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Research paper

The purification and contamination of liquid crystals by means of nanoparticles. The case of weakly ionized species

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A B S T R A C T

This letter reports the effects of nanoparticles on the concentration of mobile ions in liquid crystals with weakly ionized species. Contrary to the case of fully ionized contaminants, the regimes of the purification and contamination achieved in liquid crystal nanocolloids with weakly ionized species depend on the interplay between the ion adsorption/ion desorption and ion generation/ion recombination. The competition between these processes results in the reduction of the magnitude of the purification and contamination levels in liquid crystals with weakly ionized species as compared to similar effects in the case of full ionization of contaminants.

1. Introduction

Liquid crystal materials used in modern display and non-display technologies are typically driven by an electric field. Even a small fraction of ionic impurities can compromise an overall performance of liquid crystal devices by leading to many negative effects such as image flickering, image sticking, reduced voltage holding ratio, and slow response [1]. To ensure the specified performance of these devices, the electrical resistivity of liquid crystals should be as high as possible [1–3]. However, the high resistivity liquid crystals are prone to the uncontrolled ionic contamination. This contamination can easily happen at the stage of the device manufacturing or while operating the device [4,5]. As a result, the development of new methods of the *permanent purification* of liquid crystals is needed.

One possible solution to this issue can be found by merging liquid crystals and nanotechnology. Nanomaterials such as carbon based nano-objects (fullerenes, nano-diamond, carbon nanotubes, graphene nano-flakes), metal, dielectric, polymeric, semiconductor, and ferroelectric nanoparticles, dispersed in liquid crystals can capture some mobile ions thus reducing their concentration and providing a permanent purification of liquid crystals from ions [6 and references therein]. The purification of liquid crystals from ions (a decrease in the concentration of mobile ions) is not the only possible outcome of the dispersion of nanodopants in liquid crystals. There are some publications reporting the contamination regime (an enrichment of liquid crystals with ions) achieved in liquid crystals doped with nanoparticles [7]. Possible ionic contamination of nanodopants was considered as a major reason of the contamination regime [7,8]. More detailed analysis presented in publications [9–13] revealed the possibility of three different regimes in liquid crystal nanocolloids, namely the purification, the contamination, and no change at all. Switching between these regimes is governed by the interplay between the ionic purity of liquid crystals, the ionic purity of nanoparticles, and the ratio of the adsorption rate constant to the desorption rate constant [9–13].

Results reported in [9–13] were obtained assuming liquid crystals with *fully ionized species* (ionic contaminants). The case of liquid crystals with *weakly ionized species* was not discussed. This letter is aimed to analyse and model possible effects of nanoparticles on the concentration of mobile ions in liquid crystals with weakly ionized species. The case of weakly ionized species is compared to the case of fully ionized species.

2. Basic equations

Consider liquid crystals doped with weakly ionized species (contaminants) *AB*.

In such liquid crystals ions are generated according to the ionization-recombination process described by Eq. (1):

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$$n_{AB} \underset{K_R}{\overset{K_D}{\rightleftarrows}} n_{A^+} + n_{B^-} \tag{1}$$

where n_{AB} is the concentration of the AB species, n_{A^+} is the concentration of A^+ ions, n_{B^-} is the concentration of B^- ions, k_D is the dissociation kinetic constant, and k_R is the recombination kinetic constant [14]. At equilibrium, the rate of dissociation $k_D n_{AB}$ equals the rate of recombination $k_R n^2$ $(n_{A^+} = n_{B^-} = n)$. Consequently, assuming the weak ionization of AB species, the concentration of mobile ions n in pristine liquid crystals can be calculated as $\sqrt{k_D n_{AB}/k_R} \approx \sqrt{k_D n_{AB}^0/k_R}$, where n_{AB}^0 is the concentration of AB species prior to their partial ionization (more details on full and weak ionization of AB species can be found in Appendix A. Supplementary materials).

Nanoparticles dispersed in liquid crystals can change the concentration of mobile ions through their adsorption/desorption onto/from the nanoparticle's surface. Assuming 100% pure nanoparticles and neglecting the aggregation, the corresponding rate equations can be written as (2) and (3):

$$\frac{dn_{AB}}{dt} = -k_D n_{AB} + k_R n^2 - k_{AB}^a n_{AB} n_{NP} A_{NP} \sigma_S (1 - \Theta_\pm - \Theta_{AB}) + k_{AB}^d n_{NP} A_{NP} \sigma_S \Theta_{AB} \tag{2}$$

$$\frac{dn}{dt} = k_D n_{AB} - k_R n^2 - k_\pm^a n n_{NP} A_{NP} \sigma_S (1 - \Theta_\pm - \Theta_{AB}) + k_\pm^d n_{NP} A_{NP} \sigma_S \Theta_\pm \tag{3}$$

where σ_S is the total surface density of all adsorption sites at the surface of the nanoparticle (to simplify the discussion, σ_S is assumed the same for both AB species and a pair of A^+, B^- ions); A_{NP} is the surface area of a single nanoparticle; n_{NP} is the volume concentration of nanoparticles; k_{AB}^a is the rate constant of adsorption of neutral AB species, and k_{AB}^d is the rate constant of desorption of neutral AB species; $k_\pm^a$ is the effective rate constant of adsorption of A^+ and B^- ions, and $k_\pm^d$ is the effective rate constant of desorption of A^+ and B^- ions [12]; Θ_{AB} and $\Theta_\pm$ is the surface coverage defined for neutral species and ions, respectively. The effective rate constants of adsorption and desorption of A^+ and B^- ions were introduced in [12] assuming that nanoparticles in liquid crystals tend to restore their zero net charge. Once positive (or negative) ion is adsorbed onto the nanoparticle's surface, the positively (or negatively) charged nanoparticle restores its zero net charge through the adsorption of the counter-ion. Desorption processes can be described in a similar two-step way: once the positive (or negative) ion is desorbed from the nanoparticle's surface, the negatively (or positively) charged nanoparticle tends to restore its zero net charge through desorption of the negative (or positive) ion. It should be noted that adsorption (or desorption) followed by desorption (or adsorption) does not change the total number of mobile ions in liquid crystals [12]. Liquid crystals are typically *weakly polar* materials [1,2]. If nanoparticles are added to such systems, their total surface charge is very likely to be effectively zero because of strong electrostatic interactions between ions in *low polar* fluids [15,16]. As a result, an assumption made in [12] and briefly described above is reasonable.

The first term of Eq. (2), $k_D n_{AB}$, describes the dissociation of the AB species. The second term, $k_R n^2$, accounts for the recombination of ions. The third term, $k_{AB}^a n_{AB} n_{NP} A_{NP} \sigma_S (1 - \Theta_\pm - \Theta_{AB})$, results from the adsorption of neutral species AB onto nanoparticles. The fourth term, $k_{AB}^d n_{NP} A_{NP} \sigma_S \Theta_{AB}$, is associated with the desorption of neutral species AB from nanoparticles. In an analogous manner, the first and second terms of the Eq. (3) account for the dissociation-recombination processes, while the third, $k_\pm^a n n_{NP} A_{NP} \sigma_S (1 - \Theta_\pm - \Theta_{AB})$, and fourth, $k_\pm^d n_{NP} A_{NP} \sigma_S \Theta_\pm$, terms describe the adsorption and desorption of ions onto/from nanoparticles, respectively.

The conservation law of the total number of particles (neutral species and ions) can be written as (4):

$$n_{AB}^0 = n_{AB} + n + n^a + n_{AB}^a \tag{4}$$

where n_{AB}^0 is the total concentration of neutral AB species prior to their partial ionization in liquid crystals, and n_{AB} is the concentration of the same species weakly ionized; n^a is the concentration of ions adsorbed onto nanoparticles, and n_{AB}^a is the concentration of neutral AB species adsorbed onto nanoparticles. The concentrations n^a and n_{AB}^a are related to the above-mentioned surface coverage as $n^a = n_{NP} A_{NP} \sigma_S \Theta_\pm$ and $n_{AB}^a = n_{NP} A_{NP} \sigma_S \Theta_{AB}$, respectively.

Assuming the equilibrium $\left(\frac{dn_{AB}}{dt} = 0 \text{ and } \frac{dn}{dt} = 0\right)$ the concentration of mobile ions in liquid crystal nanocolloids as a function of the nanoparticle's loading can be found by solving Eqs. (2)–(4) for n. In this case Eqs. (2) and (3) are simplified since the rate of dissociation equals the rate of recombination, and the rate of adsorption equals the rate of desorption.

In actual experiments, the weight concentration of nanoparticles ω_{NP} is widely used. An approximate relationship between the volume concentration, n_{NP}, and the weight concentration, ω_{NP}, can be written as $n_{NP} \approx \omega_{NP} \frac{\rho_{LC}}{\rho_{NP}} \frac{1}{V_{NP}}$, where ρ_{LC} (ρ_{NP}) is the density of liquid crystals (nanoparticle), V_{NP} is the volume of a single nanoparticle.

Parameters used to model the concentration dependence of mobile ions in liquid crystals with weakly ionized species are listed in Table 1. Spherical nanoparticles of the radius R_{NP} and density ρ_{NP} are considered. To compare weak and full ionization cases, the initial concentration of fully ionized contaminants in liquid crystals was set to the equilibrium concentration of ions in pristine liquid crystals with weakly ionized species, $\sqrt{k_D n_{AB}^0/k_R}$.

Table 1
Parameters used to model curves shown in Figs. 1–4.

$n_{AB}^0,\ \mathrm{m^{-3}}$	$\frac{k_R}{k_D},\ \mathrm{m^3}$	$K_{AB} = \frac{k_{AB}^a}{k_{AB}^d},\ \mathrm{m^3}$	$K_\pm = \frac{k_\pm^a}{k_\pm^d},\ \mathrm{m^3}$	$\sigma_S,\ \mathrm{m^{-2}}$	$R_{NP},\ \mathrm{m}$	$\frac{\rho_{NP}}{\rho_{LC}}$
10^{20} (Figs. 1 and 2) 0 (Fig. 3) 10^{18} (Fig. 4)	10^{-16}	0 10^{-24} 10^{-23}	10^{-23}	0.5×10^{18}	10^{-8}	3.3

Unit conversion

Concentration	Surface density of adsorption sites	Constants $\left(K_{AB},\ K_\pm,\ \frac{k_R}{k_D}\right)$	Size
$1\ \mathrm{m^{-3}} = 0.166 \times 10^{-26}\ \frac{\mathrm{mol}}{\mathrm{L}}$	$1\ \mathrm{m^{-2}} = 10^{-18}\ \frac{\mathrm{sites}}{\mathrm{nm^2}}$	$1\ \mathrm{m^3} = 10^3\ \mathrm{L}$	$1\ \mathrm{m} = 10^9\ \mathrm{nm}$