



# Adsorption of ions onto nanosolids dispersed in liquid crystals: Towards understanding the ion trapping effect in nanocolloids



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## ABSTRACT

The ion capturing effect in liquid crystal nanocolloids was quantified by means of the ion trapping coefficient. The dependence of the ion trapping coefficient on the concentration of nano-dopants and their ionic purity was calculated for a variety of nanosolids dispersed in liquid crystals: carbon nanotubes, graphene nano-flakes, diamond nanoparticles, anatase nanoparticles, and ferroelectric nanoparticles. The proposed method perfectly fits existing experimental data and can be useful in the design of highly efficient ion capturing nanomaterials.

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## 1. Introduction

The majority of modern liquid crystal devices are driven by an electric field. To fulfil strict industrial requirements, the electrical conductivity of liquid crystals should be of the order of  $10^{-12}$  S/m or less [1,2]. Even a small fraction of ions in liquid crystals can compromise an overall electro-optical performance of liquid crystals leading to such negative effects as image sticking, image flickering, reduced voltage holding ratio, and slow response, to name a few [2]. Methods of chemical design, along with techniques of the physical–chemical purification, is a general, yet expensive and time consuming way to produce the high resistivity liquid crystals [3]. However, even highly purified liquid crystals can get contaminated (enriched with ions) at the stage of the device fabrication and/or while operating the device. This uncontrolled contamination can increase the electrical conductivity of liquid crystals by more than two orders of magnitude [4,5]. Therefore, the development of a simple method of the permanent purification of liquid crystals is of utmost importance to both research and industrial communities.

Recent progress in liquid crystal nanoscience provides a solution to this issue. In short, nano-dopants dispersed in liquid crystals can capture ions, thus reducing the concentration of mobile ions and restoring electro-optical performance. Nano-dopants can be made of various materials: carbon based nano-objects (carbon nanotubes, graphene nano-flakes, fullerenes, nano-diamond); metal,

dielectric, polymeric, semiconductor, and ferroelectric nanoparticles [3 and references therein].

For practical applications, the ability of nanosolids to capture ions in liquid crystals should be quantified. One must know how much ion trapping nanomaterials are needed to reduce the concentration of ions in liquid crystals to the desired level. Unfortunately, this practically important aspect is heavily underexplored. To quantify the ion capturing process, the ion trapping coefficient  $k$  was introduced [6]. This coefficient can be defined through the following equation (1):

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

where  $n_0$  is the concentration of ions in pristine liquid crystals (prior to their mixing with nanosolids), and  $n$  is the concentration of ions in liquid crystals doped with nanosolids (liquid crystal nanocolloids). At a sufficient concentration, ideal ion-trapping nanosolids are characterized by the ion trapping coefficient  $k = 1$ . In actual liquid crystal nanocolloids,  $0 < k < 1$  is typically the case.

The ion trapping effect is not the only possible outcome of the dispersion of nanosolids in liquid crystals. There are also publications reporting effects opposite to the ion trapping scenario. Some nanosolids dispersed in liquid crystals increase rather than decrease the concentration of mobile ions [3 and references therein]. These two possible regimes (contamination and purification) are characterized by different values of the ion trapping coefficient. This coefficient is positive in the case of the purification regime. In the contamination regime, the ion trapping coefficient is negative,  $k < 0$ . The adsorption and desorption of ions onto/from nanosolids dispersed in liquid crystals are major physical processes leading to these regimes (contamination and purification).

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It was shown that both purification and contamination regimes depend on the ionic purity of nanosolids [7–10]. 100% pure nanosolids lead to the decrease in the concentration of mobile ions in liquid crystals. Nanosolids contaminated with ions prior to dispersing them in liquid crystals can result in three different regimes, namely contamination, purification, and no change in the concentration of mobile ions [7–10].

So far, the ion trapping coefficient  $k$  was determined at a single concentration of nanosolids only [6]. There is no data on the concentration dependence of this coefficient. In addition, the effect of the ionic purity of nanosolids on the ion trapping coefficient was not explicitly discussed in the literature. This letter is aimed to cover the above-mentioned aspects. Moreover, contradictory experimental data obtained by independent research groups [3,11–13] will be discussed in the framework of the same approach. The ion trapping performance of ‘real’ (contaminated) and ‘ideal’ (100% pure) nanosolids dispersed in liquid crystals will be compared.

## 2. Basic equations

To calculate the ion trapping coefficient (1), the concentration of mobile ions in liquid crystal nanocolloids as a function of the nanodopant’s loading should be found. This can be done by applying recently developed formalism based on the Langmuir adsorption isotherm and assuming a certain degree of the ionic contamination of nanosolids [7–10]. To account for possible ionic contamination of nanosolids (they can carry some ions prior to dispersing them in liquid crystals), the contamination factor  $\nu$ ,  $0 \leq \nu \leq 1$ , will be used. This factor is dimensionless and it equals the fraction of the adsorbing sites at the nanosolids’ surface occupied by ion-contaminants prior to dispersing them in liquid crystals [7–10]. Once contaminated nanosolids are dispersed in the liquid crystal host, the process of an ion adsorption/ion desorption results in the change of the concentration of mobile ions in liquid crystals. According to [7–10], the concentration of mobile ions  $n$  in liquid crystal nanocolloids can be found by solving Eq. (2) for  $n$ :

$$\sigma_S A_{NP} n_{NP} \frac{Kn}{1+Kn} + n = n_0 + n_{NP} A_{NP} \sigma_S \nu \quad (2)$$

where  $\sigma_S$  is the total surface density of all adsorbing sites at the surface of the nanosolid;  $A_{NP}$  is the surface area of a single nanosolid;  $n_{NP}$  is the volume concentration of nanosolids;  $K = k_a/k_d$ ,  $k_a$  is the rate of adsorption, and  $k_d$  is the rate of desorption;  $n_0$  is the initial concentration of ions in liquid crystals (prior to mixing them with nano-dopants); and  $\nu$  is the above-mentioned contamination factor. Eq. (2) is a result of the conservation law applied to the total number of ions. In other words, a total concentration of the adsorbed,  $\sigma_S A_{NP} n_{NP} (Kn/(1+Kn))$ , and mobile,  $n$ , ions in liquid crystal nanocolloids (left side of Eq. (2)) equals the initial concentration of ions in liquid crystals,  $n_0$ , plus the concentration of ions  $n_{NP} A_{NP} \sigma_S \nu$  carried by contaminated nanosolids (right side of the same equation).

The weight concentration of nanosolids  $\omega_{NP}$  can be used instead of the volume concentration  $n_{NP}$ . An approximate relationship between  $n_{NP}$  and  $\omega_{NP}$  can be written as  $n_{NP} \approx \omega_{NP} (\rho_{LC}/\rho_{NP}) (1/V_{NP})$ , where  $\rho_{LC}(\rho_{NP})$  is the density of liquid crystals (nanosolids),  $V_{NP}$  is the volume of a single nanosolid. No aggregation of nanosolids in liquid crystals is assumed. Once the concentration of mobile ions is found, Eq. (1) is used to compute the ion trapping coefficient.

## 3. Results and discussion

Existing experimental data reviewed in [3] indicate that nanosolids made of the same materials can both trap and release ions in liquid crystals. The major factor governing this process is an ionic purity of nanosolids that can be quantified by means of the

contamination factor [7–10]. To show an impact of the ionic purity of nanosolids on their ion trapping coefficient  $k$ , experimental data (the dependence of the concentration of mobile ions  $n$  on the nanodopant’s loading  $\omega_{NP}$ ) [14] were modelled using Eq. (2). The results are shown in Figure 1a. An inset depicts the concentration dependence of the ion trapping coefficient computed by means of Eq. (1) for the same materials. The following parameters were used to achieve the best fit:  $\sigma_S = 10^{18} \text{ m}^{-2}$ ,  $K = 5 \times 10^{-23} \text{ m}^3$ ,  $\nu = 0.0849$ .

These parameters ( $\sigma_S$ ,  $\nu$ ,  $K$ ) represent important characteristics of nanosolids and liquid crystals exhibiting ionic electrical conductivity. The total surface density of all adsorbing sites at the nanosolid’s surface,  $\sigma_S$ , characterizes the ion-adsorbing capability of nanosolids. A typical order of magnitude of this parameter is  $10^{17} - 10^{18} \text{ m}^{-2}$  [9]. The parameter  $\sigma_S$  times the surface area  $A_{NP}$  of a single nanosolid defines the maximum number of ions this single nanosolid can trap. The contamination factor  $\nu$  is related to the ionic purity of nanosolids. It equals 0 if nanosolids are 100% pure. Very often, actual nanosolids are not 100% pure and relatively small values of  $\nu$  can be reasonably expected [9]. The constant  $K = k_a/k_d$ , is a ratio of the rate of adsorption  $k_a$  to the rate of desorption  $k_d$ . The greater this ratio, the more pronounced is the ion trapping effect [7]. A nanosolid exhibiting ideal ion trapping properties can be described by  $k_d \rightarrow 0$  thus  $K \rightarrow \infty$ . The value of this constant can vary in broad diapason ( $10^{-20} - 10^{-25} \text{ m}^3$ ), depending on materials used [9].

The negative sign of the ion trapping coefficient indicates that nanosolids (carbon nanotubes) dispersed in ferroelectric liquid crystals lead to additional contamination of liquid crystals (Figure 1a). It should be noted that the same nanosolids characterized by zero contamination factor (100% pure carbon nanotubes) will act as ion capturing agents, thus reducing the concentration of mobile ions in liquid crystals as shown in Figure 1b. In this case, the ion trapping coefficient is positive and asymptotically approaches its highest value ( $k \rightarrow 1$ ) with an increase in the concentration of nanosolids (an inset, Figure 1b).

Figure 1a and b unambiguously shows a detrimental effect of the ionic purity of nanosolids on their ion trapping coefficient. If this factor is not controlled by experimentalists, the results can vary dramatically.

The applicability of the approach expressed by Eqs. (1) and (2) to deduce the ion trapping coefficient of various nanosolids dispersed in liquid crystals was verified further (Figures 2–4). The ion trapping coefficient of liquid crystals doped with graphene nano-flakes [9,15] is shown in Figure 2a for ‘100% pure’ ( $\nu = 0$ ) and ‘contaminated’ ( $\nu = 8.6 \times 10^{-6}$ ) cases. Similar curves were plotted for liquid crystals doped with carbon nanotubes (Figure 2b) [9,16]. As can be seen from Figure 2, even minor contamination of nanosolids ( $\nu \sim 10^{-6}$ ) leads to the substantial ( $\sim 2$  fold) decrease in their ion trapping coefficient.

Another interesting example involves liquid crystals doped with diamond nanoparticles [9,17]. It was found that liquid crystals doped with diamond nanoparticles can exhibit both increased and decreased concentration of mobile ions in liquid crystals [17]. Eqs. (1) and (2) were used to deduce the concentration dependence of the ion trapping coefficient of these nanoparticles for both contamination and purification regimes, as shown in Figure 3a and b. Again, the modelled curves are presented for ideal (or ‘100% pure’,  $\nu = 0$ ) and real (or ‘contaminated’,  $\nu = 0.01$  (Figure 3a), and  $\nu = 0.25$  (Figure 3b)) cases.

Ion trapping coefficients of liquid crystals doped with anatase [18] and ferroelectric [19,20] nanoparticles exhibit similar trends. The concentration dependence of ion trapping coefficients of these materials is shown in Figure 4.

As can be seen from Figures 1–4, the sign of the ion trapping coefficient determines the type of the regime reached in experiments. The purification regime is characterized by the positive ion

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