

EVALUATION OF THE DEBYE LENGTH FOR A NEMATIC LIQUID CRYSTAL ALIGNED WITH CONDUCTIVE POLYMERS

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S-au efectuat măsuratori de conducție electrică în vederea estimării densității de ioni și a lungimii de ecranare Debye în probe de cristal lichid nematic aliniat cu polimeri conductori. Studiul a fost efectuat pe celule simetrice standard, de tip sandwich, cu cristal lichid nematic 5CB orientat planar prin intermediul unor filme de polipirol dopat cu anioni de diferite dimensiuni și geometrii moleculare. Admițând că, într-o probă, ionii prezenti în cristalul lichid sunt identici cu excepția semnului sarcinii electrice, s-au determinat densitățile de ioni și lungimile Debye la echilibru termodinamic, pentru fiecare probă. S-a observat o descreștere a lungimii Debye cu creșterea grosimii filmului de polimer conductor.

Electric conduction measurements were performed to estimate ionic charge densities and Debye screening length within a nematic liquid crystal aligned with conductive polymers. The study has been carried out on standard sandwich symmetric cells filled with nematic liquid crystal 5CB. Planar orientation was induced using thin films of polypyrrole doped with ions having different molecular sizes and geometries. By assuming that, in a sample, the ions are identical except for the sign of the electrical charge, the ion densities and the Debye lengths in thermodynamical equilibrium for each cell were determined. Decreasing values of Debye lengths for increasing thickness of same alignment conductive polymer films are revealed for long enough periods of triangular applied voltages.

Keywords: nematic liquid crystal, conducting polymers, Debye length

1. Introduction

The optical properties of liquid crystals are exploited in information displays, LCD. With the aid of an external electric field one can control the optical transmission of the display. In general, the application of an external electric field across a film of liquid crystal having a positive dielectric anisotropy ($\Delta\epsilon > 0$) will give rise to a reorientation of the director axis, which tends to align

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along the field direction. The response of the nematic director to the applied field is a threshold phenomenon and depends on the strength of the field, on the dielectric anisotropy ($\Delta\epsilon$) and elastic constants of the liquid crystal and, very important, on the boundary anchoring effects.

Fast electro-optic response times measured at switching off the electric field have been obtained in nematic cells oriented with plasma polymerized conducting polymers. Such remarkable properties are probably related to an accumulated charge at the polymer film-liquid crystal interface, due to the ions transferred from the polymeric films [1]. To this charge accumulation is connected an electric field distribution across the sample. The coupling of this field with the anisotropic dielectric properties of the liquid crystal gives rise to a dielectric energy density localized near the limiting surfaces [2]. This energy renormalizes the anisotropic part of the interfacial energy favouring the nematic relaxation to the initial orientation.

In order to characterize the electric properties of a nematic liquid crystal (NLC) aligned by a doped polymer, the electric current response with respect to applied voltage for each sample submitted to a triangular potential with different amplitudes and periods has been measured. The amount of the transferred charges was calculated from current-voltage characteristics. The density of ions in the bulk and the Debye length were evaluated by considering the following assumptions: (1) only two kinds of ions, one positive and one negative, identical in all other aspects, are present in the cell, (2) the cell is limited by perfectly blocking electrodes, (3) ionic recombination and adsorption phenomena are negligible. In the absence of an external electrical field, the liquid crystal is locally and globally neutral. When an electric field is applied, ions move under the effect of the electric force until an equilibrium distribution is reached. The sample is still globally neutral, but locally charged. In very pure liquid crystals, the electric field created by the distribution of ions inside the sample may extend over a region of some 100 μm in depth [3]. For pure liquid crystals, the Debye length is found to be about 100 nm [4, 5].

Our aim is to evaluate the Debye length in nematic samples aligned with a conducting polymer, namely doped polypyrrole. Samples preparation and experimental set-up are described in Sec.2. In Sec.3 the obtained results are presented. A comparison between Debye length for nematic samples with different types of ions and thicknesses of the aligned layers is reported. The last part of the paper is devoted to conclusions.

2. The physical system and the experimental set-up

The study has been carried out on 8 symmetric cells. The basic component of the cell is a thin layer, 36 μm in thickness, of positive uniaxial nematic liquid

crystal: 4-*n*-pentyl-4'-cyanobiphenyl (5CB). The liquid crystal is sandwiched between two glass plates coated on the inner sides with a transparent conductive layer of ITO (indium tin oxide). An initial planar orientation of the nematic director was obtained using unidirectional rubbed conducting polymer substrates deposited on the ITO layers. Such alignment layers (30 nm, 60 nm and 90 nm in thickness) of polypyrrole (PPy) films doped with different anions - perchlorate (ClO_4^-), p-toluenesulfonate (tosylate, TSO^-), nitrate (NO_3^-), perfluorobutanesulfonate ($CF_3CF_2CF_2CF_2SO_3^-$) and trifluoro-methanesulfonate ($CF_3SO_3^-$) - were obtained by electrochemical polymerization [6]. The chosen doping anions have different structures and molecular sizes.

Employing the experimental set-up described in [7], the current to applied voltage response of each sample submitted to an external triangular excitation of amplitude 3V_{PP} and different periods has been measured. A deviation from the linear behaviour of the current has been observed for long enough periods (>5s) of the applied voltages. This is connected to a charge accumulation at nematic-polymer interface due to the carrier injection from the doped polymer layer into the liquid crystal [7]. We hypothesized that this charge accumulation leads to formation of an electrical Debye layer within the liquid crystal near the surface.

3. Results and discussions

Under the assumptions that there is no recombination and the electrodes are perfectly blocking, the magnitudes of the stored charges were obtained from current - voltage characteristics following the standard procedure [7]. The density of ions in thermodynamical equilibrium was evaluated by assuming that the ions are identical in all aspects, except for the sign of the electrical charge [8]. The obtained values are reported in Table 1.

Table 1
Densities of ions for different periods of the applied voltage for all types of investigated dopants

T(s)	N·10 ²⁰ (m ⁻³)				
	$CF_3CF_2CF_2CF_2SO_3^-$	$CF_3SO_3^-$	ClO_4^-	TSO^-	NO_3^-
1	1.6	0.8	1.4	0.2	0.3
5	13.7	13.4	19.1	1.7	2.8
10	41.5	30.5	28.2	3.9	7.3
50	243.2	100.8	101.9	20.7	30.6
100	420.1	140.3	148.9	61.1	50.2
200	713.0	274.2	283.9	106.2	90.8

Further, the length of Debye, defined by $\lambda_{Debye} = \sqrt{\frac{\varepsilon k_B T}{2Nq^2}}$ was evaluated. In the definition of λ_{Debye} , $k_B T$ is the thermal energy, N the density of ions, q the electrical charge of the monovalent ions and ε the dielectric constant of the liquid crystal.

Due to the anisotropy of the liquid crystals, the dielectric constant depends on the nematic orientation described by the liquid crystal director \mathbf{n} . The measurements being performed for applied voltages with amplitudes below the Freedericksz threshold transition, no reorientation of nematic molecules occurs. For the analysed samples, planar aligned, the dielectric constant is that one perpendicular to the director, $\varepsilon = 6.7 \cdot \varepsilon_0$ [9], where ε_0 is the dielectric constant for free space. The values obtained for the length of Debye for each type of anion depend on the period of the applied voltage as shown in Fig.1.

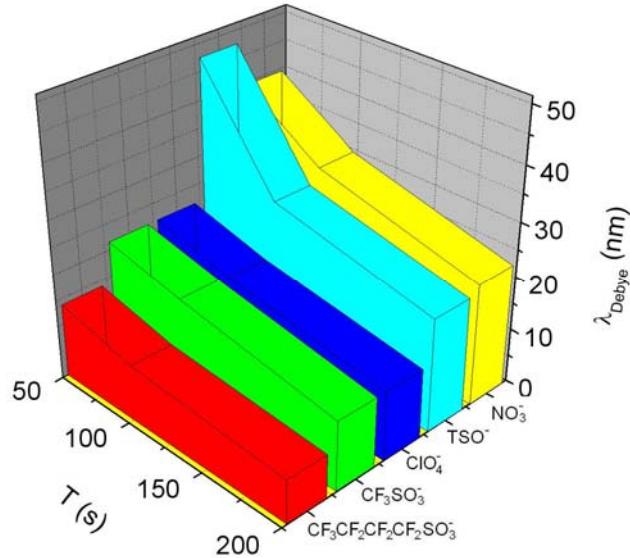


Fig.1. Variation of the Debye length with the applied voltage period at the same amplitude $3V_{PP}$, for different types of dopant anions

As one can see, for short periods (≤ 5 s) of the applied voltages, the ion densities and Debye lengths are in good agreement with values of pure 5CB reported in literature [4,5].

An increase of the period of the applied voltage decreases the Debye screening length; that is, the penetration depth of the electric field of the diffuse layer decreases and the average value of the electric field near the NLC-polypyrrole film interface increases.

A comparison between Debye lengths estimated for alignment polymer films of different thickness is shown in Fig.2.

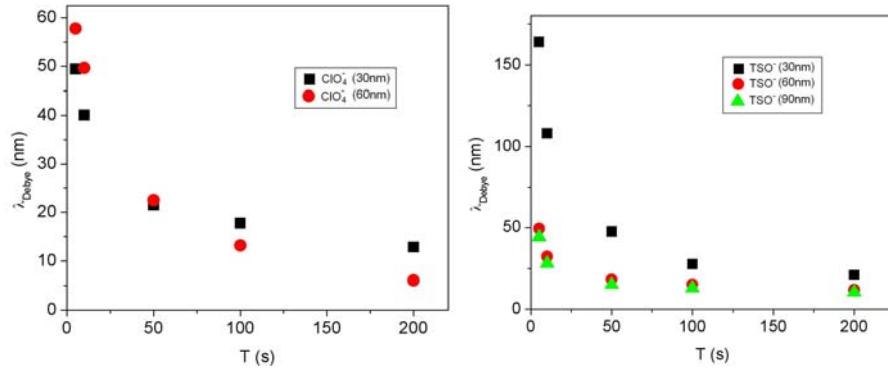


Fig.2. Dependence of the Debye length on the period of the applied voltage for
 (a) PPy doped with ClO_4^- 30 nm and 60 nm in thickness,
 (b) PPy doped with TSO^- 30 nm, 60 nm and 90 nm in thickness

The results indicate that the Debye length values decrease with increasing thickness of the same alignment conductive polymer films, for long periods (≥ 100 s for PPy doped with ClO_4^- and ≥ 5 s for PPy doped with TSO^-) of the triangular applied voltages. This behavior leads to the conclusion that the penetration of the electric field into the liquid crystalline phase depends on the amount of ions present in the polymeric film.

4. Conclusions

We analyzed the electrical properties of nematic liquid crystals planar aligned with conductive polypyrrole layers. From the measured current in a circuit

containing the sample it is possible to evaluate the density of ions present in the liquid crystal. This density is larger than the one present in a liquid crystal aligned with a dielectric polymer and it is proportional with the thicknesses of the doped polypyrrole. These results confirm the hypothesis that the ions from the aligned layers are transferred into the nematic cell.

From the experimental date we evaluate also the Debye length. The obtained values show that the nematic sample can be considered as a distribution of ions which varies in time depending on the applied electric field.

The Debye lengths obtained for same thickness of alignment films doped with different anions depend on the size and molecular geometry of the ions.

For low periods (≤ 1 s) of the applied voltages, the ion densities and Debye lengths are in agreement with values of pure 5CB reported in literature.

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