The electroconvection in nematic liquid crystals with short range smectic C order and negative electroconductivity anisotropy

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Abstract. The electroconvective instability (ECI) in nematic liquid crystals (NLCs), appearing beyond smectic C at cooling known as N with short range smecic C order, presents a unique electrooptical phenomenon due to generation and frustration of the smectic layering, which manifests inside the N temperature range. We found that the response time in this material is about an order shorter than those in the classical nematics. For the first time in NLCs were detected harmonics higher than fourth order. A twist type instability is suggested for this material.

1. Introduction

Anisotropic, uniaxially symmetric fluid, like nematic liquid crystals (NLCs) which have a locally preferred direction described by the director field \( \mathbf{n}(r,t) \), with \( \mathbf{n}^2=1 \), are rich in pattern forming phenomena [1-4]. Under standard conditions, nematic LCs of positive conductive (\( \sigma_\parallel=\sigma_\perp>0 \)), negative dielectric (\( \varepsilon_\parallel=\varepsilon_\perp<0 \)) (\( \parallel \) and \( \perp \) mean parallel and perpendicular to the nematic director \( \mathbf{n} \)) anisotropies and planar orientation (the director is along the x direction of the LC cell’s plane \( xy \)), the system in the presence of d.c. or a.c. electric field, applied in z direction, turns into electroconvection (EC), appearing like normal rolls (NRs) pattern with wave vector \( \mathbf{q} \) parallel to the equilibrium director orientation \( \mathbf{n}\parallel x \). This EC is well described by classical one-dimensional 1D Carr–Helfrich (CH) theory [5], but it is not applicable for the description of the more complicated 3D EC patterns. Recently a lot of papers were published [2-4], aiming to introduce more clarity in the scope of combinations of the sign and magnitude of \( \varepsilon_a \) and \( \sigma_a \), LC geometry (from planar to homeotropic). The EC characterizes with diversity of pattern manifestations, thus it was divided into two categories, standard and non-standard EC (sEC and nsEC) respectively depending on the possible EC driving mechanism (CH or other one still unknown). Till now a justification of the driving mechanism for the most of the nsECs does not exist.

Some experimental investigations concerning the measurement of the director’s twist azimuthal angle in the xy plane and the trends of threshold field on the temperature as well as on the frequency could throw a new light in the understanding of the complicated field of the EC driving mechanisms. The nematic with short range smectic C (S_c) order is a suitable LC system where the twist angle variation by electric field parameters and the temperature reveals the EC mechanism in these materials i.e. the twist instability mechanism. The instability in the N with short range smectic order is strongly
influenced by the generation and frustration of the smectic layers inside the N phase. Furthermore, the smectic order fluctuations in the Ns, where quasi-smectic supramolecular N complexes form undoubtedly influenced the character of the EC instability, and provoke inversion of the sign and magnitude of $\varepsilon_a$ and $\sigma_a$ as a result of the easy distribution of the charges in the layer’s planes.

We will analyze the results of the 9th homologue of p,n-alkyloxybenzoic acid (9OBA), which is Ns with short range $S_C$ order built by hydrogen bonded in dimers molecules. Using both microtextural-polarization and the laser diffraction method at normal and oblique illumination, we will put into practice a real-time quantitative access to the electric field induced director field amplitude variations. Furthermore, analyzing the threshold and polarization characteristics of the patterns, their decay from EC to the ground non-excited state and the existence of the Fourier modes with frequencies harmonic to the electric field frequency, we will test the possible EC mechanism of this LC material.

2. Experimental results and discussion

4, n-nonyloxybenzoic acid (9OBA) display N phase between 118°C and 146°C and $S_C$ between 118°C and 92°C. The substance was filled between two parallel glass plates whose surfaces express xy plane and are coated with transparent electrodes, indium tin oxide (ITO) uni-directionally rubbed in x direction providing initial director orientation $n_x$. The cell thickness $d=12\mu m$.

The temperature of the sample was varied with a rate of 0.1 °C min$^{-1}$ by a hot stage temperature controller Linkam TMS 90. An ac field $E=(0,0,E_z)$ of frequency $f$ was applied across the sample. The EC patterns in the $xy$ plane were observed by use of a video camera Hitachi and by a microscope Zeiss NDU2.

The analysis of EC instability in 9OBA requires a description of the $\varepsilon_a$ and $\sigma_a$ temperature variation within the N phase. For 9OBA $\varepsilon_a$ varies between 0.03 and 0.011 at temperature variation between 146 and 118°C. The maximum value of $\varepsilon_a$ is 0.04 at 129°C and just at $T_{NC}$ the $\varepsilon_a$ sign sharply change from positive to negative. So $\varepsilon_a$ is positive but small as the average value in the N region is $\varepsilon_a=0.013$ [6-8].

The $\sigma_a$ variation in the N temperature range of 9OBA is as follows: from $-0.4x10^{-11}(\Omega^{-1}\text{cm}^{-1})$ at 144°C it decrease to $-0.5x10^{-11}(\Omega^{-1}\text{cm}^{-1})$ at 118°C, i.e always negative in the nematic temperature range. An weak anomaly of $\sigma_a$ one notes at 129°C, which we mark out with $T^*$. We emphasize that the electric behaviour of 7th and 8th homologues of p,n-alkyloxybenzoic acid differs from that of the 9th homologue, since their electroconductivity anisotropies are positive, while in 9OBA $\sigma_a<0$ in the entire N region. This could be assign to the longer molecule of 9OBA, providing easy realization of compact (co-ordination of the monomers, closed and open dimers fluctuations in space and time with trend to generate quasi-smectic layer) smectic like supramolecular complexes, still below $T_{NI}$. It is a result of the decrease of $\sigma_1$, with respect to $\sigma_a$, providing more easy charge distribution within the grown smectic layer. This effect depends on the tilt angle $\omega$ (the angle between the layer’s normal N and the director), as the sign of $\sigma_a$ could be positive if $\omega\approx\pi/4$, or negative if this angle is smaller than $\pi/4$ [6]. For 9OBA $\omega\approx34^\circ$, while for 8OBA and 7OBA it is 55° and 50° respectively (bigger than the limit for the sign inversion). This angle dependent $\sigma_a$ sign causes the negative signs of $\sigma_a$ and provoke a EC in 9OBA (although the dimeric molecular structure) different from those of other N with short range $S_C$ order, which display positive electroconductivity. Thus the investigated here 9OBA, we can categorize as EC case where $\varepsilon_a$ is positive and small and $\sigma_a$ is negative.

We used for the diffraction a low power He-Ne laser ($\approx 1\text{mW}$) of wavelength $\lambda_a=632.8\text{nm}$. In order to study the relaxation of EC patterns the intensity of the diffracted light was monitored.

We concentrated on the EC instability below the characteristic temperature $T^*=130°C$ at 12 $\mu m$ for the studied here substance 9OBA, aiming to analyze this instability in the N region where the EC sets in the expected big enough quasi-smectic supramolecular clusters.

At threshold voltage 24V, 80Hz stripe domains (rolls) forming an angle $\pm 45^\circ$ with respect to $n_{yz}$ are seen at 125°C. At a further overthreshold voltages the stripe domains, after fluctuations normal to the roll’s axes, transform (figure 1) to a regular square pattern.
At 122°C $\sigma_\parallel$ reaches very high negative value meaning that the quasi-smectic layers are enough large to be able to ensure an easy charge distribution inside the layers. This indicates an underlined twist type instability appearing directly at threshold voltage and reveals as a regular cell-like (square form) domains arrayed in two directions including angle $\approx 45^\circ$ with x direction, similar to that at 125°C.

Both decay and response times have been scanned, extracted and measured by recording the odd and even diffraction intensities $I_{\pm 1}$ and $I_{\pm 2}$ at normal or oblique illumination respectively, taking into consideration that the oblique illumination is more effective one in respect to put into practice an real time access to the director amplitude at the EC onset [9-11].

The decay time is an important parameter, which is able to reveals the LC system dynamics since the EC patterns allow us to keep track of the pattern relaxation by means of the fringe intensities decay during the system transition to the equilibrium ground state.

In figure 2 we indicate, as an example, a typical 2D diffraction pattern corresponding to the EC pattern shown in figure 1. The angle of oblique illumination $\alpha$ is 10°. Increasing the voltage above threshold we indicate in figure 3(a), (b) (as an example) the response and decay curves obtained when applied different increasing over-threshold U values. As seen the response time decreases from 1000ms at 23.5V to 80ms at 25V. At the same time the decay time at 25V is $\approx$100ms, meaning equalization of the response and decay times, which is important for LCD technique.

Furthermore, we found for the first time, that the smectic layer generation in the N phase changes the director modulation characteristics of the EC instability, as well as the nonlinearity of the system, thus leading to inducing of the forth harmonic of the excited ac electric field (4f), coexisting with the second harmonic one 2f with a higher magnitude.

Using microtextural polarization analysis we estimated the amplitude of the azimuthal $n$ modulation $\varphi_0$ at varying the over-threshold voltages by rotation the sample between crossed polarizers. If the director was chosen to be at the polarizer direction, before EC, then in the EC regime the bright regions expresses a rotation of the polarization plane of the light deviation by the $n$ projection, while the dark regions expresses that this projection rests close to this plane. So the twist out of the tilt plane inverses the dark and bright domain lines, and the polarization direction. This is the base of the detection of the twist spatial modulation of the director (spatial variation of the effective refractive index).
Figure 2. The 2D diffraction pattern of 9OBA. T=125º, U=26V, f=80Hz.

Figure 3. (a) The response times at increasing over-threshold voltages at T=122ºC, f=80Hz. ‘On’ and ‘off’ on the graphics present switch on and switch off of the electric field. (b) The decay times corresponding to the response ones.
The azimuthal $\varphi(U)$ dependences at 80Hz for the temperature 122$^\circ$ is indicated in figure 4. The azimuthal $n$ modulation varies as $\varphi(U)=\varphi_o\left((U^2-U_{th}^2)/U_{th}^2\right)^{1/2}$. The measured azimuthal angle variation indicates periodic twist fluctuation (periodic going out of $n$ from the vertical $xz$ plane) and is expected to be initiated from the coupling of the charge spread out in the $xy$ plane and the director field, thus resulting flow field $\mathbf{v}=(v_x,v_y,v_z)$, which actually is 3D phenomenon. As a result the process of the closing of the rolls in square (figure 1) or hexagonal localized states could be due namely to such in-plane director rotation and corresponding flow in the $xy$ plane, which acts simultaneously with that acting in $xz$ plane. The distribution of the 2D far-field diffraction field intensity from the domain picture expresses two-dimensional director modulation, which is $n$ azimuthal deflections and can be presented as $\varphi(x,y)\sim\varphi_o\cos(q_xx+q_yy)$, where $q_x$ and $q_y$ are the periodicities of the pattern. All these suggests a twist type EC instability in N with short range $S_C$ order and $\sigma_a<0$ (9OBA), resembling that of $S_C$ phase [12].

![Figure 4. The azimuthal angle variation at over-threshold voltage increasing at $T=122^\circ$C, $f=80$Hz.]

As indicated in figure 3 the decay of the EC pattern is exponential. At larger amplitude of the director we leave the linear regime and both amplitude and phase grating effects of the $n$ modulation are important. On the other hand by oblique incidence we detected very small near threshold director deflections and in such way we have time to increase the scope of the deflection angle $\varphi$ values and in turn to increase the possibility to co-ordinate the controlled switching period of time with the higher over-threshold driving voltage. Thus we keep the sharpness of the fringe.

On the base of the time-dependent director’s fluctuation amplitude $\varphi(t)$ we expresses the intensity of light diffracted by the EC domains as a Fourier expansion $I(m,t)=I_o+A_2\cos(2\omega t)+A_4\cos(4\omega t)+...$, where $m$ is the diffraction order and $A_2$ and $A_4$ are the voltage-dependent coefficients of the detected by us second and fourth harmonics. We neglect the observed in the experiment even harmonics with higher order, which will be considered in a future work.

At 122$^\circ$C $\sigma_a$ reach very high negative value (as we described above) meaning that the quasi-smeectic layers are enough large to be able to ensure an easy charge distribution inside the layers. This indicates underlined twist type instability at this temperature which reveals as cell-like domains arrayed in two directions including angle 45$^\circ$ with $x$ direction.

3. Conclusion
In conclusion, we described the special feature of the electroconvection instability in the dimeric N phase with short range $S_C$ order of the ninth homologue of the p,n alkylxybenzoic acid. This feature dues to the negative electroconductivity anisotropy underlined below a definite temperature ($T^*$) inside
this N phase. Since the anisotropy of the dielectric constant is small and positive, we assigned the EC in this LC material to category $\epsilon_a>0$, $\sigma_a<0$, but with specific pattern, threshold and dynamical characteristics. In the studied here material 9OBA the magnitude of the conductivity anisotropy falls always below zero. This feature due to the smaller tilt angle (34°) in 9OBA providing a negative conductivity anisotropy and EC instability closer to that in smectic C phase.

By polarization analysis of azimuthal in-plane ($x,y$) director deflection in EC regime, we suggested twist type character of this instability, which is still not embraced by the contemporary 3D standard model, although this twist instability was discovered long ago for $S_C$. We stated also that the minimization of the free energy in the formed $S_C$ supramolecular complexes is fulfilled by a rotation of director on a cone, around the layer’s normal similar to that in $S_C$ and decisively favours the twist fluctuations.

Our measurements of the response and the decay times showed that in general the response times in the region below $T^*$ of 9OBA are shorter than that in the classical $N_s$, as the ratio of the response and decay times is $\approx 1$. That means equalization of both response and decay times in 9OBA, which is preferable in the LC display techniques.

A fourth frequency harmonic, which is roughly an order weaker than the second one, was detected for the first time in nematic state.

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