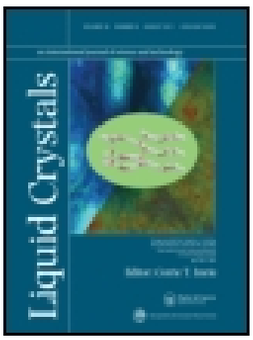

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Polar anchoring energy and tilt angle measured by magneto-optical technique in nematic doped with ionic surfactant

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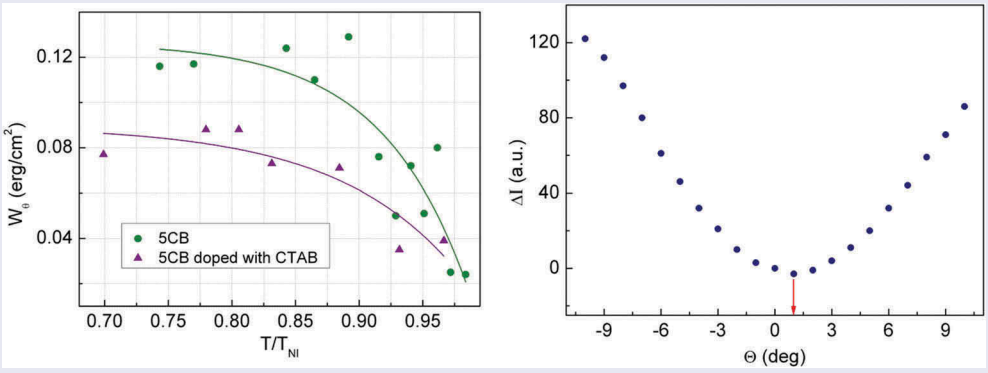
ABSTRACT

The surface anchoring of a nematic doped with the ionic surfactant has been investigated and compared with the one in the undoped sample. The director tilt angle at the substrates coated with the orienting polymer film has been determined by the null method in a rotating magnetic field. The Frederiks transition in a magnetic field has been chosen as a convenient technique to measure the polar anchoring energy W_θ. The temperature dependences of anchoring energy have been obtained for the various nematic cells. The W_θ values for nematic doped with the ionic surfactant are less than for the undoped one. The factors affecting the measurement accuracy have been discussed. The accuracy is higher for the thinner nematic layers and weaker anchoring energy.



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KEYWORDS
Nematic; ionic surfactant; tilt angle; anchoring energy; magnetooptics

1. Introduction

Liquid crystals (LCs) are the materials whose properties can be controlled by the various external factors such as electric or magnetic field, temperature, etc [1,2]. In practice, LC is usually placed between two substrates. The surface anchoring of LC molecules with the substrates specifies the director configuration, which, in turn, assigns the bulk properties of the LC layer. The director tilt angle θ_0 (the angle between a director and a substrate surface) and the polar anchoring energy W_θ are the independent parameters describing an interaction of LC with a surface. Besides, the temperature dependences of W_θ allow getting the important data on the interaction between LC and solid surface [3,4]. Various methods have been proposed to measure the parameters θ_0 [5] and W_θ [2] among which the methods using an electric or magnetic field are the most effective [6]. For example, the parameter θ_0 can be measured by the magnetic null method in which the LC cell is rotated until the director is oriented parallel to the magnetic field. The determination of θ_0 is carried out by measuring the capacitance [7,8], optical transmission [9,10] or the angle of total internal reflection [11]. The polar anchoring energy W_θ can be determined by measurement of the threshold [3,4,12–14] or the saturation [12,15–17] fields of Frederiks transition in the electric or magnetic fields. In addition, the anchoring energy can be obtained based on the analysis of the dependences of birefringence and capacitance of LC cell on the applied voltage [15,18,19]. Currently, the above-mentioned methods to measure W_θ are widely used in research [20,21] and have some advantages and disadvantages.

The effect of various additives on the response of LC materials to the external influences is of great interest. The additives in LC can not only improve the response

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of the system, but also allow realising the new orientational transitions in liquid crystals. For instance, the additive of ionic surfactant into LC initiated a transformation of the director configuration by the electrically controlled ionic modification of the surface anchoring [22–25]. In this method, the applied DC voltage induces the modification of the boundary conditions due to the variation of the surface density of ions. Since the surfactant ions are adsorbed at the interface, their influence on the polar anchoring energy is an important issue [26,27]. The measurement of W_θ by a magnetic field is more suitable than the electric field which can cause the parasitic effects of ion redistribution [15]. In this article we determine the tilt angle θ_0 and the polar anchoring energy W_θ of a nematic LC doped by the ionic surfactant with a polymer surface using the magneto-optical methods.

2. Experimental technique

The experiment was carried out with sandwich-like cells. These cells consisted of two glass substrates covered by the polymer films of polyvinyl alcohol (PVA) which specify the planar surface anchoring for LC. Spin coater HO-TH -05 (HOLMARC) was used to form the polymer films on the substrates by spin coating. Then the polymer films were uniaxially rubbed by Rubbing machine HO-IAD-BTR-01 (HOLMARC) to assign the uniform director orientation on the PVA films. The substrates were assembled into cells so that the rubbing directions of the polymer films at the top and bottom surfaces were antiparallel. The cell gap thickness d was set using teflon films and measured by means of the interference technique with the spectrometer HR4000CG-UV-NIR. One pair of cells had the gap thicknesses d_1 = 13.6 μm and d_2 = 13.9 μm (thick samples) while the other samples had d_3 = 5.0 μm and d_4 = 4.8 μm (thin samples). The cells with d_1 and d_3 were filled with undoped nematic 4-pentyl-4′-cyanobiphenyl (5CB), the samples with d_2 and d_4 were filled with 5CB containing 0.78 wt. % of ionic surfactant cetyltrimethylammonium bromide (CTAB).

Measurements of θ_0 and W_θ were carried out using the magnetooptical setup (Figure 1). To determine θ_0 the beam of He-Ne laser *L*' (LGK 7634, LASOS) (λ = 0.633 μm) passed through the polariser *P*', the LC cell *S*', the crossed analyser *A*' and was detected by the photodiode *F*' (Scheme 1 in Figure 1). The signal from the photodiode was measured by the voltmeter. The angle between the rubbing direction of the PVA films and polarisers was equal to ±45°. LC cell was fixed at the rod between the electromagnet poles and adjusted so that the incident laser beam was perpendicular to the substrates. The rubbing direction of the cell substrates coincided with the axial line of the electromagnet poles and lied in the rotation plane of the electromagnet placed on the stage *R*. The rotation angle Θ was set by the dial *G* with the diameter of 640 mm and changed in the range from −10 to +10° in steps of 1°. The magnetic field of about 18

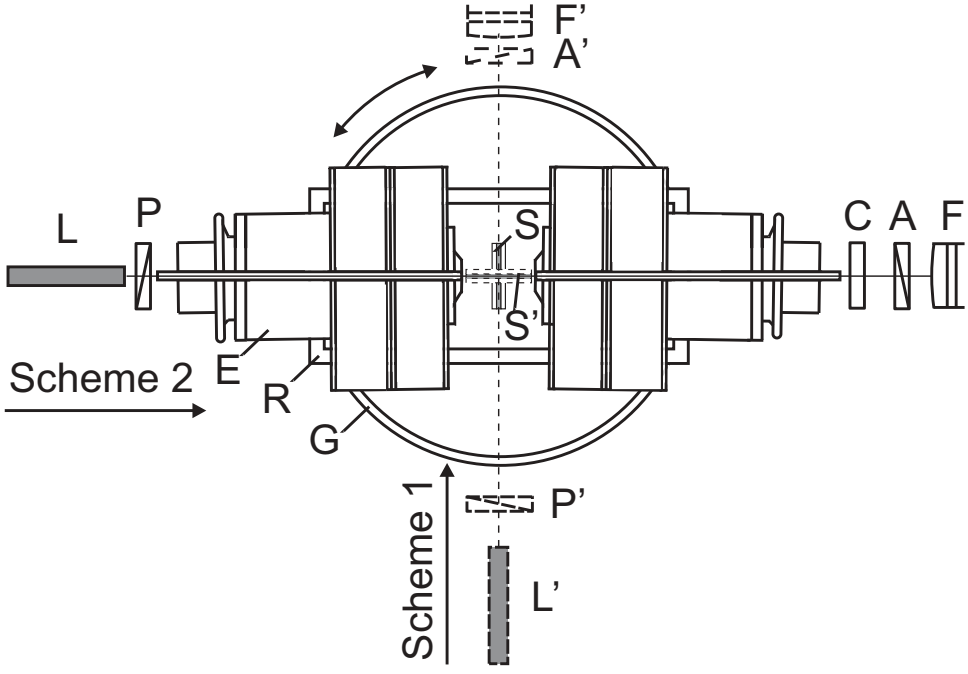

Figure 1. Scheme of magnetooptical setup. *L, L'* – He-Ne lasers; *P, P'* – polarisers; *E* – electromagnet; *S, S'* – LC cells; *C* – quarter-wave plate; *A, A'* – analysers; *F, F'* – photodiodes; *R* – rotating stage; *G* – dial. Schemes 1 and 2 are the optical schemes for measuring the tilt angle θ_0 and polar anchoring energy W_θ, respectively.

kOe was applied to the sample for each value of the angle Θ and the minimal change in the light intensity ΔI_{min} was found. In this case, the initial director orientation was approximately parallel to the magnetic field lines and the angle Θ was equal to the director tilt angle θ_0.

To determine W_θ the beam of He-Ne laser *L* (R-39727, Newport Corporation) (λ = 0.633 μm) passed parallel to the axial line of the electromagnet poles through the polariser *P*, the LC cell *S*, the quarter-wave plate *C*, the analyser *A* and was detected by the photodiode *F* (Scheme 2 in Figure 1). LC cell was put into the constant-temperature cuvette placed between the drilled electromagnet poles so that the initial director orientation was perpendicular to the magnetic field lines. The angle between the incident light polarisation and LC director was equal to 45°. The temperature *T* within the cuvette was monitored by the copper-constantan thermocouple, and the magnetic field strength *H* was measured by the Hall probe. The temperature and magnetic field were stabilised with accuracy ± 0.5%. The values of light intensity *I* and magnetic field strength *H* proportional to the signals from the photodiode and Hall probe, respectively, were measured by the voltmeters, and the dependences *I* (*H*) were recorded automatically. The *H* value was varied from 0 to 24 kOe, and the scanning rate was equal to 1 kOe/min.

In the initial state, the light intensity was set to zero at a certain temperature. To adjust the optical system in this way, LC cell was firstly placed between the polarisers and the minimal light transmission was obtained by the analyser rotation. In this case, the major axis of the polarisation ellipse of the light passed through the LC cell was perpendicular to the analyser. Then the quarter-wave plate was placed between the sample and analyser so that the fast or slow axis of the plate was parallel to the analyser. It provided the linear polarisation of light after the quarter-wave plate. Finally, the zero light transmission was set by the analyser rotation.

The anchoring energy W_θ was calculated from the expression [28]

$$ctg\left(\frac{H_{th}}{H_{th}^{\infty}}\frac{\pi}{2}\right) = \frac{H_{th}}{H_{th}^{\infty}}\frac{\pi K_{11}}{W_\theta d} \quad (1)$$

where K_{11} is the splay elasticity constant of LC; *d* is the thickness of the nematic layer; H_{th} is the threshold value of the magnetic field strength measured in the experiment; H_{th}^{∞} is the threshold value of the magnetic field strength at $W_\theta \to \infty$. H_{th}^{∞} was determined as [1, 2]

$$H_{th}^{\infty} = \frac{\pi}{d}\sqrt{\frac{K_{11}}{\Delta\chi}} \quad (2)$$

where Δχ is LC diamagnetic anisotropy.

3. Results and discussion

Figure 2 shows the dependence of light intensity variation Δ*I* on the rotation angle Θ of the electromagnet when a magnetic field is applied to the sample. The cell under study was filled with 5CB, and the LC layer thickness was 13.6 μm. It is possible to find the intersection point of the decreasing and increasing parts of the dependence Δ*I* (Θ) by rotating the electromagnet in the opposite directions. This point corresponds to the director tilt angle θ_0. The data presented in Figure 2 show that θ_0 is about 1°. The same θ_0 values were obtained for other samples, including LC cells filled with 5CB doped by the ionic surfactant.

The dependences *I*(*H*) for different temperatures *T* of the samples with the LC layer thicknesses of 13.9, 13.6, 5.0, and 4.8 μm were obtained for the determination of polar anchoring energy. Figure 3 shows the dependences *I(H)* for thin layers of undoped 5CB and 5CB doped with the ionic surfactant CTAB. It is seen that the ionic impurity does not significantly change the shape of *I(H)* dependences. For both samples, the increase of the reduced temperature T/T_{NI} (T_{NI} is the nematic-isotropic transition temperature) leads to decreasing the threshold field of Frederiks transition. At that, the slope of curves *I*(*H*) near the threshold increases. Similar dependences *I*(*H*) at the various reduced temperatures were obtained for the samples with the LC layer thicknesses of 13.9 and 13.6 μm. In these cells, the threshold of Frederiks transition was lower because of the thicker LC layers.

The H_{th} values were determined from the experimental curves *I*(*H*). The temperature dependences of $H_{th}d$ for LC

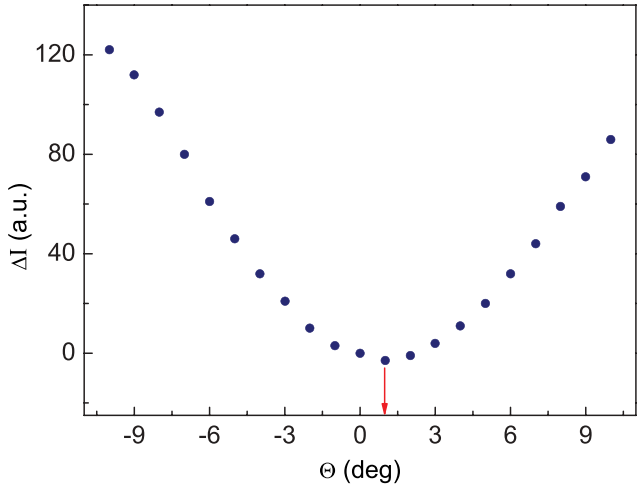

Figure 2. (Colour online) Dependence of the light intensity variation Δ*I* on the electromagnet rotation angle Θ when the magnetic field is applied to LC cell filled with 5CB. The nematic layer thickness is 13.6 μm. The red arrow indicates the director tilt angle θ_0 equal to 1°.

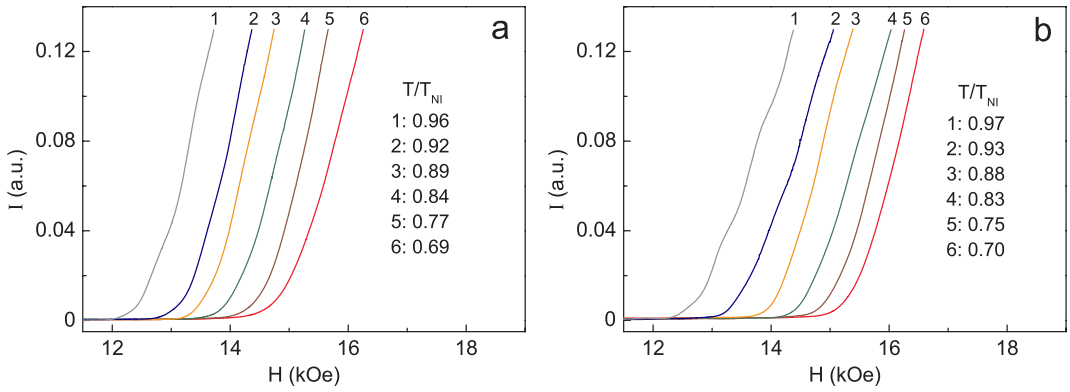

Figure 3. (Colour online) Dependences of the light intensity I on the magnetic field strength H obtained at the various reduced temperatures T/T_{NI} for the thin layers of undoped 5CB (a) and 5CB doped with the ionic surfactant CTAB (b). Hereinafter, T_{NI} is the nematic-isotropic transition temperature. The LC layer thicknesses of 5CB and 5CB with CTAB are 5.0 and 4.8 μm, respectively.

cells with thick (13.6 and 13.9 μm) and thin (5.0 and 4.8 μm) nematic layers are shown in Figures 4 and 5. It is seen that the spread of experimental points for thick LC layers (Figure 4) is larger than for the thin ones (Figure 5). The Frederiks threshold field decreases when the reduced temperature increases for all investigated samples.

The obtained values of the threshold magnetic field strength H_{th} were used to calculate the polar anchoring energy W_θ from the expression (1). The values of H_{th}^{∞} were calculated from the expression (2), where K_{11} and $\Delta\chi$ were taken at the certain reduced temperatures T/T_{NI} from [29]. The temperature dependences of W_θ for the thin LC layers of 5CB and 5CB doped with CTAB are presented in Figure 6. One can see that the increase of the reduced temperature causes a significant decrease of the polar anchoring energy. The observed

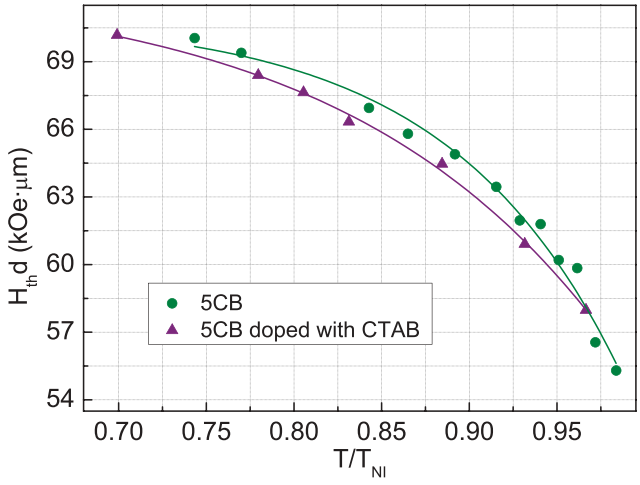

Figure 5. (Colour online) Temperature dependences of $H_{th}d$ for the thin layers of 5CB and 5CB doped with the ionic surfactant CTAB. The solid lines are the approximations. The LC layer thicknesses of 5CB and 5CB with CTAB are 5.0 and 4.8 μm, respectively.

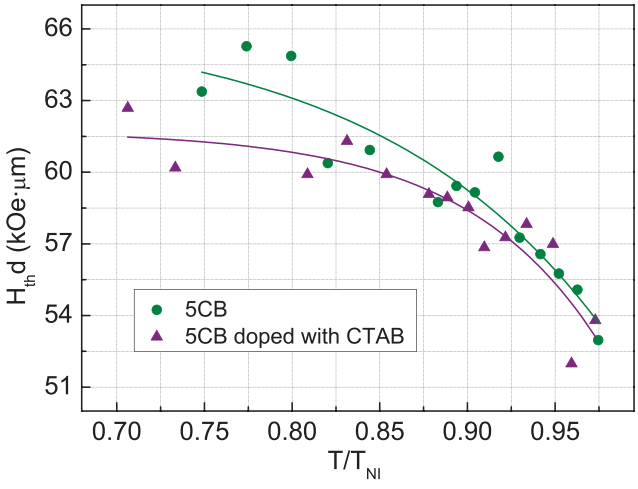

Figure 4. (Colour online) Temperature dependences of $H_{th}d$ for the thick layers of 5CB and 5CB doped with the ionic surfactant CTAB. The solid lines are the approximations. The LC layer thicknesses of 5CB and 5CB with CTAB are 13.6 and 13.9 μm, respectively.

increase in the slope of the dependences $I(H)$ in the threshold area (Figure 3) is probably connected with this fact. The lower polar anchoring energy leads to the sharper change of the director orientation in the central area of the cell with increasing the magnetic field [30] and, consequently, the light intensity rises faster. The polar anchoring energy is in the range 10^{-2}–10^{-1} erg/cm^2 that is in a good agreement with the data presented in [31]. The polar anchoring energy for 5CB doped with the ionic surfactant is less than for the undoped LC. It might be connected with the fact that CTAB is the homeotropic surfactant and it causes the weakening of the planar anchoring of LC molecules with the substrates. As mentioned above, the experimental values spread of H_{th} for the thick LC layers is larger than for the thin ones. A calculation of the polar

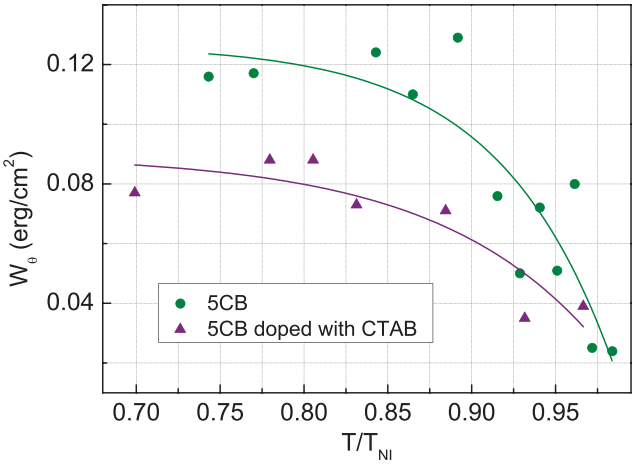

Figure 6. (Colour online) Temperature dependences of the polar anchoring energy for the thin layers of 5CB and 5CB doped with the ionic surfactant CTAB. The solid lines are the approximations. The LC layer thicknesses of 5CB and 5CB with CTAB are 5.0 and 4.8 μm, respectively.

anchoring energy based on the threshold magnetic field strengths H_{th} results in even wider spread of the points for the temperature dependences of W_θ. For this reason, the reliable W_θ data for the thick LC layers were not obtained.

The possible factors affecting the accuracy of θ_0 and W_θ measurements have been considered to analyse the obtained results. The electromagnet rotation to determine θ_0 allows more precisely detecting the transmitted light since the possible errors caused by a sample rotation might be larger. The errors of the anchoring energy measurement are caused by the inaccuracies in the determination of H_{th}. An uncertainty of the experimental H_{th} values is produced by a rounding of $I(H)$ dependences near the threshold (Figure 3). It has been shown in [28] that the abrupt threshold of director reorientation is observed when the director tilt angle on the alignment layers is zero. When the tilt angle is non-zero, there is no abrupt threshold. The performed θ_0 measurements by the magnetic null method have shown that the director tilt angle is about 1°. This value could not significantly distort the dependences $I(H)$. The rounding of $I(H)$ curves near the threshold can also be caused by the formation of the double electrical layer arising from the ion surfactant adsorption at the interfaces [26,27]. However, no significant differences in $I(H)$ near the threshold were observed for undoped 5CB and 5CB doped with the ionic surfactant, and this fact does not allow suggesting the existence of the ordered near-surface layers.

The threshold magnetic field strength was determined as the point where the light transmission starts to differ from the initial zero value. The small temperature fluctuations also lead to the error of H_{th} determination since they change the birefringence Δn of nematic and, consequently, the light intensity I. The intensity of the light passed through the LC cell placed at angles ± 45° between crossed polarisers is expressed by

$$I = I_0 sin^2\left(\frac{\pi d \Delta n}{\lambda}\right) \quad (3)$$

where I_0 is the intensity of the linearly polarised light incident on the LC cell, d is the thickness of LC layer and λ is the wavelength of the incident light [2].

Figure 7 demonstrates the calculated dependence of I (Δn) when the temperature of LC cell filled with 5CB changes by 10°C. The calculation was performed using the expression (3), and the Δn values at the certain reduced temperatures were taken from [32]. It is seen that the same Δn change leads to the different variations of the light intensity ΔI. For example, the Δn change by 0.0014 results in $\Delta I_1 = 0.1$ in the middle range of I and $\Delta I_2 = 0.02$ for I near zero. Therefore, to increase the accuracy of H_{th} determination, the quarter-wave plate was used in the optical scheme (Scheme 2 in Figure 1). This plate along with analyser allowed adjusting the initial light transmission to zero value.

The dependences of W_θ on the reduced magnetic field $h = H_{th}/H_{th}^{\infty}$ for LC layers with d = 13.9 μm and d = 4.8 μm have been calculated (Figure 8) to analyse the experimental accuracy of W_θ determination. The calculations have been performed using the expressions (1) and (2). In the case of a rigid surface anchoring ($W_\theta \to \infty$) the value of the reduced magnetic field tends to unity and a small error in the determination of the threshold

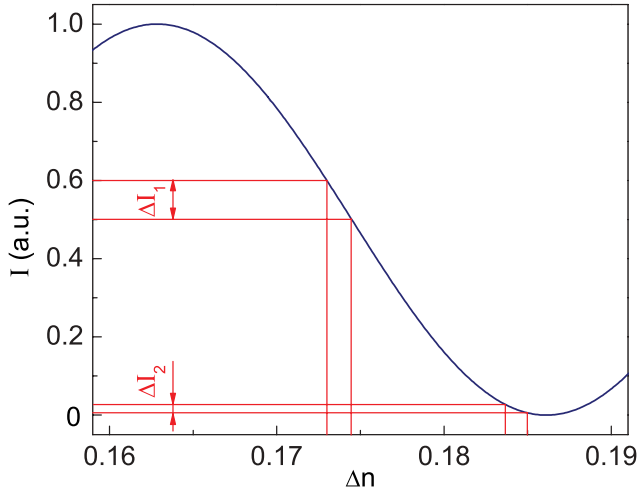

Figure 7. (Colour online) Dependence of the light intensity I on the birefringence of nematic Δn calculated from the expression (3). The LC layer thickness d = 13.6 μm. The wavelength λ = 0.633 μm.

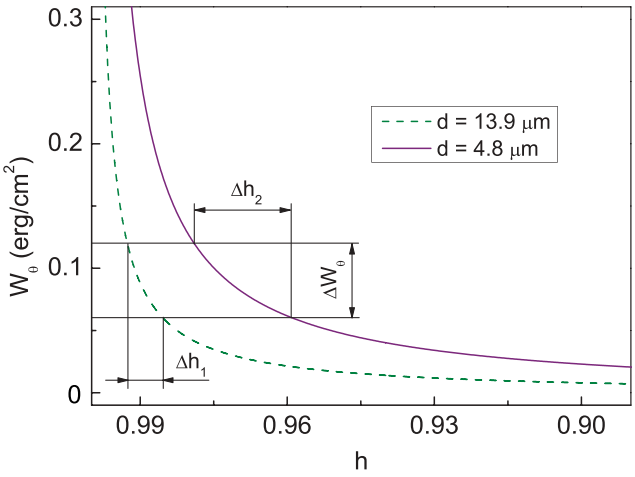

Figure 8. (Colour online) Calculated polar anchoring energy W_θ versus the reduced magnetic field h for LC layers with thicknesses 13.9 and 4.8 μm.

magnetic field strength results in the significant uncertainty of W_θ. The reduced magnetic field tends to zero when the surface anchoring is weak ($W_\theta \to 0$), and the measurement error of the threshold magnetic field strength influences insignificantly on W_θ. The reliable W_θ data are in the range of low values of anchoring energy. At the same time, the accuracy of W_θ determination depends on the LC layer thickness. For example, the error of Δh_1 determination equal to 0.008 leads to an uncertainty of the polar surface energy $\Delta W_\theta \cong 0.08$ erg/cm^2 in the thick LC layer. However, the same ΔW_θ uncertainty is obtained when the error of Δh_2 is 0.02 in the thin LC layer. Thus, the accuracy of W_θ measurement can be improved by using the thinner nematic layers and, consequently, higher magnetic fields.

4. Conclusions

The surface anchoring of nematic 5CB both with and without the ionic surfactant CTAB has been tested in the cells whose substrates were coated with orienting polymer films. The director tilt angle θ_0 at the substrates and polar anchoring energy W_θ have been measured in the various LC cells. The angle θ_0 determined by the null method in the rotating magnetic field is about 1°. The anchoring energy W_θ has been obtained using the threshold magnetic fields of Frederiks transition. Unlike methods using an electric field, a magnetic field avoids the ions redistribution in the cell during the experiments. The temperature dependences of W_θ have been obtained. It has been revealed that the increase of the reduced temperature leads to the decrease of the polar anchoring energy. W_θ for 5CB doped with the ionic surfactant is lower than for the undoped one. It is explained by that CTAB as homeotropic surfactant added to the nematic weakens the planar anchoring specified by the PVA films. Analysis of the factors affecting the measurement accuracy showed that an insertion of the compensator in the optical scheme decreases the influence of temperature fluctuations. Besides, the measurement accuracy of W_θ is higher for thinner LC layers and weaker anchoring energy.

Disclosure statement

No potential conflict of interest was reported by the authors.

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