Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Ionic impurities in nematic liquid crystal displays

M. R. Costa; R. A. C. Altafim; A. P. Mammana

To cite this Article Costa, M. R. , Altafim, R. A. C. and Mammana, A. P.(2001) 'Ionic impurities in nematic liquid crystal displays', Liquid Crystals, 28: 12, 1779 — 1783

To link to this Article: DOI: 10.1080/02678290110078757

URL: http://dx.doi.org/10.1080/02678290110078757

LIQUID CRYSTALS, 2001, VOL. 28, NO. 12, 1779–1783

Ionic impurities in nematic liquid crystal displays

M. R. COSTA*, R. A. C. ALTAFIM
Dept. of Electrical Engineering, School of Engineering at São Carlos,
University of São Paulo, São Carlos, Brazil

and A. P. MAMMANA
Information Display Laboratory (LMI),
National Institute of Information Technology (ITI), Campinas, Brazil

(*Received 30 December 2000; accepted 8 June 2001*)

This paper shows that the dielectric anisotropy of conductivity in cells composed of nematic liquid crystal E7 (NLC-E7) is related to the fact that the diffusion constant (D) is greater in a cell with homeotropic alignment than in one with homogeneous alignment ($D_{\parallel} > D_{\perp}$). This behaviour can be understood by the study of the dielectric properties of the NLC based on the ionic hopping behaviour and on the analysis of the electrical conductivity in relation to the voltage applied.

1. Introduction

The study of the dielectric properties of nematic liquid crystals (NLCs) at low and high frequencies is of great importance for optical or electrical applications, such as display devices, spatial light modulators and sensors; and in new technology development, such as TN-TFTs and PDLCs [1–4].

The dielectric properties at low frequencies have received special attention, due to the charge carrier transport process that affects display performance [5].

The NLC dielectric behaviour at low frequencies has been linked to cells without an alignment layer for the electrode polarization [6]. Thus, these mechanisms depend upon the materials used and the cell manufacturing process, which can vary significantly.

For the study of anisotropic behaviour in NLC cells, special attention was paid to the complex permittivity behaviour at low frequencies (< 1 kHz), measuring it in cells composed of NLC-E7 (Merck Ltd., UK) and manufactured with both homogeneous and homeotropic alignments.

In homogeneous and homeotropic cells with NLC-E7 dielectric dispersion mechanism may be understood through the hopping model proposed by Iwamoto [7], and explained by the molecular alignment that facilitated the movement of ionic impurities from the electrodes for long distances in NLCs.

An equation that might estimate the impurity concentration and the diffusion constants when these cells are put under applied voltage variation is proposed. Diffusion constants, static dielectric constants and ionic impurity concentration are estimated. The homogeneous and homeotropic behaviour under temperature variation conditions have been observed.

2. Methodology

The nematic liquid crystal studied was the commercial compound E7 (Merck Ltd., UK) The cells were constructed with 1 mm soda-lime glass substrates covered with circular gold electrodes with an area of 0.78 cm^2. The homogeneous and homeotropic gaps were measured by interferometry; the values found were 12.50 μm and 12.00 μm, respectively. For homeotropic alignment a thin silana (ZLI-3124 MERK liquicoat) layer was used.

The complex permittivity was obtained by the impedance measurement of both newly made cells using a Solartron-SI1260 bridge in the 0.1 kHz to 10 MHz frequency range.

Correction for border effects in the cell capacitors was obtained by an empirical method that resulted in residual errors less than 1.1% [8]. The voltage used was 50 mV (rms), much lower than the Fréedericksz transition. A thermal analysis over the range 20–80 ± 1°C was performed on both homogeneous and homeotropic samples.

---

*Author for correspondence;
e-mail: marcosrc@sel.eesc.sc.usp.br

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2001 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290110078757

3. Experiments and results

3.1. *Frequency analysis*

Figure 1 shows the complex permittivity behaviour $[\varepsilon'(\omega) - i\varepsilon''(\omega)]$ of the homogeneous and homeotropic cells, determined by the Solartron bridge, on the as-prepared NLC cells.

Debye relaxation behaviour could be observed in the high frequency range, 10^4–10^7 Hz, with molecular rotation around the NLC axis [1, 9].

NLC static behaviour was seen in the medium range frequencies, 10–10^4 Hz, exactly where it is possible to obtain parallel and perpendicular dielectric permittivities $\varepsilon'_\parallel = 19.16$ and $\varepsilon'_\perp = 5.42$, and conductivities $\sigma'_\parallel = 5.7 \times 10^{-10}$ and $\sigma'_\perp = 2.6 \times 10^{-10}\ \Omega^{-1}\,\mathrm{cm}^{-1}$. This defines the static region of NLC-E7 as having an anisotropy of $\Delta\varepsilon = 13.74$ and a conductivity relation $\sigma'_\parallel / \sigma'_\perp \cong 2$ at 22°C.

In low frequency regions, 10^{-1}–10 Hz, $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ vary with frequency in proportion to $f^{3/2}$ and f^{-1}, respectively. This behaviour of $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ was observed by Murakami and Naito [6] analysing NLC-5CB with ITO electrodes up to a frequency of 0.5 Hz; it is caused by the electrode polarization, as described by the Uemura [10] diffusion equations.

Nevertheless, when the diffusion model proposed by Uemura [10] is used to explain the dielectric behaviour of NLC-E7 at low frequencies a divergence at very low frequencies (<1 kHz) is observed. This is because a complex permittivity reduction occurs at frequencies lower than 1 Hz (figure 1) in both alignments, different from that observed by Murakami [6] in NLC-5CB. In addition, figure 1 shows that this reduction is higher in homeotropic alignment than in homogeneous alignment.

The dielectric dispersion mechanism observed at low frequencies in NLC-E7 may be the result of a non-linearity between the polarization and the electric field caused by the movement of ionic impurities. These impurities would be moving long distances in the cells until they reached the electrodes, where they would be blocked.

This non-linear behaviour can be understood through ionic hopping modelling. To represent the NLC-E7 behaviour through hopping ionic movement a recent model proposed by Iwamoto was chosen [7]. This model was first applied to the study of dielectric dispersion in isolated films. In this model, the complex permittivity equations are expressed by

$$(\varepsilon' - \varepsilon_s)\varepsilon_0 \equiv \left(\frac{8q^2nL^2}{\pi^4 k_B T}\right)\left[\left(\frac{1}{1+z^2}\right) + \left(\frac{1}{9^2+z^2}\right) + \left(\frac{1}{25^2+z^2}\right) + \dots\right] \qquad (1)$$

and

$$\varepsilon''\varepsilon_0 \equiv \left(\frac{8q^2nL^2}{\pi^4 k_B T}\right)\left[\left(\frac{z}{1+z^2}\right) + \left(\frac{z/9}{9^2+z^2}\right) + \left(\frac{z/25}{25^2+z^2}\right) + \dots\right] \qquad (2)$$

where $z = (2L^2/\pi D)f$; n, is the ionic concentration, q is the electronic charge, D is the diffusion constant, L is the cell thickness, k_B is the Boltzmann constant, T is the environmental temperature and ε_0 is the vacuum dielectric permittivity. It should be noted that these equations were obtained by considering the diffusion process and neglecting the space charge field effect at the electrodes and electrostatic interaction among ions.

Adjustments to figure 1 by means of equations (1) and (2) at 100 Hz frequency were performed through the Levenberg–Marquardt non-linear regression method and are shown in figure 2. The estimated ionic concentration and diffusion constant adjusted parameters for NLC-E7 are given in table 1.

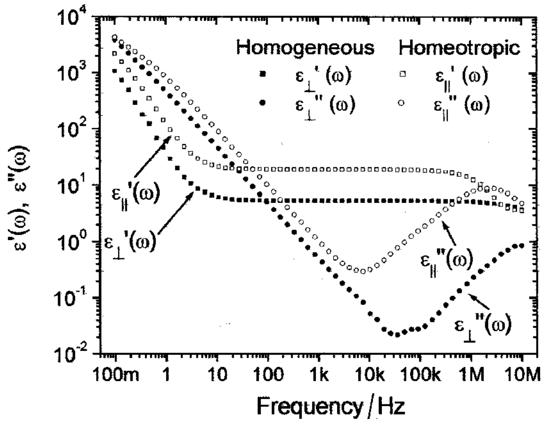

Figure 1. Frequency dependence of the $\varepsilon'(\omega) - i\varepsilon''(\omega)$ of NLC-E7 for homogeneous and homeotropic cells at 22°C.

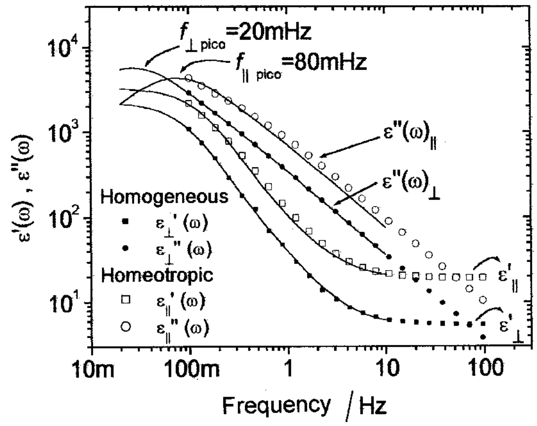

Figure 2. Low frequency dependence of the $\varepsilon'(\omega) - i\varepsilon''(\omega)$ of NLC-E7 for homogeneous and homeotropic cells at 22°C.

Table 1. Diffusion constant D and ionic concentration n for homogeneous and homeotropic cells at 22°C.

Cell type	$D/\mathrm{cm}^2\,\mathrm{s}^{-1}$	n/cm^{-3}
Homogeneous	2.83×10^{-8}	1.42×10^{15}
Homeotropic	7.05×10^{-8}	1.30×10^{15}

Comparing the data for the two cells, it can be seen that the ionic concentrations are close, while the diffusion constants are very different.

The higher diffusion constant in the homeotropic cell indicates that in this alignment the NLC-E7 molecules facilitate diffusion of impurities, causing them to reach the electrodes faster than in the homogeneous cell. Thus the molecular structure in NLC-E7 cells channels ionic impurities through long distances until they reach the electrodes. These accumulated impurities in the electrodes can lead to dynamic instabilities in the NLC cells [11–13].

3.2. *Voltage analysis*

It was observed that the conductivity anisotropy in NLC-E7 cells seems to be related to the diffusion constant, and it is higher in homeotropic cells than in homogeneous ones, or $D_\parallel > D_\perp$. Therefore, since the motion of ionic impurities in NLC-E7 cells is directly dependent on the diffusion constants and on the molecular structure of the cell, the motion of these impurities should be affected by the application of an external electric field. Figure 3 shows the variation of electrical conductivity in the homogeneous cell under the action of an external electrical field.

Figure 3 shows that the electrical conductivity of NLC-E7 is static, corresponding to the perpendicular electrical conductivity ($\sigma'_\perp$), up to the NLC-E7 Fréedericksz voltage (V_{th}), $V < V_{\mathrm{th}}$. Above the Fréedericksz voltage ($V > V_{\mathrm{th}}$) the conductivity depends on the applied electrical voltage, probably tending to the parallel electrical conductivity ($\sigma'_\perp$).

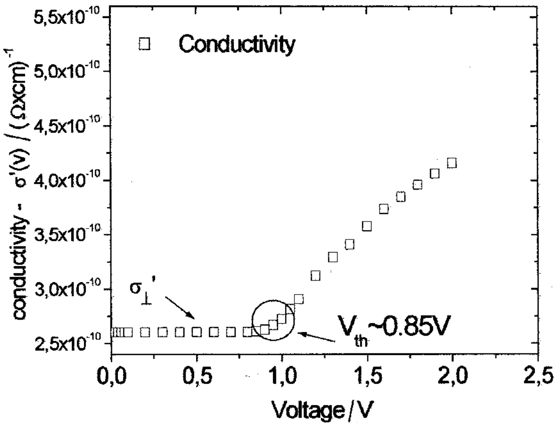

Figure 3. Electric conductivity of NLC-E7 as a function of voltage (1 kHz, 22°C).

It is known that $\sigma'(\omega) = \varepsilon''(\omega)\varepsilon_0\omega$, where $\omega = 2\pi f$, from which can be derived

$$\sigma'(\omega) \equiv \left(\frac{16q^2L^2}{\pi^3 k_{\mathrm{B}}T}\right)\left[\left(\frac{1}{\frac{1}{Bf^2}+B^2}\right)+\left(\frac{1}{\frac{9^3}{Bf^2}+9B}\right)+\left(\frac{1}{\frac{25^3}{Bf^2}+25B}\right)+\ldots\right] \tag{3}$$

where $B = (2L^2/\pi D)$.

To obtain the static limit $\sigma'(\omega)$, $f \to \infty$ is used, resulting in:

$$\sigma' \equiv \left(\frac{8nq^2D}{\pi^2 k_{\mathrm{B}}T}\right)\left[1+\left(\frac{1}{3^2}\right)+\left(\frac{1}{5^2}\right)+\left(\frac{1}{7^2}\right)+\ldots\right]. \tag{4}$$

The series $[1+(1/3^2)+(1/5^2)+(1/7^2)+\ldots]$ can be interpreted through Bernoulli numbers as follows:

$$\left[1+\left(\frac{1}{3^{2n}}\right)+\left(\frac{1}{5^{2n}}\right)+\left(\frac{1}{7^{2n}}\right)+\ldots\right] \equiv B_n\left[\frac{(2^{2n}-1)\pi^{2n}}{2(2n)!}\right] \tag{5}$$

For $n=1$, $B_1 = 1/6$ and the series becomes $\pi^2/8$. Therefore equation (4) leads to

$$\sigma' \equiv \frac{nq^2D}{k_{\mathrm{B}}T} \tag{5}$$

and according to the frequency analysis in homeotropic and homogeneous cells, it can be simplified as

$$\sigma'_{\perp,\parallel} \equiv \frac{nq^2D_{\perp,\parallel}}{k_{\mathrm{B}}T}. \tag{6}$$

The observed behaviour, after using the Fréedericksz voltage in figure 3, is similar to a raising sigmoidal Hill curve, as follows:

$$y = \left(\frac{x^\alpha}{\gamma + x^\alpha}\right)y_{\mathrm{Max}} \tag{7}$$

where α and γ are adjustment parameters.

Combining equations (6) and (7) and normalizing the Fréedericksz voltage axis, the following empirical equation is obtained:

$$\sigma'(V/V_{\text{th}}) = \frac{nq^2}{k_B T}\left\{\Delta D\left[\frac{\left(\frac{V}{V_{\text{th}}}-1\right)^{\alpha}}{\gamma+\left(\frac{V}{V_{\text{th}}}-1\right)^{\alpha}}\right]+D_{\perp}\right\}, \quad \text{for } V \geqslant V_{\text{th}} \tag{8}$$

where $\Delta D = D_{\parallel} - D_{\perp}$.

Normalizing the graph in figure 3 (V/V_{th}) and setting the ionic concentration n and the perpendicular diffusion constant $D_{\perp}$ for adjustments, it is possible to adjust and extrapolate the graph through equation (8). This behaviour is illustrated in the graph of figure 4 and the adjustment result is presented in table 2.

The figure 4 graph shows that estimated values for parallel diffusion constant ($D_{\parallel}$) is close to the estimated values in hopping equations (1) and (2), indicating that in NLC-E7 the anisotropic behaviour of the electrical conductivity is due to the diffusion of ionic impurities favoured by molecular arrangement of the nematic structure. However, in NLC cells, the structure depends on temperature, so that thermal variation of conductivity anisotropy should be observed.

3.3. *Thermal analysis*

When the parallel and perpendicular electrical conductivity behaviours are analysed for NLC-E7 under different temperature conditions figure 5 is obtained. It is observed that both conductivities, $\sigma'_{\perp}(T)$ and $\sigma'_{\parallel}(T)$, rise with temperature. This rise is expected, as this is a thermally activated ionic process. However, $\sigma'_{\perp}(T)$ shows a greater rise than $\sigma'_{\parallel}(T)$.

According to the model adopted via equation (6), it is verified that the factors that influence static thermal conductivities are the ionic concentration and diffusion constants. Therefore, both factors may be influencing the behaviour observed in figure 5.

The effect of temperature on the ionic concentration and diffusion constants in homogeneous and homeotropic cells is deduced from equations (1) and (2), and presented in figure 6.

Figure 6, shows that the diffusion constants increase with rise in temperature, while the ionic concentration is relatively independent of temperature in both types of cell in the nematic range. The ionic concentration independence is normally to be expected when ions are

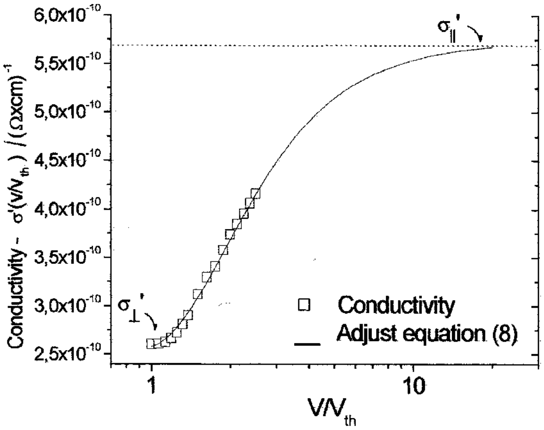

Figure 4. Adjustment of the electric conductivity of NLC-E7 as a function of voltage (1 kHz, 22°C).

Table 2. Estimate of the parallel diffusion constant $D_{\parallel}$ from equation (8).

From table 1		Estimated		
n/cm^{-3}	$D_{\perp}$/cm^2 s^{-1}	$D_{\parallel}$/cm^2 s^{-1}	α	γ
1.42×10^{15}	2.83×10^{-8}	6.30×10^{-8}	1.50	1.86

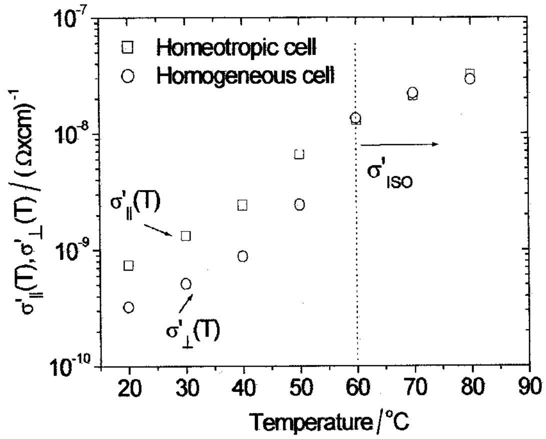

Figure 5. Graph of the conductivities ($\sigma'_{\parallel}, \sigma'_{\perp}$) of NLC-E7 between 20°C and 80°C (1 kHz).

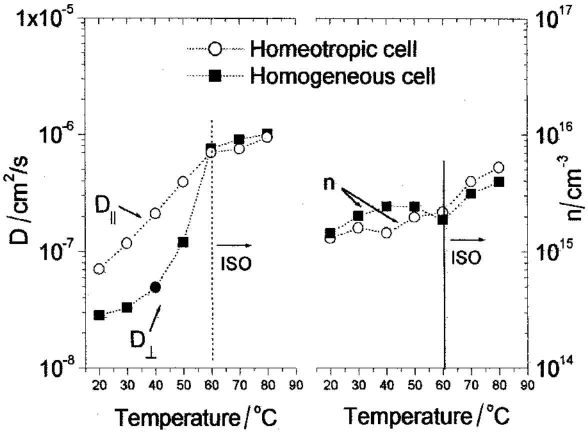

Figure 6. Graphs of the diffusion constant and ionic concentration of NLC-E7 for homogeneous and homeotropic cells between 22°C and 80°C (1 kHz).

not associated with their counterions in the NLC bulk, i.e. there is no association–dissociation reaction. This behaviour has been observed by Murakami [6] in cells composed of NLC-5CB and with ITO electrodes. Therefore, since the ionic concentration is practically independent of nematic temperature range, the diffusion constant is probably the most significant factor in the rise in parallel and perpendicular conductivities with temperature.

It is interesting to observe that the parallel diffusion constant ($D_{\parallel}$) has a greater rise than the perpendicular diffusion constant ($D_{\perp}$) in the nematic phase. This is probably because the diffusion constant is dependent on both structure and temperature of the material.

The effect of temperature on a liquid crystal is measured through the order parameter $S(T)$ [14]. Since this parameter influences both homogeneous and homeotropic cells equally, its action will favour impurity diffusion in the transition from a homogeneous cell to the isotropic phase as well as block the impurities transition from a homeotropic cell to the isotropic phase. Therefore, the greatest increase in diffusion, shown in figure 6 to the homogeneous cell rather than the homeotropic cell, is probably due to the loss of nematic structure, caused by rise in temperature. This favours impurity diffusion in the homogeneous cell and its blockage in homeotropic cells.

4. Conclusion

In the present paper an explanation of the anisotropic behaviour of NLC-E7 electrical conductivity is given through ionic hopping analysis. This is in spite of the mechanism of electrical conductivity in polar liquids such as NLCs being very complex [15].

It has also been demonstrated that NLC-E7 electrical conductivity anisotropy is probably caused by the long distance motion of ionic impurities in the cell, as these impurities move more easily in cells with homeotropic alignment than in cells with homogeneous alignment.

It was verified that ionic impurities travel to the electrodes faster in homeotropic cells rather than in homogeneous cells; the diffusion constant was considered the most significant fact in the anisotropic electrical conductivity of NLC-E7.

The ionic impurity concentration and diffusion constants in homogeneous and homeotropic cells were estimated for the nematic phase. NLC-E7 dielectric constants and static conductivities were estimated as $\varepsilon'_{\parallel} = 19.16$, $\varepsilon'_{\perp} = 5.42$; $\sigma'_{\parallel} = 5.7 \times 10^{-10}$, $\sigma'_{\perp} = 2.6 \times 10^{-10}\,\Omega\,\mathrm{cm}^{-1}$. These data define an anisotropy of $\Delta\varepsilon = 13.74$ and a relation between the conductivities $\sigma'_{\parallel}/\sigma'_{\perp} \cong 2$ at 22°C for NLC-E7 in the medium frequency range ($100\,\mathrm{Hz} < f < 1\,\mathrm{kHz}$).

We would like to thank FAPESP for financial support, and Dr B. J. Mass for his assistance in the preparation of this paper.

References

[1] Coffey, W. T., Crothers, D. S. F., Kalmykov, Yu. P., and Waldron, J. T., 1995, *Physica A*, **213,** 551.

[2] Mada, H., and Nishkawa, A., 1993, *Jpn. J. appl. Phys.*, **32,** L1009.

[3] Jacob, T., Klement, D., Schuler, B., Tarumi, K., and Sawada, A., 1998, *Displays and Vacuum Electronics*, ITG Conference, Germany, April 29–30, 1998, pp. 41–46.

[4] Jadzyn, J., and Czechowski, G., 1999, *Liq. Cryst.*, **36,** 453.

[5] Sawada, A., Sato, H., Nakazono, U., Naemura, S., and Manabe, A., 1999, *SID '99 Dig.*, 190–193.

[6] Murakami, S., and Naito, H., 1997, *Jpn. J. appl. Phys.*, **36,** 2222.

[7] Iwamoto, M. I., 1995, *J. appl. Phys.*, **77,** 5314.

[8] Schaumburg, G., 1997, *Dielectrics Newsletter*, pp. 5–10.

[9] De Jeu, W. H., 1978, *Solid State Phys., Suppl.*, **14,** 109.

[10] Uemura, S., 1974, *J. polym. Sci.*, **12,** 1177.

[11] Naito, H., Yoshida, K., Okuda, M., and Sugimura, A., 1993, *J. appl. Phys.*, **73,** 1119.

[12] Naito, H., Okuda, M., and Sugimura, A., 1991, *Phys. Rev. A*, **44,** R3434.

[13] Mada, H., and Yamada, H., 1994, *Jpn. J. appl. Phys.*, **33,** 5886.

[14] Buka, A., and de Jeu, W. H., 1982, *J. Phys. (Paris)*, **43,** 361.

[15] Schmidt, F. W., 1994, in *Electrical Insulating Liquids*, ASTM, Chap. 2.