THE CARR-HELFRICH EFFECT IN LIQUID CRYSTAL MBBA DOPED WITH SWCNTS

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Influence of single-walled carbon nanotubes (SWCNTs) with concentration of 0.5wt.% on the Carr-Helfrich electrohydrodynamic instability (*EHDI*) in nematic liquid crystal 4-methoxybenzylidene-4'-butylaniline (*MBBA*) is investigated. It is shown that the inclusion of this dopant into liquid crystal leads to decreasing of the threshold voltage of Williams domains formation. In addition, an increase in the threshold voltage is observed at low frequencies. Critical frequency of disappearance of the *EHDI* increases for the MBBA+SWCNTs colloid with respect to the pure MBBA. In this case, a increase of time characteristics in the colloid is observed owing to strong interaction of the nanotubes with the liquid crystal molecules.. The experimental results are explained on the base of the Carr-Helfrich theory for electrohydrodynamic instability in nematic liquid crystal.

1. INTRODUCTION

Electro-optic effects in liquid crystals (*LC*) are subdivided into field and current ones. Field effects are concerned with the reorientation of *LC* molecules under the action of an electric field. Current effects are the result of motion of macroscopic volumes of a liquid crystal. In this case, various types of electrohydrodynamic instability (*EHDI*) appear. One of them is the formation of so-called Williams domains. Regular vortex motion is observed at application of a sine-form electric field to homogeneously oriented nematic LC with negative dielectric anisotropy. They have a form of long rolls perpendicular to the initial planar alignment of the director and are observed as alternating dark and light bands under a polaizating microscope. For the first time, theoretical description of this effect was given by Carr [1] and Helfrich [2]. Therefore, it is often called the Carr - Helfrich effect.

In earlier times, we investigated the influence of conductive and non-conductive small particles with dimensions compared with the wavelength of the incident light and the corresponding bands of the Williams domains in nematic *LC* [3]. It was shown that the existence of particles in *LC* reduces the threshold voltage of the *EHDI* formation at application of electric field. Meanwhile, the limiting frequency of the EHDI disappearance increases at the additive of silver particles while aluminum oxide particles reduce it. A presence of particles changes rise and decay times in comparison with the pure *LC*.

Single-walled carbon nanotubes (SWCNTs) have a diameter comparable to cross-section of elongated *LC* molecules. Rod-like particles of SWCNTs in nematic *LC* cause the effective orientational coupling with *LC* molecules [4].

The aim of the work is the study of influence of SWCNTs on the Carr - Helfrich effect in nematic liquid crystal 4-methoxybenzylidene-4'-butylaniline.

2. EXPERIMENTAL

We used nematic liquid crystal 4-methoxybenzylidene-4'-butylaniline (MBBA) from the firm Merck with negative dielectric anisotropy as a matrix. The temperature range of the nematic phase of this LC is usually located between 21°C and 47°C.

Single-walled carbon nanotubes (SWCNT) (US, Research Nanomaterials, In.) were added into the liquid crystal with concentration of 0.5wt. %. Then obtained mixture was shaken in a vortex mixer for 1 hour at temperature 50°C, followed by sonication with dispergator Ultrasonic Cleaner NATO *CD*-4800 (China) for 4 hours.

The cell had a sandwich structure and consisted of two plane-parallel glass plates whose inner surfaces were coated with thin transparent and conductive indium-tin-oxide (*ITO*) layer. Planar orientation of molecules was attained by coating the inner substrate surfaces with rubbed polyimide layers. For obtaining of homeotropic orientation of *LC* molecules, we used the surfactant (polysiloxane). The cell thickness was fixed with calibrated 20μm polymer spacers for measurements. Both the colloid and the pure *LC* were injected into the empty cell by capillary action at the isotropic state. To increase the dispersion, the cells with the colloid were placed at electric field of 40 V to achieve turbulence and were kept for 2 days. In this case, no aggregation of particles was observed. The filled cell was kept in the special heater with temperature regulator *GL*-100 (China).

Dielectric and conductivity measurements were carried out by the Precision LCR Meter 1920 (IET Labs. Inc., USA) at the frequency of 2kHz and temperatures 24°C. In such a case, applied voltage was *0.5V* for both *LC* molecular orientations.

A set-up for measurements of electro-optic parameters was assembled on the base of the Carl Zeiss polarization microscope (model 720, Germany). The electric impulses of the special form applied to

the cell from the functional generator (model G6-28, Russia). A light, passing through the cell, fell on the photo diode and was registered by digital storage oscilloscope (model 6022BE, Hantek, China).

The threshold voltage of Freedericksz effect was determined from an electro-optic response using unipolar triangular impulses in quasi-static regime while switching times of Williams domain formation were done by application of unipolar rectangular impulses. The voltage of Williams domains displaying was visually defined by observation under polarization microscope (fig.1).

3. RESULTS AND DISCUSSION

he frequency dependence of the threshold voltage for the formation of Williams's domains in the pure *LC* and the colloid at 24°C is shown in fig.2. As can see, the asymptotic value of the threshold voltage at static electric field is equal to 6.4*V* for the pure *LC* while it decreases down to 6.1V with the additive of SWCNTs. Moreover, critical frequency of disappearance of the EHDI increases for MBBA+SWCNTs with respect to the pure *LC*. In

addition, an increase in the threshold voltage is observed at low frequencies.
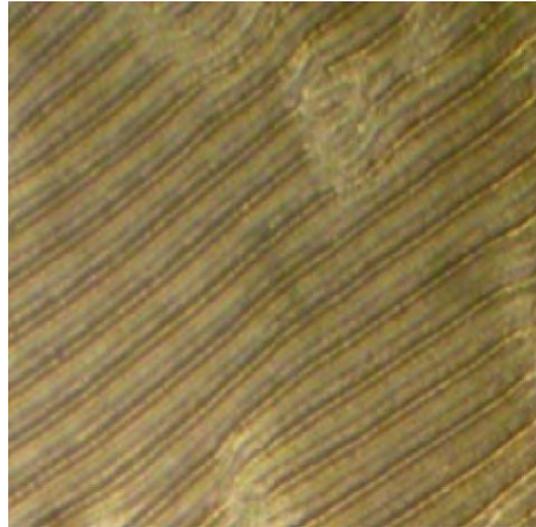

Fig.1. The image of Williams domains under the polarization microscope.
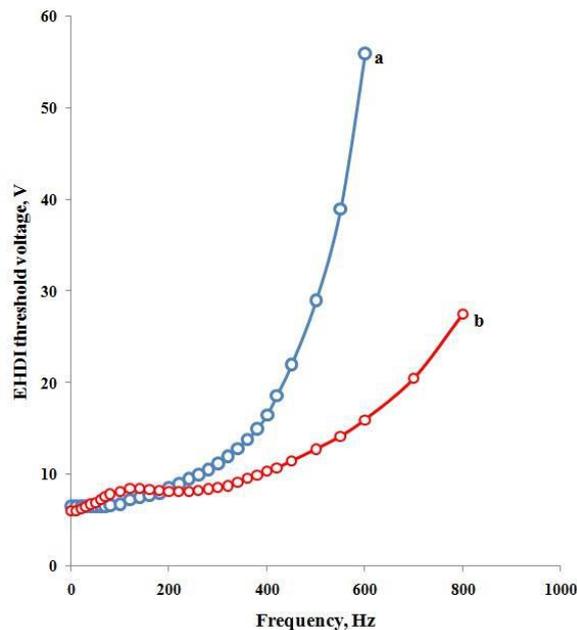

Fig.2. Frequency dependence of the threshold voltage of Wiliams domain formation: (a) pure MBBA; (b) MBBA+SWCNTs.

It is known that the ions are charge carriers in liquid crystal. In this case, the mobility along long molecular axis is more than one across this direction.

Thereby, electric conductivity in one direction is greater than in the another. The space charge is formed owing to this anisotropy because of ion division. Electric field applied to the *LC* layer acts on the charges. It imparts the formation of macroscopic flows in two reciprocal directions which generate the torque acting on the *LC* molecules. In addition, the dielectric torque is originated under the action of the transverse field because of the distribution of the space charge. At certain conditions, the torque formed

by the motion of charges preponderates over other torques and the system becomes unstable. At low frequencies of an applied field, the instability mode is characterized by oscillation of the space charge with the same frequency. The motion of the space charge lags behind in the phase of the field frequency with its increasing. It leads to reduction in the force of the external field on the space charge. The torque corresponding to conductivity decreases and it is necessary to increase the external field for realization of instability. Therefore, the threshold voltage sharply increases at approaching to the critical frequency f_c connected with the dielectric relaxation time τ_c as [5]:

$$f_c = \frac{\sqrt{\xi^2 - 1}}{2\pi\tau_c} \tag{1}$$

where ξ^2 is the gain parameter which is defined as follows [6]:

$$\xi^2 = -\frac{\varepsilon_{II}^2}{\varepsilon_\perp \Delta\varepsilon} \frac{\eta_B}{\eta} \left(\frac{\varepsilon_\perp}{\varepsilon_{II}} - \frac{\sigma_\perp}{\sigma_{II}} \right) \tag{2}$$

where ε_{II} and $\varepsilon_\perp$ are the longitudinal and transverse components of the dielectric permittivity of liquid crystal, respectively; $\Delta\varepsilon$ is the dielectric anisotropy; σ_{II} and $\sigma_\perp$ are the specific conductance along and across

the director, relatively; η_B is the viscosity relevant for bend deformations; η is translation viscosity which is defined by following combination of Leslie viscosity coefficients [7]: $\eta=(1/2)(\alpha_4+\alpha_5-\alpha_2)$.

In order to estimate the critical frequency for the pure *LC* and the colloids, the values of dielectric permittivity and specific conductance were measured in the middle frequency range (*2kHz*) since the corresponding parameters at these frequencies determine the bulk properties of the *LC* and the colloid [8]. Experimental values are resulted in the Table 1.

Table 1.

Dielectric permittivity, dielectric anisotropy and specific conductance of the pure MBBA and the colloid at the frequency of *2kHz*.

	ε_{II}	$\varepsilon_\perp$	$\Delta\varepsilon$	σ_{II}, 10^{-8} S/m	$\sigma_\perp$, 10^{-8} S/m
Pure MBBA	4.60	5.19	-0.59	11.0	7.4
MBBA+SWCNTs	4.75	5.09	-0.34	14.2	9.1

As can be seen from the table, the additive of fullerenes into MBBA reduces the longitudinal component of dielectric permittivity and specific conductance while the presence of SWCNTs increases the corresponding parameters. There is a strong dipole-dipole interaction between SWCNTs and *LC* molecules in the MBBA+SWCNTs, leading to an increase in the order parameter [9] and the longitudinal component of dielectric permittivity. Owing to the percolation effect [10], the electron hopping conductivity dominates over the ionic one, leading to an increase in the specific conductance.

Let us assume that the ratio of viscosity of different types changes in the same manner with the additive of fillers. Hence, the ratio $k=\eta_B/\eta$ for the pure *LC* and the colloids has the same value. Using (2) and the experimental values of the parameters, one can obtain the values of gain parameters which are equal to 3.14k and 5.61k for MBBA and MBBA + SWCNTs, correspondingly. Moreover, the presence of SWCNTs descreases the dielectric relaxation time of nematic *LC*. Considering the above, we find that SWCNTs increase the critical frequency of the disappearance of Williams domains. It consistent with the corresponding experimental results.

According to [6], the threshold voltage for the formation of Williams domains is defined as:

$$U_W^2 = -\frac{4\pi^3 K_{33}}{\varepsilon_\perp \Delta\varepsilon(\xi^2 - 1)} \tag{3}$$

In order to calculate the threshold voltage, it is first necessary to find the value of the bend elastic constant which can be determined from the following

expression for the threshold voltage of the Freedericksz effect [7].

$$U_F = \pi\sqrt{\frac{K_{33}}{\varepsilon_0 |\Delta\varepsilon|}} \tag{4}$$

The experiment shows that the homeotropic-planar transition begins in the pure LC at voltage of 3.7 V while it is equal to 4.4*V* with the additive of fullerenes and SWCNTs, respectively. Simple calculations give the values of $7.25\cdot10^{-12}N$ and $5.91\cdot10^{-12}N$ for MBBA and MBBA+SWCNTs. Using (3), we obtain the following relations: $U^2_s/U^2_p = 1.49$ (3.14 k-1)/(5.56 k-1), where U_p and U_s are the threshold voltages of Williams domains formation in MBBA and MBBA+SWCNTs, accordingly. Considering that k is approximately equal to 2 [6] for MBBA and slightly changes, depending on its purity, it is easy to show that the indicated ratios are less than 1. In other words, the calculations indicate to a decrease in the threshold voltage at the additive of dopand and qualitatively good agree with the experiment.

One can note that conducting SWCNTs at low frequencies of the external field prevent formation of the space charge, playing a role of traps for moving ions. For that reason, the threshold voltage increases at these frequencies.

The dependence of switching times of the Williams domain formation on the applied voltage for both the pure *LC* and the colloid is presented in fig.3. Apparently, a rise time decreases with increasing of the applied voltage in all cases and these dependences qualitatively correspond to the expression [11]:

$$\tau_{on} = \frac{\beta \eta_B d^2}{U^2 - U_W^2} \qquad (5)$$

where β is the coefficient depending on properties of

the pure *LC* or the colloid; *d* is the cell thickness; *U* is the voltage of applied field. As can be seen, an additive of SWCNTs into the pure *LC* increase a rise time as well as a decay time at all voltages.
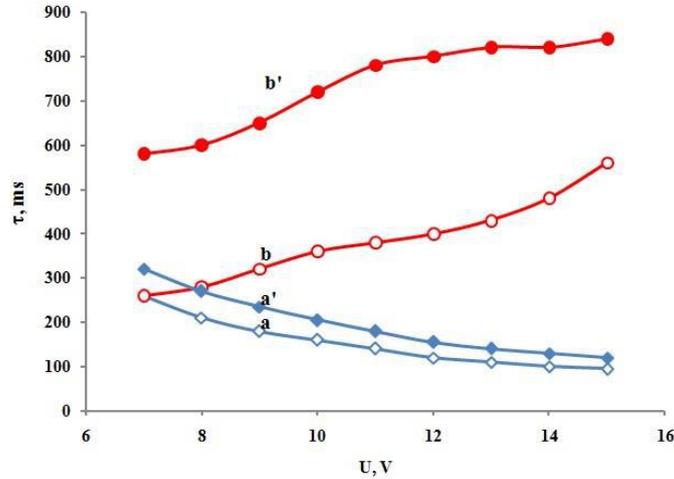

Fig.3. Voltage dependences of switching times of the EHDI effect: (a) a rise time of the pure MBBA; (a') a rise time of the colloid; (b) a decay time of the pure MBBA; (b') a decay time of the colloid.

Possible explanation for the increase of time characteristics in the MBBA+SWCNTs colloids may be because of the strong interaction of the nanotubes with the *LC* molecules, which increases the inertia of the corresponding pair, reacting to the voltage as a whole.

4. CONCLUSION

It is shown that the additive of SWCNTs into the nematic liquid crystal MBBA with the concentration

of *0.5wt.%* leads to a decrease in the threshold voltage of Williams domain formation. Owing to an increase of the longitudinal component of dielectric permittivity and amplification of electric conductivity in the MBBA+SWCNTs colloid, the critical frequency of disappearance of the EHDI increases for the colloid with respect to the pure *LC*. Time characteristics increase in MBBA+SWCNTs by reason of strong interaction of the nanotubes with the *LC* molecules.

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