



Anionic-cationic surfactant mixture providing the electrically controlled homeotropic surface anchoring of liquid crystals☆

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ARTICLE INFO

Article history:

Received 14 November 2018

Received in revised form 5 February 2019

Accepted 27 February 2019

Available online 28 February 2019

Keywords:

Polymer dispersed liquid crystal

Nematic droplet

Ionic surfactant

Anchoring transition

Director configuration

Optical texture

ABSTRACT

In search of a substance able to function as an anionic surfactant applied for the electrically-induced anchoring transitions in liquid crystals, the compound 4-heptyloxybenzoate benzyl dodecyltrimethylammonium (HOBDDDA) has been synthesized. Its orienting influence on nematic liquid crystal 4-pentyl-4'-cyanobiphenyl (5CB) has been tested. HOBDDDA dissolved up to 1.4% in 5CB droplets dispersed in polymer film does not change the tangential surface anchoring inherent to polyvinyl alcohol matrix used. Homeotropic surface anchoring is realized if the HOBDDDA content exceeds 1.7%. The molecules of the surfactant in 5CB dissociate into anions and cations. The anions modify the surface anchoring under the action of DC electric field both in the normal and inverse mode. The mixture of HOBDDDA and cetyltrimethylammonium bromide can function as a binary ionic-cationic surfactant which significantly expands the prospects for using the ionic-surfactant method to control liquid crystal materials.

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1. Introduction

Liquid crystals (LCs) are the molecular liquids with an anisotropy of the orientational structure, optical, electrical and other physical properties making them by promise material for using in various optoelectronic devices [1–3]. Liquid crystals are studied and applied in the different systems such as the flat capillary [4], polymer dispersed liquid crystals (PDLC) [5], emulsions, fibers, etc. [6]. Optical properties of LC materials depend mainly on the orientational ordering of LC molecules, which, in turn, is specified by the anchoring of its molecules at the interface. Surface anchoring of LC can be controlled by the specially chosen and treated orienting layers of specific chemical composition [4,7–9]. For example, in flat capillaries the using of thin polymer film as orienting layer allows obtaining the homogeneous or structured interface and the appropriate anchoring by the rubbing or photoalignment method. The homeotropic boundary conditions both in the conventional LC cells and in another more complex LC systems such as droplets dispersions, colloids, capillaries, etc. can be realized using some surfactants. In this case the ordered long alkyl chains of surfactant molecules

orient the LC molecules [7,10,11]. The parameters of orienting layer and, consequently, the surface anchoring can be varied by changing the concentration of surfactant dissolved in LC [12] or in the ambient solution [13], pH of the ambient medium [14,15], temperature [16] or upon UV irradiation [17,18]. Using of ionic surfactants allows modifying the orienting influence of definite interface area due to the applied voltage which changes the ion concentration at the corresponding part of droplets [19–22] or on the substrate of flat LC cells [23–25]. Such anchoring transitions cause the transformation of orientational structures which cannot be obtained by using the Frederiks effect [26,27]. This approach to control a director configuration is known as the ionic-surfactant method [19–27]. The method was realized previously only with cationic surfactant cetyltrimethylammonium bromide (CTAB), that limits the application of this method, since the modification of boundary conditions occurs only near one of the electrodes. To change the boundary conditions near both electrodes, it is necessary to apply simultaneously the anionic and cationic surfactants. This work is aimed at the synthesis of anionic homeotropic surfactant which in composition with CTAB can function as a binary anionic-cationic surfactant for electrically controlled anchoring transitions.

2. Materials and methods

PDLC films based on the nematic LC 4-pentyl-4'-cyanobiphenyl (5CB) (Merck), the polymer polyvinyl alcohol (PVA) (Mowiol 28-99,

☆ The article belongs to the special issue on The problems of solvation, complex formation and crystallization challenging the development of smart materials.

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Aldrich) plasticized with a glycerin, the cationic surfactant CTAB (Sigma) and the anionic surfactant 4-heptyloxybenzoate benzyl dodecyltrimethylammonium (HOBBDDBA, see Fig. 1) have been produced and studied [28].

The HOBBDDBA was synthesized in Belarusian State Technological University according to the following process: 6.3 mmol of 4-heptyloxybenzoic acid, 10.6 mmol of KOH and 10 mmol of dodecyltrimethylammonium chloride were mixed in the 100 ml of water at 40 °C. The reaction mixture was stirred for 25 min and cooled in the refrigerator. The crystalline product was filtered, washed with water and dried in the vacuum exicator. Yield 88%, m. p. 99°C. Data of NMR spectrum of the substance is presented in the Supplementary.

The weight ratio of 5CB:HOBBDDBA was varied in the range from 1:0.01 to 1:0.03. The weight ratios of PVA:GI and PVA:5CB were 1:0.27 and 1:0.11, correspondingly, for all samples. The HOBBDDBA, presented in Fig. 1, was dissolved in 5CB at temperature 70 °C for 5 min followed by cooling to room temperature without further purification. The samples for study were prepared by the emulsion technique [5]. Nematic 5CB doped with the HOBBDDBA was added in the water solution of polymer and glycerin. After that the mixture was mechanically stirred resulting in the formation of droplets, the size of which is varied from few microns to tens of microns. The obtained emulsion was poured out onto the glass substrate coated with two transparent ITO electrodes separated by 600 μm gap and then was dried. Such an arrangement of electrodes allows applying DC electric field in the plane of PDLC film.

The optical textures of the nematic droplets were examined by means of the polarizing optical microscope (POM) in crossed polarizers and with switching-off analyzer. For used materials the ordinary refractive index of nematic n_o is near to the refractive index of polymer matrix n_p . It allows determining the director orientation at the droplet interface in the geometry without analyzer [29]. In this case the droplet border is clearly seen owing to light scattering at those areas where the director is parallel to the polarizer, and vice versa it is almost invisible where the polarization of incident light is perpendicular to the director.

3. Results and discussion

3.1. The normal mode of ionic-surfactant method

The polymer PVA plasticized with a glycerine specifies the tangential boundary conditions for nematic 5CB [5]. The director configuration appearing in the droplets of nematic doped with surfactant depends on its concentration. So, the bipolar director configuration with two surface point defects (boojums [16]) is formed in the LC droplets at the weight ratio 5CB:HOBBDDBA = 1:0.014 and at lower surfactant content (Fig. 2a).

Such orientational structure corresponds to the tangential surface anchoring. When the initial orientation of bipolar axis is along the direction of applied electric field, one of boojums close to the anode is collapsed under the action of DC electric field (Fig. 2b). This is proved by rising light scattering at the corresponding droplet border, that means local change of the boundary conditions from tangential into homeotropic ones. Similar transformations are observed in the normal

mode of ionic-surfactant method [19]. The relatively sharp transition between regions with tangential and homeotropic anchoring is typical for the sample under study. Sufficiently narrow extinction lines observed in crossed polarizers (Fig. 2b, bottom row) is proved it. Thus, under the action of DC voltage the bipolar director configuration is transformed into the structure with boojum and surface ring defect with a preferred splay deformation (splay-type ring defect) (Fig. 2c) dividing the regions with different boundary conditions. The observed transformations of optical textures show that HOBBDDBA dissociates into ions, and anions HOB^- provide the controlled surface anchoring under the action of DC electric field similarly to the processes occurred in [19–22] due to cationic CTAB surfactant. At the same time, the cations BDDBA^+ do not change the boundary conditions.

Orientalional structure transformation shown in Fig. 2 is caused by only modification of boundary conditions near of anode. Consequently, the director orientation corresponds to the initial bipolar configuration in the most part of droplet (Fig. 2b). The same situation is observed when the bipolar axis is initially aligned at any angle to the direction of applied field. Fig. 3 demonstrates the bipolar droplet with axis orthogonal to the electric field. Modification of boundary conditions occurs near of the anode as in the above described case (Fig. 2) while both point defects remain (Fig. 3). As a result, we observe the optical texture (Fig. 3d–e) of complex asymmetric structure with two boojums and the ring surface defect dividing the homeotropic anchoring region from the tangential one. The plane of ring defect is perpendicular to the applied field, and the defect has areas characteristic of both wedge and twist distortions smoothly transforming from one to other along the defect line similar to the disclination ring in nematic layer [30].

Thus, the scenario presented in Fig. 3 is realized generally at any orientation of bipolar axis relatively to E-vector. However, a structure with one boojum is formed eventually when one of the boojums is initially on the part of droplet surface where the boundary conditions are changed [19].

The area of droplet surface with the modified boundary conditions depends on the value of applied voltage (Fig. 3). There are a threshold field below which the surface anchoring doesn't change from tangential to homeotropic one (Fig. 3a) and a saturation field above which the part of surface with modified boundary conditions is practically independent of the field value (Fig. 3e). At intermediate values of field, the part of modified surface smoothly increases as the field rises (Fig. 3b–d). The value of threshold field increases as the droplet size or the surfactant content decrease. However, there is a minimal concentration of surfactant at which this effect is possible. In the compositions under study, the modification of boundary conditions occurs when the content of HOBBDDBA is >1%. When HOBBDDBA is 1.7% and more, the homeotropic anchoring is initially formed in the droplets. In the range of HOBBDDBA concentration from 1% to 1.7%, the part of droplet surface with electrically controlled boundary conditions at saturation field increases as the surfactant content rises.

3.2. The inverse mode of ionic-surfactant method

The homeotropic boundary conditions are realized in the nematic droplets formed in the PDLC with the weight ratio 5CB:HOBBDDBA =

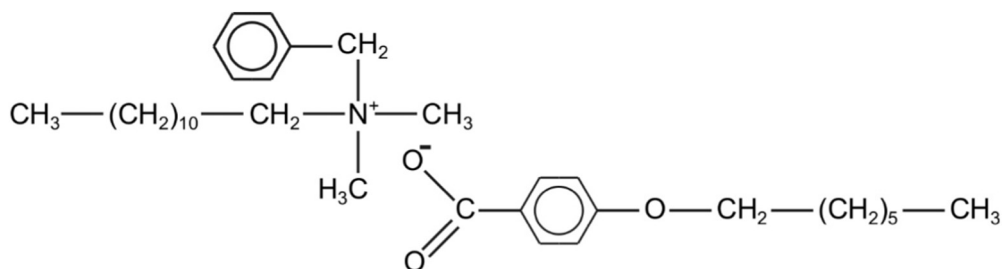


Fig. 1. Chemical formula of 4-heptyloxybenzoate benzyl dodecyltrimethylammonium (HOBBDDBA).

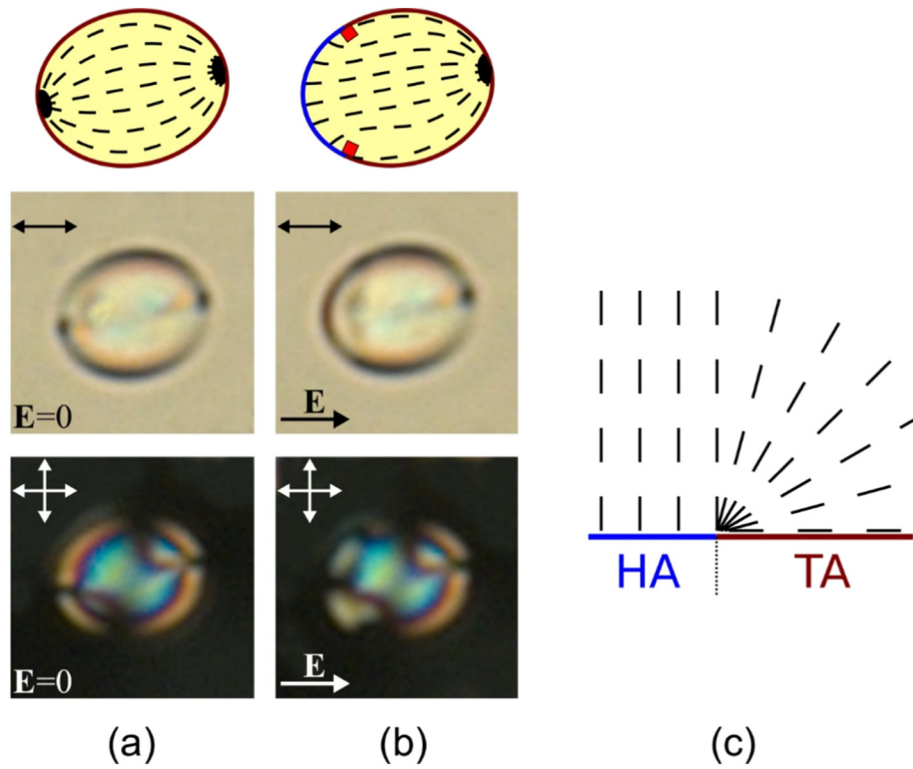


Fig. 2. POM images of 5CB nematic droplet doped with anionic surfactant HOBBDDBA in the weight ratio 5CB:HOBBDDBA = 1:0.014 in the initial state (a) and under DC electric field of $0.07 \text{ V}/\mu\text{m}$ directed from left to right (b). Photos are taken with switched-off analyzer (middle row) and in crossed polarizers (bottom row). The droplet's sizes along the major and minor axes are 10 and $8 \mu\text{m}$, respectively. The director configurations in the central section of the droplet are presented at the top row. A scheme of cross-section of the splay-type ring defect dividing the areas with homeotropic (HA) and tangential (TA) surface anchoring (c). Hereinafter, the polarizer orientation is indicated by the double arrows. The direction of electric field E is shown by the single arrow.

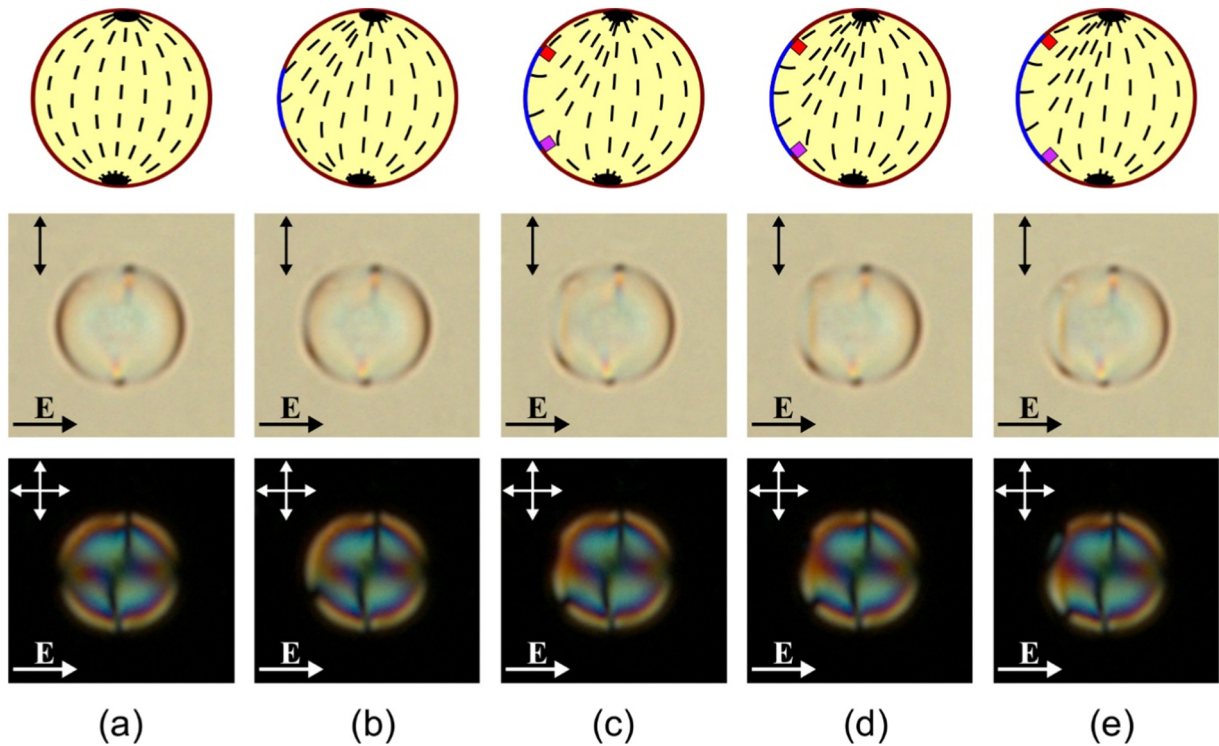


Fig. 3. POM images of 5CB nematic droplet doped with anionic surfactant HOBBDDBA in the weight ratio 5CB:HOBBDDBA = 1:0.014 under DC electric field $E \leq 0.030 \text{ V}/\mu\text{m}$ (a), $E = 0.035 \text{ V}/\mu\text{m}$ (b), $E = 0.045 \text{ V}/\mu\text{m}$ (c), $E = 0.055 \text{ V}/\mu\text{m}$ (d) and $E \geq 0.065 \text{ V}/\mu\text{m}$ (e) directed from left to right. Photos are taken with switched-off analyzer (middle row) and in crossed polarizers (bottom row). The droplet's size is $12 \mu\text{m}$. The director configurations in the central section of the droplet are presented at the top row.

1:0.017 and at the higher concentration of the surfactant. As a result, the radial director configuration with a bulk point defect (hedgehog) is formed in the droplets (Fig. 4a). A change of droplet orientational structure occurs under DC electric field of $0.09 \text{ V}/\mu\text{m}$ (Fig. 4b). This transformation is caused by the modification of boundary conditions from homeotropic to tangential ones at the droplet border near the cathode. Thus, in this case, the inverse regime of ionic-surfactant method is observed [20].

In the droplet shown in Fig. 4b, the surface anchoring is modified at the part of border corresponding approximately to 75% of major axis. At that, the homeotropic boundary conditions are kept on the remaining part of droplet. Therefore, the point defect hedgehog in the droplet bulk, defect boojum on the surface and the bend-type ring defect dividing the areas of tangential and homeotropic anchoring are observed in the modified structure.

The structures shown in Fig. 2b and in Fig. 4b possess the boojum and the surface ring defect. At that, the structure of ring defects is different for these director configurations. In the first case (Fig. 2b) the splay deformation occurs preferably near the core of ring defect and the director lines enter in the core (Fig. 2c). In the second case (Fig. 4b) the director has preferably the bend deformation near the defect core and the director lines go along a hyperbolic path (Fig. 4c). This difference in the structure of the ring defects leads to the keeping the hedgehog in bulk for the second case. The analogous structures were observed in [20,21], when the inverse regime of ionic-surfactant method based on CTAB was realized.

3.3. The binary mixture of anionic and cationic surfactants

The change of boundary conditions from the homeotropic to tangential ones at the most part of droplet surface is possible in the inverse regime of ionic-surfactant method. Clearly, using the anionic surfactant HOBDDA the boundary conditions changes at the droplet border

close to the cathode (Fig. 4), and the cationic surfactant CTAB modifies the surface anchoring at the droplet border close to the anode [20]. One can suppose, that a combination of the anionic and cationic surfactants will result in the modification of boundary conditions, for example, in the central part of droplet with simultaneous keeping homeotropic anchoring at the areas both near the cathode and the anode. To test this assumption the nematic 5CB was doped with 1% HOBDDA in common with 0.5% CTAB by weight. In the initial state, the radial director configuration (Fig. 5a) corresponding to the homeotropic boundary conditions is realized in the LC droplets. Under DC electric field the complicated director configuration characterized by the inhomogeneous boundary conditions is formed (Fig. 5b). The homeotropic boundary conditions are kept near the cathode and anode on the borders approximately corresponding to 45% and 17% of droplet diameter, respectively. Surface anchoring is modified from homeotropic to tangential at the remaining central band of droplet surface.

A tangential anchoring changes into homeotropic one quite sharply as in the cases described above, therefore, here the pair of ring surface defects appears. At that, the point defect is located simultaneously both in bulk and in the plane of one of ring defects (right part of droplet in Fig. 5), whose structure is similar to the ring defect observed in Fig. 4b, c (bend-type ring defect). The second ring defect (left part of droplet in Fig. 5) is the splay-type ring defect (Fig. 2b, c). Thus, the structure with a hedgehog and pair of the different surface ring defects is formed in the LC droplet. After switching-off electric field the region with tangential surface anchoring gradually decreases and, finally, disappears (the ring defects approach each other and annihilate). As a result, the orientational structure is returned to the initial state (Fig. 5a).

4. Conclusion

The electrically controlled ionic modification of surface anchoring in 5CB droplets using the anionic surfactant HOBDDA was studied. It was

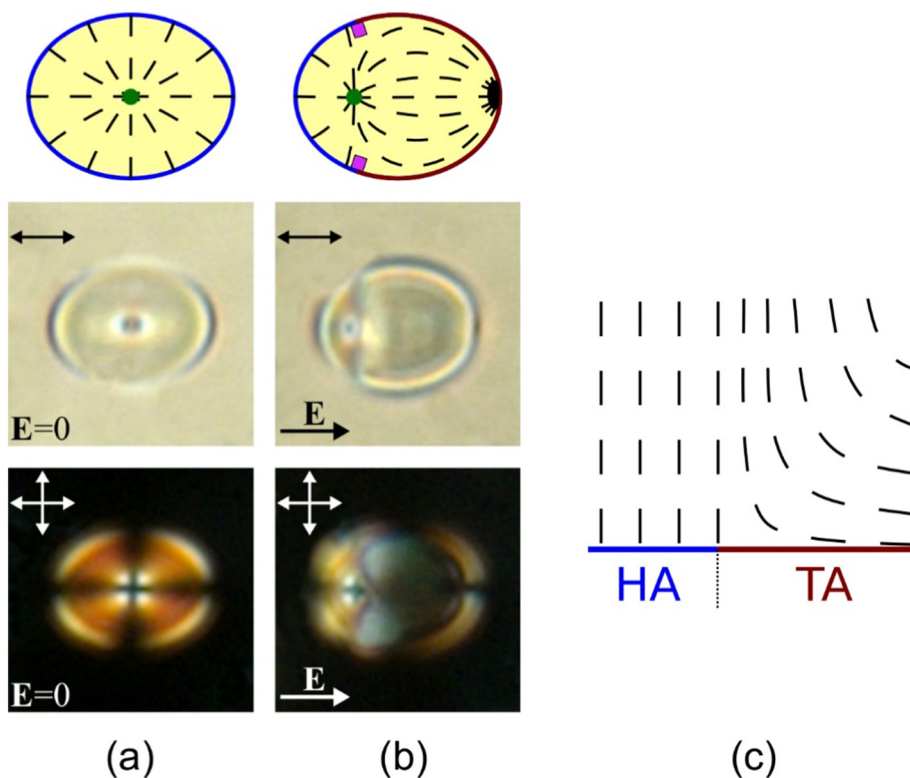


Fig. 4. POM images of 5CB nematic droplet doped with anionic surfactant HOBDDA in the weight ratio 5CB:HOBDDA = 1:0.017 in the initial state (a) and under DC electric field of $0.09 \text{ V}/\mu\text{m}$ directed from left to right (b). Photos are taken with switched-off analyzer (middle row) and in crossed polarizers (bottom row). The droplet's sizes along the major and minor axes are 12 and $9 \mu\text{m}$, respectively. The director configurations in the central section of droplet are presented at the top row. The cross-section of bend-type ring defect dividing the areas with homeotropic (HA) and tangential (TA) surface anchoring (c).

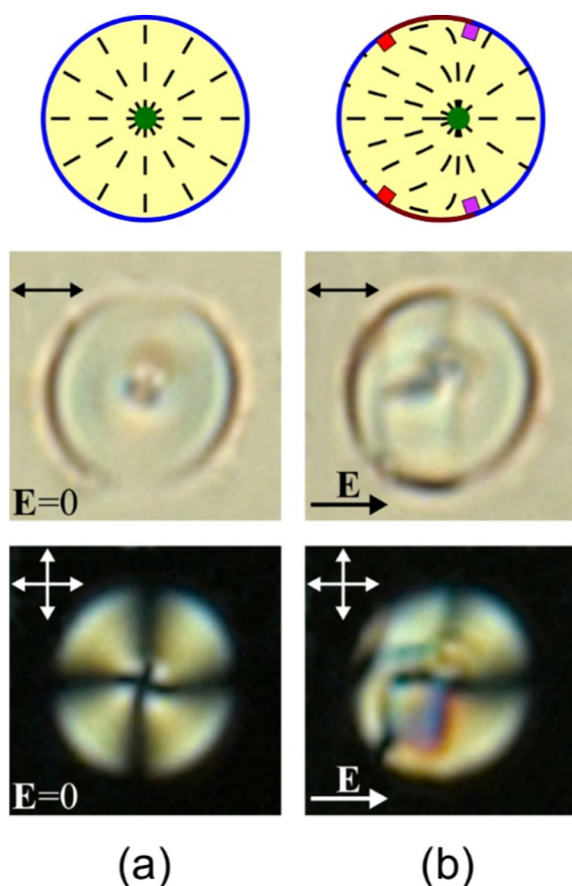


Fig. 5. POM images of 5CB nematic droplet doped with a mixture of the anionic surfactant HOBBDDA and cationic surfactant CTAB with weight concentrations 1% and 0.5%, respectively, in initial state (a) and under DC electric field of 0.07 V/μm directed from left to right (b). Photos are taken with switched-off analyzer (middle row) and in crossed polarizers (bottom row). The droplet size is 10 μm. The director configurations in central section of droplet are presented at the top row.

shown that this substance specifies the homeotropic alignment for 5CB at the PVA surface plasticized by glycerin at the 1.7% and more concentration of HOBBDDA in nematic by weight. The 1.4% content of HOBBDDA in 5CB operates as anionic surfactant modifying the tangential boundary conditions into homeotropic ones near the anode. The inverse regime of ionic-surfactant method is observed at 1.7% of HOBBDDA in 5CB. The orientational structure transitions in the droplets under study occur at low driving fields (<0.1 V/μm). At that the response time is several seconds, the relaxation time doesn't exceed 10 s. The combination of HOBBDDA and CTAB acts as anionic-cationic surfactant which can modify surface anchoring simultaneously at both parts of LC droplets (and, consequently, at both substrates of flat LC cells) near the anode and cathode.

That is, the electrically controlled surface anchoring transitions were first implemented using anionic surfactant both in the normal and inverse mode. Binary mixture based on HOBBDDA and CTAB can function as the universal anionic-cationic surfactant that operates significantly the possibilities of ionic-surfactant method to operate liquid crystal materials.

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molliq.2019.02.132>.

Acknowledgments

The reported study was supported by the Belarusian Republican Foundation for Fundamental Research (project No X16P-110) and Russian Foundation for Basic Research (RFBR) (project No 16-53-

00073). Mikhail N. Krakhalev and Vitaly S. Sutormin acknowledge financial support from RFBR, Government of Krasnoyarsk Territory, Krasnoyarsk Regional Fund of Science (project No 18-42-243006).

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