Al_2O_3$  nanoparticles was marginally changed exhibiting both decrease (from  $9.52 \times 10^{-7} S/m$  to  $7.76 \times 10^{-7} S/m$  at a temperature of 23 °C and the concentration of 0.2 wt%) and increase (from  $9.52 \times 10^{-7} S/m$  to  $1.21 \times 10^{-6} S/m$  at a temperature of 23 °C and the concentration of 0.6 wt. %) [182]. Complicated behavior of the same nematic liquid crystal 5CB doped with  $TiO_2$  nanoparticles (0.1–2 wt. %) was also reported in [183,184]. An increase in the concentration of  $TiO_2$  nanoparticles from 0 wt% to 0.2 wt% led to the unexpected increase in the concentration of ions  $n$  (from  $3.5 \times 10^{21} m^{-3}$  to  $4.2 \times 10^{21} m^{-3}$  at a temperature of 30 °C), the diffusion coefficient  $D$  (from  $1.4 \times 10^{-11} m^2/s$  to  $2.1 \times 10^{-11} m^2/s$ ), and the electrical conductivity  $\sigma$  (from  $3.0 \times 10^{-7} S/m$  to  $5.4 \times 10^{-7} S/m$ ) of the 5CB [183]. However, further increase in the concentration of nanoparticles from 0.2 wt. % to 1 wt. % resulted in the decrease of the above-mentioned parameters as compared to their values at the concentration of 0.2 wt. %:  $n$  dropped to  $1.0 \times 10^{21} m^{-3}$ ;  $D$  changed to  $\sim 1.5 \times 10^{-11} m^2/s$  almost returning to its original value  $1.4 \times 10^{-11} m^2/s$ ;  $\sigma$  decreased to  $1.0 \times 10^{-7} S/m$ . For concentrations higher than 1.0 wt. %, the saturation of the measured parameters  $n$ ,  $D$ , and  $\sigma$  was observed [183]. These experimental facts suggest that the contamination process dominates at the low concentration of nanoparticles in liquid crystals, and the purification of liquid crystals comes into effect at higher concentrations of nanoparticles. An important conclusion for practical applications is to use purified nanoparticles as dopants for liquid crystals (according to [183,184],  $TiO_2$  nanoparticles were not purified before their use as dopants for liquid crystals). The non-monotonous behavior of the measured electrical parameters as a function of the nanoparticles loading deserves additional experimental and theoretical studies [183,184].

The removal of ionic impurities through the adsorption of ions at the surface of  $Al_2O_3$  nanoparticles dispersed in ferroelectric liquid crystals KCFLC 7S at the concentration of 1.0 wt. % was reported in [185]. The ion trapping effect in ferroelectric liquid crystals doped with  $ZrO_2$  [186],  $TiO_2$  [187], and  $MgO$  [188] nanoparticles was also discussed. According to [186,187], the applied electric field polarized the nanoparticle, and ions in liquid crystals were trapped at the surface of the polarized nano-dopant.

Semiconductor nanoparticles in liquid crystals were also studied from the perspective of the ion capturing processes [191–194]. Table 5 provides a short summary of the obtained results.

**Table 5.** Effect of semiconductor nanoparticles on the electrical properties of liquid crystals.

Nanoparticles	Liquid Crystals *	Results	Ref.
<i>CdSe</i>	FLC	Decrease in the concentration of ions	[191,192]
<i>CdS</i>	FLC	Decrease in the conductivity	[193]
<i>CdSe / ZnS</i>	NLC	Release of the trapped ions under the action of the electric field	[194]

\* NLC—nematic liquid crystals; FLC—ferroelectric liquid crystals.

The ion capturing effect in ferroelectric liquid crystals Felix 16/100 doped with semiconductor *CdSe* quantum dots (0.05–2 wt. %), deduced from the ~two-fold reduction in the electrical conductivity and complex dielectric permittivity, was reported in [191,192]. A similar trend was found in ferroelectric liquid crystal KCFLC10R doped with *CdS* nanorods (0.1–0.3 wt. %) [193]. However, the reduction in the electrical conductivity was more than five-fold (from  $2.7 \times 10^{-6} S/m$  to  $0.5 \times 10^{-6} S/m$  at a temperature of 30 °C) [192].

The ion trapping followed by the aggregation of the agglomerate “semiconductor nanoparticle/trapped ions” in nematic liquid crystals was discussed in [194]. This process can become very important in the case of liquid crystal cells driven by high electric fields.

### 3.4. Ferroelectric Nanoparticles in Liquid Crystals

The ion trapping is a result of strong attractive interactions between ions and a single nanoparticle in liquid crystals. The permanent dipole of ferroelectric nanoparticles makes them superior to the conductive, dielectric, and semiconductor nanomaterials. The spontaneous polarization  $P_s$  of the ferroelectric nanoparticle (its absolute value equals the surface charge density  $\sigma$ ) generates a very high electric field  $E_s$ , which, in the vicinity of the surface, can be estimated as Equation (11) [195]:

$$E_s = \frac{\sigma}{2\varepsilon_0\varepsilon} = \frac{P_s}{2\varepsilon_0\varepsilon} \quad (11)$$

This equation, for the barium titanate ( $P_s = 28 \mu\text{C}/\text{cm}^2$  [115,196]) immersed in a dielectric liquid ( $\varepsilon = 10$ ), yields  $E_s \approx 1.6 \times 10^9 \text{ V}/\text{m}$ . The estimated value of the electric field is high enough to trap ions in liquid crystals.

The ion trapping by means of various ferroelectric nanoparticles embedded in liquid crystals was explored in papers [197–200] summarized in Table 6.



**Table 6.** Effect of ferroelectric nanoparticles on the electrical properties of liquid crystals.

Nanoparticles	Liquid Crystals *	Results	Ref.
$LiNbO_3$	FLC	Ion trapping	[197]
$Sn_2P_2S_6$	NLC	Increase in the conductivity	[198]
$BaTiO_3$	NLC	Decrease in the concentration of ions	[199,200]
$SbSI, Sn_2P_2S_6$	NLC	Ion trapping and reduction of the screening effect	[200]

\* NLC—nematic liquid crystals; FLC—ferroelectric liquid crystals.

Dielectric and electric properties of ferroelectric liquid crystals doped with  $LiNbO_3$  nanoparticles (0.01–0.1 wt. %) were studied in [197]. Ferroelectric nanoparticles were produced by applying the method of the ball mill [201–203], followed by the harvesting procedure [204]. Experimental data were in favor of the ion trapping phenomenon. The estimated concentrations of ions deduced from the conductivity measurements were  $1.06 \times 10^{22} m^{-3}$  (non-doped FLC),  $8 \times 10^{21} m^{-3}$  (FLC nanocolloids, 0.01 wt. %), and  $3 \times 10^{21} m^{-3}$  (FLC nanocolloids, 0.1 wt. %) [197].

Effect of  $BaTiO_3$  ferroelectric nanoparticles on the ion transport in the nematic liquid crystal 5CB was reported in [199]. By introducing relatively low quantities of  $BaTiO_3$  nanoparticles, the concentration of mobile ions in 5CB was reduced by a factor of  $\sim 1.5$  (at a concentration of 0.115 wt. %), and by a factor of 2.3 (at a concentration of 0.275 wt. %). Further increase in the concentration of nanoparticles (up to 0.525 wt. %) did not lead to the corresponding decrease of the ion concentration because of the aggregation of nanoparticles. However, at this level of nanoparticle loading, the concentration of ions was still  $\sim 1.3$  times smaller than that of the pure (non-doped) 5CB [199]. The measured values of the electrical conductivity (at a temperature of 25 °C) were  $2.95 \times 10^{-9} S/m$  (non-doped NLC),  $1.9 \times 10^{-9} S/m$  (NLC nanocolloids, 0.115 wt. %),  $0.9 \times 10^{-9} S/m$  (NLC nanocolloids, 0.275 wt. %), and  $1.4 \times 10^{-9} S/m$  (NLC nanocolloids, 0.525 wt. %) [199].

The quantification of the ion trapping in liquid crystals by means of ferroelectric nanoparticles was done in [200] by applying the Poisson-Boltzmann (PB) equation solved in [205]. The concentration of the trapped positive (or negative) ions,  $n_{T,i}$ , was estimated as Equation (12) [200]:

$$n_{T,i} = n_{NP} Ad \frac{P_s^2}{2\epsilon\epsilon_0 kT} \quad (12)$$

where  $n_{NP}$  is the concentration of ferroelectric nanoparticles;  $A$  is the area of the nanoparticle's surface;  $d$  is the thickness of the ionic monolayer (the monolayer of the trapped ions at the nanoparticle's surface);  $P_s$  is the spontaneous polarization of the nanoparticle;  $k = 1.38 \times 10^{-23} J/K$ ;  $\epsilon$  is the dielectric permittivity of the surrounding medium;  $\epsilon_0 = 8.854 \times 10^{-12} F/m$ ; and  $T$  is the temperature. The parameter  $Ad \frac{P_s^2}{2\epsilon\epsilon_0 kT}$  is dimensionless and tells us how many positive (or negative)

monovalent ions can be trapped by a single ferroelectric nanoparticle. This parameter depends on the materials' characteristics of the nanoparticle (the spontaneous polarization), its size ( $A \propto R_{NP}^2$  where  $R_{NP}$  is the radius of the nanoparticle), the temperature, and the dielectric properties of the surrounding medium (liquid crystals). Considering the cylindrical  $BaTiO_3$  nanoparticle immersed in liquid

dielectric ( $R_{NP} = 20 \text{ nm}$ ,  $d \approx 10^{-10} \text{ m}$ ,  $P_s = 28 \mu\text{Cu}/\text{cm}^2$ ,  $\varepsilon = 10$ ), the parameter  $Ad \frac{P_s^2}{2\varepsilon\varepsilon_0 kT}$  equals  $1.4 \times 10^4$ . The typical concentration of ferroelectric nanoparticles in liquid crystal colloids is  $n_{NP} = 10^{18} - 10^{20} \text{ m}^{-3}$ . These numbers multiplied by a  $10^4$  factor yield  $10^{22} - 10^{24} \text{ m}^{-3}$ , which is even greater than the reported ion concentration in liquid crystals 5CB or E7 (see Table 1). As a result, even low concentrations of ferroelectric nanoparticles (equivalent to the volume fraction of the order of  $10^{-3} - 10^{-4}$ ) are enough to purify liquid crystals from ions [200].

The expression Equation (12) predicts a linear dependence of the concentration of trapped ions on the concentration of ferroelectric nanoparticles. This dependence is valid only in the regime of low concentrations of nanoparticles when aggregation phenomena can be ignored. The aggregation sets a limit on the recommended concentration of nanoparticles which should not exceed the critical concentration  $n_c$ . The critical concentration is of the order of  $10^{19} \text{ m}^{-3}$  ( $n_c$  can be estimated by finding the distance at which the thermal energy is comparable to the magnitude of the electrostatic interactions between two nanoparticles) [200]. Nevertheless, the Equation (12) can be applied to real systems with the aggregation in the form of Equation (13) which can be obtained from Equation (12) by replacing the concentration and the spontaneous polarization of nanoparticles with their effective values (the effective concentration  $n_{NP,eff}$ , and the effective spontaneous polarization  $P_{S,eff}$ ) [200]:

$$n_{T,i} = n_{NP,eff} Ad \frac{(P_{S,eff})^2}{2\varepsilon\varepsilon_0 kT} \quad (13)$$

It is worth mentioning that the aggregation of nanoparticles can decrease the effective concentration drastically. For example, the simplest model of the aggregation based on a reversible second order reaction predicts  $n_{NP,eff} \propto \sqrt{n_{NP}}$  [200]. The methods of fabrication, uncontrollable contamination during the preparation/storage, and surfactants used to stabilize nanoparticles in liquid crystals can also decrease the effective spontaneous polarization. All these factors reduce the capability of nanoparticles to trap ions as can be seen from Equation (13).

By treating thermotropic liquid crystals LC13739 [206] with ferroelectric micro-particles at the high level of loading (1 wt. % and 10 wt. %) their electrical conductivity was reduced from  $2.7 \times 10^{-8} \text{ S/m}$  to  $1.0 \times 10^{-9} \text{ S/m}$  (1 wt. %), and  $7.0 \times 10^{-10}$  (10 wt. %) [200]. Since ferroelectric micro-particles were filtered out once the treatment was completed, the observed reduction in the electrical conductivity is equivalent to the 27-fold and 39-fold decrease in the concentration of ions in liquid crystals. This experimental fact points out to the possibility of the conversion of the low-resistivity (or contaminated) liquid crystals to the high-resistivity liquid crystals by treating them with ferroelectric materials.

Not all ferroelectric materials are good candidates for liquid crystal purification. Some materials such as  $\text{Sn}_2\text{P}_2\text{S}_6$  are very tricky, as they are prone to charging [207], and a certain degree of caution is needed to interpret the experimental data [198,207].

### 3.5. Organic and Other Nanomaterials in Liquid Crystals

Papers reporting the electrical properties of liquid crystals doped with organic materials (conducting nano-fibers and polymeric nanoparticles), montmorillonite nano-clay, and  $\text{ZnO}_{1-x}\text{S}_x$  are summarized in Table 7 [208–219].

**Table 7.** Effect of organic and other nanomaterials on the electrical properties of liquid crystals.

Nanomaterials	Liquid Crystals *	Results	Ref.
Conducting nanofiber	NLC	Increase in the conductivity	[208,209]
Polymeric nanoparticles	FLC	Decrease in dielectric losses	[210]
Nanoclay (montmorillonite)	NLC	Ion trapping, time dependent properties, and aggregation	[211–217]
$ZnO_{1-x}S_x$	FLC	Increase in the conductivity	[218,219]

\* NLC—nematic liquid crystals; FLC—ferroelectric liquid crystals.

Conducting polyaniline nano-fibers (PANI) embedded in liquid crystals (5CB and CCN-47) led to a noticeable increase in the electrical conductivity and its anisotropy [208,209]. The anisotropy of the conductivity was increased by ~10 times (5CB doped with PANI nanofibers at the concentration of 0.2 wt. %), and ~20 times (CCN-47 doped with PANI nanofibers at the concentration of 1.5 wt. %). Such an increase was explained due to the contribution of both ionic and electronic conductivities [208,209].

The decrease in the dielectric losses  $\delta$  and increase in the resistivity of ferroelectric liquid crystals (Felix and CS series) doped with polymeric nanoparticles made of PBA (the copolymer of polybenzene and anthracene; 0.1–10 wt. %) was reported in [210]. The trapping of ions by PBA nanoparticles was proposed to explain the measured decrease in  $\delta$  [210].

Very interesting electrical behavior was found in liquid crystal systems doped with montmorillonite platelets [211–217]. Montmorillonite is a type of smectic clays characterized by a sandwich “tetrahedral-octahedral-tetrahedral” structure made of aluminosilicate lamellar materials. Typically, an octahedral  $Al_2O_3$  (or  $MgO$ ) is sandwiched between two tetrahedral  $SiO_2$  sheets [215]. It was reported that relatively low concentrations of PK-802 sodium montmorillonite (less than 1.0 wt. % w) dispersed in liquid crystals (E7) led to the partial suppression of the screening effect, and the reduced charge density (from  $300.62 \text{ nC/cm}^2$  to  $20.50 \text{ nC/cm}^2$ ). These effects were attributed to the charge transfer and trapping by the nano-clay [211,212,215]. A very small amount of highly purified montmorillonite CL120 (0.03–0.30 wt. %) dispersed in the nematic liquid crystal E7 decreased the electrical conductivity (from  $2.3 \times 10^{-8} \text{ S/m}$  to  $9.1 \times 10^{-9} \text{ S/m}$  at the optimal concentration of 0.07%) and the concentration of mobile ions (from  $5.5 \times 10^{17} \text{ m}^{-3}$  to  $5.0 \times 10^{16} \text{ m}^{-3}$  at the same concentration) in liquid crystals. It was also observed that the efficiency to trap ions by nano-clay was varying in time [213]. More efficient ion trapping in liquid crystals can be achieved by combining low concentrations of nano-clay with comparable amounts of carbon nanotubes [214]. Higher concentrations of montmorillonite in nematic liquid crystals (up to 5 wt. %) result in the percolation phenomena and an increase of electrical conductivity [216,217].

#### 4. Conclusions

In this manuscript we reviewed recently published papers from the perspective of liquid crystal purification by means of nano-objects. Thanks to the developments in liquid crystal nanoscience, nano-objects of various origins (carbon-based, metal, dielectric, semiconductor, ferroelectric, and polymeric) can be produced and dispersed in liquid crystals. Nano-objects are known for their extremely high surface-to-volume ratio, and, in the case of strong enough attractive interactions between the surface of the nano-object and the ions in liquid crystals, can be considered promising candidates for ion trapping

and liquid crystal purification. Experimental results discussed in this review allow us to make the following conclusions:

(i) Low loading of nanomaterials such as nanoparticles in liquid crystals ( $\sim 10^{-3} - 10^{-2}$  wt%, below the percolation threshold/critical concentration) is beneficial for the observation of the ion trapping regime characterized by the decrease in the concentration of the mobile ions in liquid crystals. In this regime ions are adsorbed at the nanoparticle's surface, and the nanoparticle acts as an ion-capturing agent. A factor improving the ion capturing capabilities is the use of small nanoparticles (10–20 nm) with a high dielectric constant and/or electric dipole moment (permanent or induced by the electric field). The aggregation of nanoparticles can be reduced by the proper design of capping agents (the surface modification and functionalization). At the same time, capping agents can alter the ion trapping capabilities of nanoparticles.

(ii) High concentrations of nanoparticles can cause the aggregation, chain and network formation, and lead to the regime of the enhanced electrical conductivity. This regime can be easily reached in the case of liquid crystals doped with nanoparticles made of conductive materials (carbon-based, metal, and polymeric).

(iii) The purity of nanoparticles is a very important factor. Purified nanoparticles can act as ion capturing agents while the nanoparticles made of the same material but not purified can become an additional source of liquid crystal contamination. If the purity of the nanoparticle is unknown, the output result (whether the liquid crystal is purified or contaminated) depends on the relative contribution of the ion adsorption/ion desorption processes.

Despite the continuous flow of new publications, the physics and chemistry of ion capturing by means of nanoparticles dispersed in liquid crystals is still under-explored.

An incomplete list of current challenges is shown below:

- The chemical composition of the trapped ions (an ionic content);
- Physical mechanisms of the ion adsorption/ion desorption and charge transfer at the nanoparticle's surface;
- The selectivity of nanoparticles to trap ions of different types;
- The effects of the capping agents and high electric field on the ion capturing;
- The appropriate models of aggregation viewed from the ion capturing perspectives;
- The total number of ions a single nanoparticle can trap, and how this number depends on the material parameters and the types of ions used.

Future studies will definitely shed light on these questions, and we encourage readers to embrace the amazing science of ions and nanoscale inclusions in liquid crystals.

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## Author Contributions

Yuriy Garbovskiy conceived the idea of writing the manuscript, and defined its content. Yuriy Garbovskiy and Iryna Glushchenko analyzed the existing literature and wrote the paper. Both authors proofread and agreed on a final version of the paper.

## Conflicts of Interest

The authors declare no conflict of interest.

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