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Evaluating the Concentration of Ions in Liquid Crystal Cells: Hidden Factors and Useful Techniques

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Abstract: Many of the liquid crystal devices are driven by electric fields. Ions, typically present in molecular liquid crystal materials in minute quantities, can compromise the performance of mesogenic materials (in the simplest case, through a well-known screening effect). Even highly purified liquid crystals can be contaminated with ions during their production and handling. Therefore, measurements of the concentration of ions became an important part of the material characterization of liquid crystals. Interestingly, even a brief analysis of existing publications can reveal a quite broad variability of the values of the concentration of ions measured by different research groups for the same liquid crystals. It reflects the complexity of ion generation mechanisms in liquid crystal materials and their dependence on numerous factors. In this paper, an overview of ion generation mechanisms in liquid crystals and modern ion measurement techniques is followed by the discussion of frequently overlooked factors affecting the measured values of the ion concentration. Ion-generating and ion-capturing properties of the alignment layers (or substrates) of liquid crystal cells are considered and used to evaluate a true concentration of ions in liquid crystals. In addition, practical recommendations aimed at improving the measurements of the ion density in liquid crystals are also discussed.

Keywords: liquid crystals; electrical conductivity; ions; ion generation; ion measurement techniques

1. Introduction: Ions in Liquid Crystals

Molecular liquid crystals are tunable anisotropic materials. The orientation of mesogenic molecules making up liquid crystals can be controlled by external electric fields. As a result, their physical properties can be tuned in a desirable way. This fact enabled numerous applications of liquid crystals including ubiquitous liquid crystal displays (LCD) [1] and liquid crystal on silicon (LCoS) displays for virtual and augmented reality [2], tunable components of biomedical equipment (lenses, filters for hyperspectral imaging) [3,4], polarization and phase control devices (waveplates and retarders) [5,6], diffractive optical elements [7], spatial light modulators and beam-steering devices [8], light shutters [9,10], smart windows [11,12,13], various tunable signal processing devices operating at microwave and millimeter wave frequencies [14,15], and countless others.

Ions normally present in liquid crystals in minute quantities can alter the performance of liquid crystal devices (in the simplest case, through a well-known screening effect). In the case of displays, ions in liquid crystals can result in such undesirable side effects as image sticking, image flickering, reduced voltage holding ratio, and overall slow response [16]. Therefore, the concentration of ions should be kept as small as possible to ensure an uncompromised performance of the aforementioned liquid crystal devices. This can be achieved by synthesizing high resistivity liquid crystals and applying physical and chemical methods of their purification [17]. There are also some applications relying on ions in liquid crystals (light shutters and smart windows [9-13,18]). Such applications would benefit from the development of new reliable techniques and materials enriching thermotropic liquid crystals with ions. As a result, an understanding of possible sources of ions and mechanisms of ion generation in liquid crystals is of utmost importance regardless the type of their application. Indeed, ions in liquid crystals are being studied since the early 1960s [16,19]. Measuring the concentration of ions in liquid crystal materials became a standard component of their electrical characterization [20].

Even though numerous experimental methods were developed to measure the concentration of ions in liquid crystals, an analysis of existing publications reveals a broad range of the measured values of the concentration of ions in the same liquid crystals. Ions in liquid crystals can originate from different sources [21]. Their low concentration and high sensitivity to external (and very often uncontrolled) factors make an apparently straightforward electrical measurement a non-trivial and a tricky one. Existing experimental results unambiguously indicate that the measured values of the concentration of ions in liquid crystals depend on the cell thickness [22,23,24]. Unfortunately, the number of the reported experimental datapoints is typically very limited. As a result, the type of the dependence of the concentration of ions on the cell thickness (monotonous, non-monotonous, etc.) and physical origin of the observed behavior are often not discussed. Interestingly, as will be shown in this conference paper, a recently developed model of ion-generating and ion-capturing substrates of a liquid crystal cell [25,26,27] can provide a reasonable quantitative explanation of the observed dependence of the concentration of ions on the cell thickness. Moreover, it can be used to improve existing experimental procedures aimed at evaluating the concentration of ions in liquid crystals.

2. Generation of Ions in Liquid Crystals

An electrical characterization of liquid crystals is performed using sandwich-like cells filled with mesogenic materials [20]. Ions can be generated in the bulk of liquid crystals and on the surface of the liquid crystal cell [21]. Both sources of ion generation in liquid crystals are very important and should be considered. Possible sources of ions in molecular liquid crystals include: (i) the dissociation of neutral molecules present in the bulk of liquid crystals [28]; (ii) chemical leftovers (inorganic ionic impurities as a result of the the chemical synthesis) [29,30]; (iii) decomposition of liquid crystal materials because of aging [31]; (iv) ions generated by means of ionizing radiation (UV light [32,33], gamma-radiation [34,35]), through electro-chemical reactions [36], and by high electric fields [37,38,39]; (vi) ions introduced intentionally by doping them with ionic species [40]; (vi) nanomaterials dispersed in liquid crystals [41,42,43]; (vii) ionic contaminants can be generated in the glue used to seal the liquid crystal cell [44]; (viii) ions due to contaminated alignment layers of the cell [45,46,47,48].

3. Measuring Ions in Liquid Crystals

Ions in liquid crystals result in their finite DC electrical conductivity λ_{DC}. The electrical conductivity λ_{DC} of liquid crystals can be written as (1):

$$\lambda_{DC} = \sum_i q_i \mu_i n_i \qquad (1)$$

where q_i is the charge of the i-th ion, μ_i is the mobility of the i-th ions, and n_i is its volume concentration. Because liquid crystals are globally electrically neutral, the total charge of negative ions is compensated by the total charge of positive ions. By limiting our consideration to the case of monovalent ions, the electrical conductivity can be rewritten as (2)

$$\lambda_{DC} = |e|(\mu^+ + \mu^-)n = |e|\mu n \qquad (2)$$

where $\mu = \mu^+ + \mu^-$, $|e| = 1.6 \times 10^{-19} C$.

The electrical conductivity, the ion mobility, and the concentration of ions are basic electrical parameters needed to describe an ion transport in liquid crystals quantitatively [16]. Their values can be found experimentally by using methods of dielectric spectroscopy [23,49,50,51] and transient current measurements [16,20,52,53]. In some cases, electrical measurements can also be combined with electro-optical experiments [54].

Measuring basic parameters of ions in liquid crystals is a very nontrivial task. Consider the case of the concentration of ions in liquid crystals. According to equation (1), the concentration of ions can be found measuring their DC electrical conductivity λ_{DC} and effective mobility μ. By measuring complex impedance spectra $Z = Z' - iZ''$, complex dielectric permittivity spectra $\varepsilon = \varepsilon' - i\varepsilon''$ can be evaluated [51,55]. The obtained spectra of the complex dielectric permittivity can be used to compute complex electrical conductivity $\lambda = \lambda' + i\lambda''$ by means of a standard equation (3):

$$\lambda = i2\pi f \varepsilon_0 \varepsilon \qquad (3)$$

where f is a frequency, and $\varepsilon_0 = 8.854 \times 10^{-12} F/m$. Finally, the obtained spectra of the complex electrical conductivity should be used to extract values of the DC electrical conductivity λ_{DC} according to (4):

$$\lambda' = \lambda_{DC} + \lambda'_{AC} \qquad (4)$$

where λ'_{AC} is a real part of an alternating current (AC) electrical conductivity. The extracted value of the DC electrical conductivity is an effective quantity characterizing the filled liquid crystal cell used in measurements rather than a liquid crystal material [51]. Typically, a standard measuring cell is made of two parallel substrates separated by a distance *d*. Each substrate has a multi-layer structure including a thin conducting layer (it is typically made of an indium tin oxide (ITO)) to apply the electric field, and an alignment layer made of polymers to align liquid crystal molecules. An actual magnitude of the DC electrical conductivity of liquid crystals can be deduced by considering an equivalent electric circuit suitable for the liquid crystal cell under test [51]. If the ion mobility is known, the concentration of ions can be computed by applying equation (2). The ion mobility can be evaluated by measuring a transient current in a liquid crystal cell driven by low frequency square waves with different DC offsets [20,52].

Alternatively, the concentration of ions and their diffusion coefficients D ($D \sim \mu$) can be estimated by fitting an appropriate model to the measured impedance spectra as explained in recent publications [23,49,50].

It should be noted that transient current measurements can also provide a valuable information about the concentration of ions in liquid crystals [16,20,52,53]. In this case the measured transient current $i(t)$ can be decomposed in the capacitive current i_{cap}, conduction current i_c, and polarization switching current i_p (if liquid crystals can exhibit a ferroelectric response), according to (5):

$$i(t) = i_{cap}(t) + i_c(t) + i_p(t) \qquad (5)$$

where t is time.

By extracting the conduction current (typically it can be achieved by varying the time duration of the applied electric pulses), the concentration of ions can be estimated (6):

$$n = \frac{1}{|e|dA} \int_0^{T/2} i_c(t)dt \qquad (6)$$

where *A* is the area of electrodes of the liquid crystal cell, *d* is its thickness, and *T/2* is the integration interval. Under certain conditions, the conduction current can exhibit a maximum (it's often called an "ion bump"). The time position of this maximum t_{trans} can be used to evaluate the effective mobility of ions according to (7):

$$\mu = \frac{d^2}{V t_{trans}} \qquad (7)$$

where V is the magnitude of the applied voltage [16,20,52,53].

4. Overlooked Factors, Practical Suggestions, and Conclusions

The provided brief description of existing experimental techniques shows that finding the concentration of ions in liquid crystals is not a simple and straightforward task. The presence of alignment layers makes the evaluation of the ion density in liquid crystals even more challenging problem [23,49,51]. The development of models focused on computing the concentration of ions is highly desirable. Even though existing models can account for the presence of alignment layers [23,49,51], there are important yet overlooked factors needed to be considered. Experimental results reported by independent research groups indicate that substrates of the liquid crystal cell can either capture ions or enrich liquid crystals with ions [44-49]. These ion-capturing and ion-releasing processes depend on the cell thickness, and, if not considered, can result in an incorrect evaluation of the concentration of ions in liquid crystals. In the majority of the reported cases only one aspect, either ion trapping or ion generation by means of substrates of the liquid crystals cell, is considered. Interestingly, a simple model can account for both ion generating and ion capturing properties of substrates of liquid crystal cells [25-27,48]. This model is briefly described in this section.

Consider a symmetric sandwich-like cell. In general, alignment layers (or just bare substrates) of this sandwich-like cell can be contaminated with ions prior to filling the cell with liquid crystals. This ionic contamination can be quantified by means of the contamination factor ν_S defined as a ratio of the number of sites occupied by ionic contaminants N_i to the total number of all surface sites N_S, $\nu_S = {N_i}/{N_S}$, where $N_S = A_S\sigma_S$, A_S is the surface area of substrates, and σ_S is the surface density of these sites [25-27,48]. Once an empty cell is filled with liquid crystals, a fraction of ionic contaminants can leave the surface of alignment layers thus enriching liquid crystals with ions. At the same time, ions inherently present in liquid crystals can be captured by the surface of alignment layers. The following rate equation can be used to describe the afore-mentioned ionic processes:

$$\frac{dn_j}{dt} = -k_{Sj}^{a\pm} n_j \frac{\sigma_{Sj}}{d}\left(1 - \Theta_{S1}^{\pm} - \Theta_{S2}^{\pm}\right) + k_{Sj}^{d\pm}\frac{\sigma_{Sj}}{d}\Theta_{Sj}^{\pm} \quad (8)$$

where a subscript j stands for the dominant type of fully ionized species-contaminants in liquid crystals ($j = 1,2$); σ_{Sj} is the surface density of all surface sites of the alignment layer; n_j is the concentration (volume density) of mobile ions of the *j*-th type ($j = 1,2$); $d$is the thickness of the cell; $k_{Sj}^{a\pm}$ is the effective rate constant of the ion capturing process (in the simplest case, it can be physical adsorption) of $n_j^+$and n_j^-ions on the surface of alignment layers, and $k_{Sj}^{d\pm}$ is the effective rate constant of the ion releasing process (in the simplest case, the desorption) of $n_j^+$and n_j^-ions from the alignment layer; $\Theta_{Sj}^{\pm}$is the fractional surface coverage of alignment layers defined for the *j*-th ions [25-27,48]. The conservation law applied to the total number of ions of the *j*-th type can be written as equation (9):

$$n_{0j} + \frac{\sigma_{Sj}}{d}\nu_{Sj} = n_j + \frac{\sigma_{Sj}}{d}\Theta_{Sj}^{\pm} \quad (9)$$

where ν_{Sj} is the already mentioned contamination factor of alignment layers.

The applicability of equations (8) – (9) to describe ion capturing and ion generating processes in liquid crystals was demonstrated in several recent papers [25-27,48]. A physical reason for the applicability of equations (8)-(9) is a relatively low value of a typical surface coverage,$\Theta_S << 1$, resulting in negligibly small electrostatic interactions between ions on the surface of alignment layers. This energy can be estimated as $\frac{e^2}{4\pi\varepsilon\varepsilon_0\sqrt{(\Theta_S\sigma_S)^{-1}}} \approx 0.1kT$ (the following typical values of the parameters are used: $|e| = 1.6 \times 10^{-19}C$,$\varepsilon = 6$,$\Theta_S = 10^{-4}$,$\sigma_S = 10^{18}m^{-2}$,$\varepsilon_0 = 8.854 \times 10^{-12}\,{F}/{m}$,$T = 293K$,$k = 1.38 \times 10^{-23}\,{J}/{K}$).

Once equations (8)-(9) are solved for n_j, ($j = 1,2$), the total concentration of fully ionized species n can be calculated according to equation (10):

$$n = n_1 + n_2 \quad (10)$$

Some interesting results are shown in Figure 1 where the total concentration of ions is plotted as a function of the cell thickness.

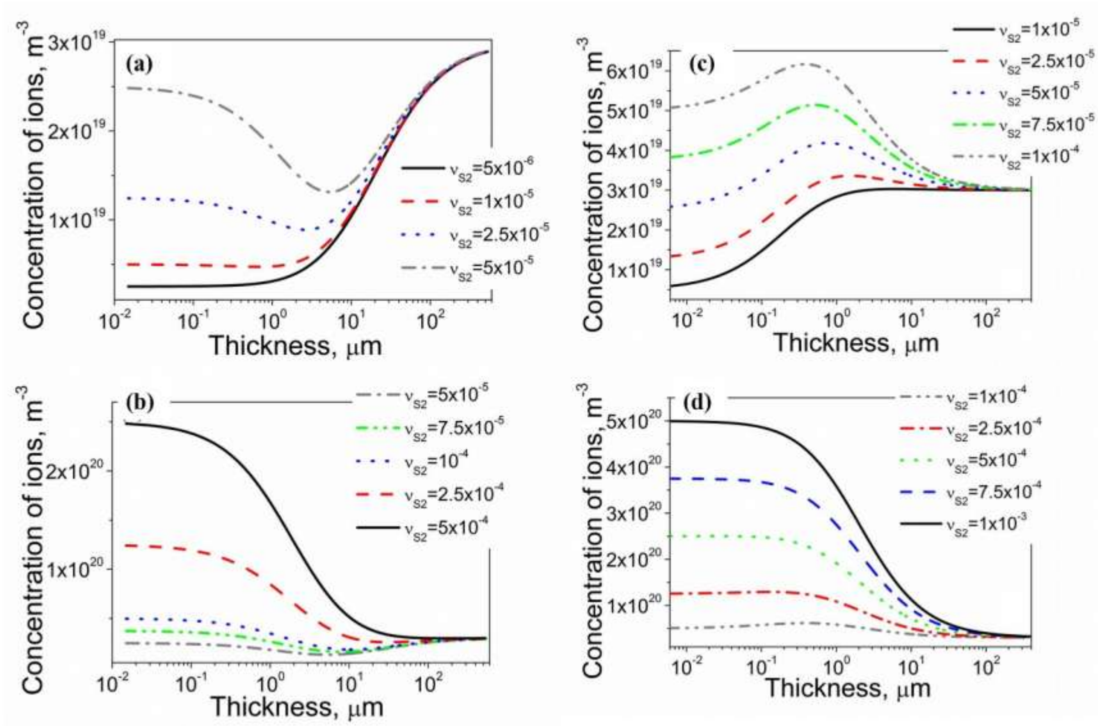

Figure 1. The total concentration of mobile ions, n as a function of the cell gap calculated at several values of the contamination factor ν_{S2}. (**a**) Monotonous increase (solid and dashed curves) followed by a non-monotonous dependence with a minimum (dotted and dashed-dotted curves). (**b**) Monotonous decrease (solid and dashed curves) followed by a non-monotonous dependence with a minimum (dotted and dashed-dotted curves). (**c**) Monotonous increase (solid curve) followed by a non-monotonous dependence with a maximum (other curves). (**d**) Monotonous decrease (all curves except double-dotted-dashed curve). Additional information can be found in paper [27].

There are several important features worth mentioning. The first obvious fact is a strong dependence of the concentration of ions on the cell thickness. In general, this dependence can vary dramatically. Depending on the interplay between parameters characterizing ion generating and ion capturing processes, the dependence of the total concentration of ions on the cell thickness can be either non-monotonous or monotonous (Figure 1).

Figure 1 leads to an important practical implication: experimental measurements of the concentration of ions should be performed by using several identical cells and varying their thickness. Measurements performed at a single value of the cell thickness do not provide enough information about ionic processes in such systems. The results shown in Figure 1 were obtained assuming a steady state. Equations (8)-(9) can also be applied to describe the kinetics of ionic processes in liquid crystal cells as was shown in recent papers [27,48].

It should be noted that the model used to model the dependence of the total concentration of ions on the cell thickness is only a reasonable approximation. Nevertheless, it can capture basic features of this dependence, and, therefore, can also guide experimental studies aimed at uncovering ionic phenomena in liquid crystals. According to Figure 1, the dependence of the concentration of ions on the cell thickness is very strong in the regime of thin cells. This fact should be considered during the selection of liquid crystal materials suitable for emerging applications utilizing very thin layers of mesogenic materials. At the same time, Figure 1 also points to a useful practical suggestion: measurements of the concentration of ions of relatively thick layers of liquid crystals can reveal a "true" concentration of ions in liquid crystals, namely, the ion density not affected by ion capturing and ion generating processes caused by the alignment layers of the cell.

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