

UDC 532.783

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DETERMINATION OF CONCENTRATIONS OF SURFACE-ACTIVE MATERIALS IN AQUEOUS SOLUTIONS AT DIFFERENT pH VALUES USING LIQUID CRYSTALS

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Determination of the content of environment polluting chemical agents is of significant importance. The goal of this study was the development of experimental approaches for detection of concentrations of surface-active molecules (surfactants) such as sodium dodecyl sulfate (SDS) and Triton X-100 in aqueous environments with varying pH level. Nematic and chiral-nematic type liquid crystals (LCs) were used as sensor materials. The pH levels in aqueous system were tuned by injection of certain amounts of acetic acid or ammonium hydroxide. In this work, we used LC thin films formed on the standard transmission electron microscopy (TEM) grids that were put in contact with aqueous subphases containing the surface-active material. The changes in the textures of the thin film LC samples were identified by polarizing optical microscopy. We have determined the influence of pH environment on the minimum concentration of surface-active materials required for the transition of the hybrid molecular alignment into homeotropic molecular alignment in the nematic LC films (or for the collapse of the nematic films). This pH influence and the change of the helical pitch in the films of chiral-nematic type under increasing concentration of the surface-active component are proposed as approaches for estimation of its concentration in the aqueous subphase.

Key words: liquid crystals, surfactants, pH of environment, collapse of the nematic films.

DOI: 10.18083/LCAppl.2017.1.34

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ОПРЕДЕЛЕНИЕ С ПОМОЩЬЮ ЖИДКИХ КРИСТАЛЛОВ СОДЕРЖАНИЯ ПОВЕРХНОСТНО-АКТИВНЫХ ВЕЩЕСТВ В ВОДНЫХ РАСТВОРАХ ПРИ РАЗНЫХ ЗНАЧЕНИЯХ pH

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В настоящее время актуальным является установление в окружающей среде содержания химических агентов, приводящих к ее загрязнению. Целью исследования была разработка экспериментальных подходов к определению с использованием ЖК концентраций поверхностно-активных веществ: додецилсульфата натрия и Тритона X-100 в водных растворах, в том числе с различным значением pH. В качестве сенсоров использованы жидкие кристаллы нематического и хирально-нематического типов. Для вариации pH среды в водную систему (субфазу) вводились соответствующие объемы растворов уксусной кислоты или гидроксида аммония. В работе

использовались тонкопленочные образцы ЖК, сформированные на стандартных сеточках, применяемых для просвечивающей микроскопии, в контакте с субфазой, содержащей поверхностно-активное вещество. Текстурные изменения тонкопленочных образцов ЖК идентифицированы методом поляризационной микроскопии. Установлено влияние pH среды на минимальную концентрацию поверхностно-активных веществ, приводящую к переходу гибридной ориентации нематика в гомеотропную (или к коллапсу пленки). Данное влияние, а также изменение шага спирали в пленках хирально-нематического типа при увеличении концентрации поверхностно-активного вещества, предложены в качестве подходов к оценке содержания его в субфазе.

Ключевые слова: жидкие кристаллы, поверхностно-активные вещества, pH среды, коллапс пленки.

Introduction

Technological progress, growth of the population and non-optimal use of natural resources lead to alarming environmental problems. Disruption of natural balance in the environment appears on local and global scales in form of deteriorating of the ecologic conditions and of the climate of Earth.

In particular, solving the challenge of identification of environmental organic pollutants, including the surface-active materials, is of high importance. The most wide-spread surfactants are of sodium alkyl sulfate type.

It is well known that the aqueous sewage waste surfactant analysis methods, such as potentiometry, chromatography, calorimetry, electro-chemistry, ionometry, are time-consuming and require sophisticated laboratory equipment. Recently new approaches were realized in sensing of chemical compounds at low concentrations using LC materials. It was demonstrated that LC sensors are capable of determining chemicals that can be present as gases [1], identifying biological molecules (proteins, oligopeptides, immunoglobulins and nucleic acids) [2, 3, 4] sensing low concentrations of surfactants, lipids and charged molecules [5, 6], single and double stranded DNA fragments on solid surfaces [7]. LC sensors were used for identification of viruses, bacteria and mammalian cells [8, 9] and so on.

The goal of this study was the development of practical approaches for detection of concentrations of surfactants such as SDS and Triton X-100 in their aqueous solutions at different pH levels.

Experimental part

In this work the anionic surfactant sodium dodecyl sulfate (SDS) and non-ionic surfactant Triton X-100 were used as received from Aldrich. The

commercially available 4-cyano-4'-pentylbiphenyl (5CB) from Sigma-Aldrich and 5CB with a chiral dopant at a weight percentage of 5 wt. % with a helical twisting power (HTP) of $4 \mu\text{m}^{-1}$ were used as sensing materials. Standard $20 \mu\text{m}$ thick transmission electron microscopy (TEM) nickel grids with hexagonal cells, in which a circle with a diameter of $200 \mu\text{m}$ can be inscribed, were employed for making the thin films of the sensing mesogens. The LC was applied onto the TEM grids to obtain thin films in the cells. Tweezers were used to set the grid with LC films in contact with the water level, which was held in a plastic container.

The plastic containers (5 ml of total volume) with a transparent glass bottom (to avoid birefringence from container parts) were filled with distilled water and placed under a polarizing optical microscope (POM). A micropipette was used for injection of small amounts of surfactant. After surfactant injection the solutions were allowed to reach equilibrium within 10 minutes.

The variations in pH level of the solution was controlled by additions of acetic acid or ammonium hydroxide. The measurement of pH was conducted with a pH-meter Ionometer laboratory I-160M, AHMEX, C0005403 produced by "Measuring equipment", Moscow, Russia. The values of pH of the subphase were measured at: 2.4, 2.9, 4.3, 4.5, 7.0, 9.6, 10.9, 11.8. A polarizing microscope LetzLaborLux 12 Pol was employed to observe and identify transitions from hybrid to homeotropic orientations of LC molecules as a test of presence of surfactants. The micro-images of the obtained texture were saved with a Digital Camera for Microscope (DCM800, 8 Mpixels).

The surfactant concentration, which lead to a transition of the Schlieren-texture of the hybrid LC alignment to a homeotropic alignment (seen as a uniform dark image between crossed polarizers), we called *minimum effective concentration of surfactant*.

Influence of pH environment on the values of minimum effective concentration of SDS in aqueous solution

It was previously shown [7], that a thin film of 5CB undergoes through a transition from hybrid to homeotropic alignments at neutral value of pH of the subphase at a concentration of SDS around 0.9 mM. However, in the conditions of real industrial and domestic water based waste the pH values may vary significantly. Thus, we have set a goal of studying the influence of pH of the subphase on the minimum concentration of SDS in solution, which can be measured using this method.

The obtained results are presented in Table 1:

As it can be seen from Table. 1, the decrease of the pH of the solution leads to a lower concentration of anionic surfactant SDS that is required to transition the LC alignment from hybrid to homeotropic state in

comparison to the case when pH environment is neutral (0.11 mM and 0.90 mM, respectively). Figure 1 demonstrates the transition of hybrid to homeotropic alignment at pH=2.9 as observed under the microscope.

As the concentration of the base is increased (up to pH \cong 10.9) the transition from hybrid to homeotropic alignment occurs at higher concentrations of SDS in solution as compared to the neutral pH environment (Fig. 2). Further increase of pH leads to the loss of hybrid-to-homeotropic transition and instead, even under lower SDS concentrations (1.31 mM), a collapse of the sensing LC film is observed (Fig. 3).

The results reported in Table 1 suggest that the minimum effective concentration of SDS (0.11 mM), under which 5CB film undergoes through a hybrid-to-homeotropic alignment transition, is observed in acid environment (in our case at pH = 2.4). The results are summarized in form of a graph in Fig. 4.

Table 1. Influence of pH of the subphase on minimum effective concentration of SDS

| pH of subphase | Minimum effective concentration of SDS, at which a transition from hybrid to homeotropic LC alignment was observed, mM |
|----------------|--|
| 2.4 | 0.11 (± 0.05) |
| 2.9 | 0.26 (± 0.05) |
| 4.3 | 0.66 (± 0.05) |
| 4.5 | 0.75 (± 0.05) |
| 7.0 | 0.9 (1.3) (± 0.05) |
| 9.6 | 1.53 (± 0.05) |
| 10.9 | 1.60 (± 0.05) |
| 11.8 | 1.31 (± 0.05) collapse |

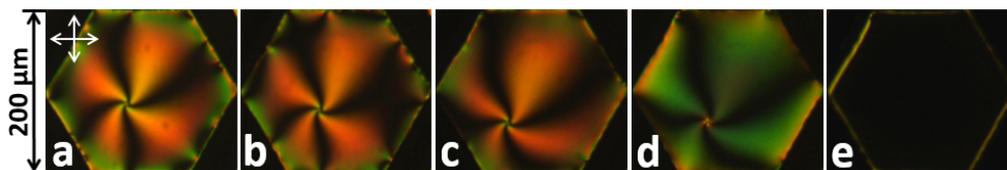


Fig. 1. Transition of 5CB molecular orientation from hybrid to homeotropic. SDS concentrations, mM: a – 0; b – 0.07; c – 0.12; d – 0.19; e – 0.26. (subphase pH = 2.9)

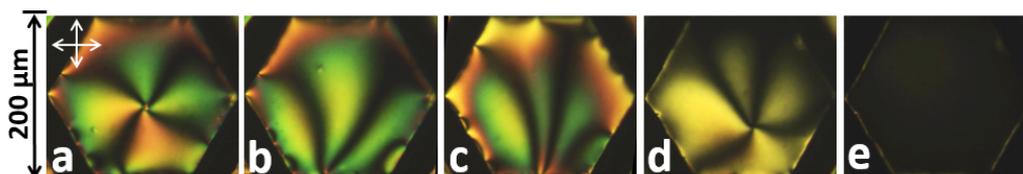


Fig. 2. Transition of 5CB molecular orientation from hybrid to homeotropic. SDS concentrations, mM: a – 0; b – 0.2; c – 0.3; d – 1.2; e – 1.5. pH = 9.6

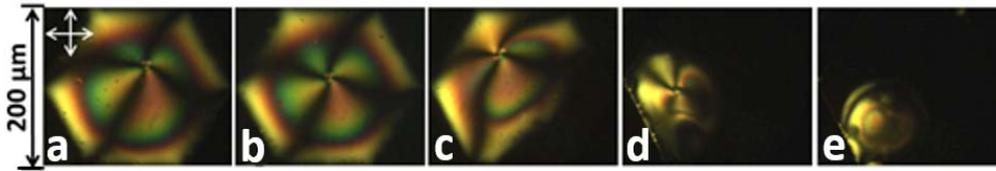


Fig. 3. Transition of 5CB molecular orientation from hybrid to homeotropic. SDS concentrations, mM: *a* – 0; *b* – 0.8; *c, d, e* – 1.3 (images taken during the process of collapse of the thin film). pH = 11.76

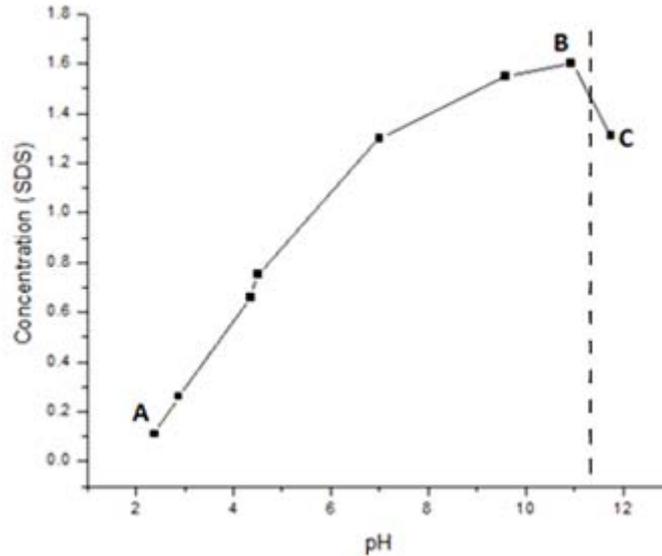


Fig. 4. Hybrid-to-homeotropic transition of 5CB film: (A-B) under variation of the pH of the environment; C – film collapse

Determination of minimum effective concentration of SDS in the subphase using the 5CB-chiral dopant system

The special “finger-print” texture of chiral-nematic phase suggests a potential opportunity to determine the influence of SDS presence not due to transition to homeotropic alignment, but due to change in the helical pitch under lower surfactant

concentrations in the subphase as compared to the transition to the homeotropic orientation of the chiral nematic. Thus, we conducted an investigation to determine the sensing properties of the film in response to concentrations of SDS in the subphase when the nematic phase is replaced with chiral nematic (N*) phase. Figure 5 presents the change in the finger-print texture as the concentration of SDS is increased in the subphase with pH = 7.0.

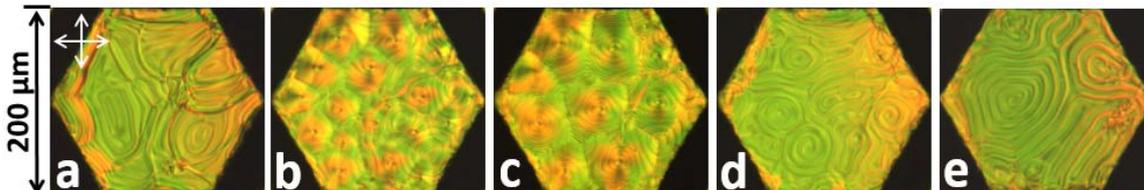


Fig. 5. Texture change of a thin film made with 5CB with a chiral dopant ($HTP = 4 \mu\text{m}^{-1}$). Growth of finger-print texture domains at increasing concentration of SDS. Surfactant concentrations, mM: *a* – 0, *b* – 0.32, *c* – 0.63, *d* – 1.18, *e* – 1.89. pH = 7.0
Changes of the finger-print texture were observed at surfactant concentrations as low as 0.08 mM

We have applied thin films of 5CB with 5 wt. % of chiral dopant onto TEM grids to develop the method of quantitative changes of N* helical pitch in response to presence of surfactants. We employed a similar protocol in observations of textural changes as in the case when the pure nematic 5CB films were used. The grid was allowed to stay in contact with SDS solution for 24 hours to ensure that a stable texture of the N* phase had established. In the case when the SDS concentration was 1.9 mM a clearly defined finger-print texture has developed as shown in Fig. 6.

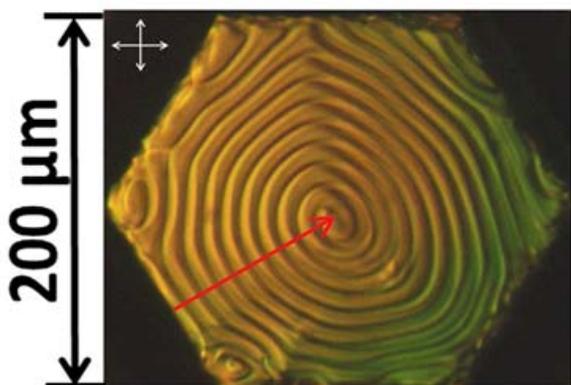


Fig. 6. "Finger-print" texture of the LC film: 5CB + chiral dopant ($HTP = 4 \mu\text{m}^{-1}$). Subphase – aqueous solution of SDS

A plot of the dependence of light intensity along the 91.5 μm long arrow drawn in Fig. 6 was obtained by using the image processing software ImageJ [<https://imagej.nih.gov/ij/download.html>]; the period of light intensity variation was extracted along the length of the arrow starting from the edge of the grid's cell towards its center. The 19.6 μm helical pitch of the finger-print texture was derived from the measurement of the periodicity in the intensity pattern (Fig. 7).

It was observed that in the beginning of the process of addition of SDS into the subphase the chiral nematic thin film develops multiple finger-print domains.

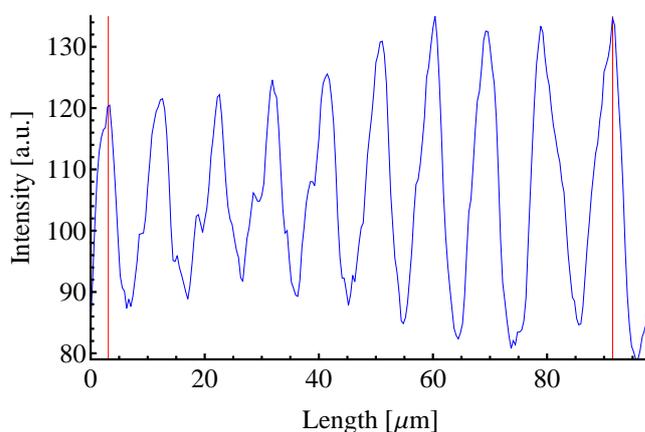


Fig. 7. Intensity profile of the finger-print texture obtained from Fig. 6

Then, as the concentration of the surfactant increases, the number of the domains decrease and the helical pitch increases. This approach can be used as well for the determination of the *minimum effective concentration of surfactant* in the subphase.

Determination of minimum effective concentration of Triton X-100 in the subphase using 5CB films

After reproducing the experiments on determination of the *minimum effective concentration of SDS* using 5CB, as well as 5CB with chiral dopant, we attempted to determine the presence and the concentration of a different surfactant, which is often encountered in domestic and industrial wastes – Triton X-100. Previously this method was not used to identify this chemical compound.

It was found that in comparison to anionic surfactant, which at high enough concentration causes the 5CB film to undergo hybrid-to-homeotropic transition, the non-ionic surfactant Triton X-100 does not facilitate the a transition to homeotropic alignment and instead at high enough concentration ruptures the sensing film (Fig. 8).

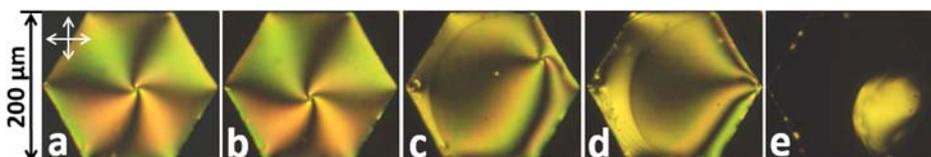


Fig. 8. Influence of Triton X-100 on the 5CB nematic film. Surfactant concentrations, mM: a – 0, b – 0.93, c, d, e – 0.94 (images taken during the process of collapse of the thin film). pH = 7.0

It is interesting to note that the collapse of the film in the neutral environment happens at lower concentrations of Triton X-100 as compared to the concentrations of SDS.

Discussion

The results from the conducted investigations, which reflect the influence of the chemical composition of the subphase onto the hybrid-to-homeotropic transition of the mesogen, are presented in Table 2.

As it is seen from Table 2, the pH level of the subphase, the type of the surfactant and the type of the

sensing LC material, all have significant influences on the transition to homeotropic alignment of the LC molecules. For example, the neutral aqueous solution of the ionic surfactant causes the LC film to transition into homeotropic alignment state at 0.9 mM, while in acidic environment the same occurs at 0.11 mM, which is a concentration that is 8 times lower.

It is interesting to notice, that the chiral nematic film is less sensitive to surfactants in both conditions: in the case of using SDS and in the case of using Triton X-100. Perhaps this is linked to the fact that the helical structure of the LC is not capable of unwinding into homeotropic alignment state in these conditions.

Table 2. Surfactant concentrations, which reflect the LC transition to homeotropic orientation

| Subphase composition | Mesogen | Surfactant concentration, mM | Presence of homeotropic transition |
|-------------------------|---------------------|------------------------------|------------------------------------|
| SDS (pH = 2.4) | 5CB | 0.11 | + |
| SDS (pH = 2.9) | 5CB | 0.26 | + |
| SDS (pH = 4.3) | 5CB | 0.66 | + |
| SDS (pH = 4.5) | 5CB | 0.75 | + |
| SDS (pH = 7.0) | 5CB | 0.90 | + |
| SDS (pH = 9.6) | 5CB | 1.53 | + |
| SDS (pH = 10.9) | 5CB | 1.60 | + |
| SDS (pH = 11.8) | 5CB | 1.31 | – (collapse) |
| SDS (pH = 7.0) | 5CB + chiral dopant | > 2.0 | – (stable “finger-print” texture) |
| Triton X-100 (pH = 7.0) | 5CB | 0.94 | – (collapse) |
| Triton X-100 (pH = 7.0) | 5CB + chiral dopant | 1.07 | – (collapse) |

The surface tensions of the nematic LC and the subphase play an important role in establishing the difference in the surfactants’ influence on the LC films. Tomilin M.G. [10] showed, that if surface tension of LC is larger than the surface tension of the

substrate $\sigma_{LC} > \sigma_{sub}$, then the molecules adopt homeotropic alignment. If $\sigma_{LC} < \sigma_{sub}$, then the LC molecules assume planar alignment. If $\sigma_{LC} \approx \sigma_{sub}$, then the LC molecules assume a tilted orientation in the film (Fig. 9).

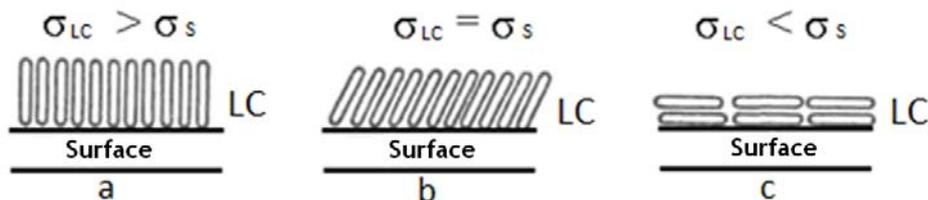


Fig. 9. LC molecular alignment on substrates having dissimilar surface tension values: a – homeotropic, b – tilted, c – planar

In our case we have observed changes in the features of the film texture and the change in the color of the Schlieren texture: from colored to dark (non-birefringent). The color of the Schlieren texture varies due to changes of the tilt of the LC molecules. Previously this effect was successfully applied to visualize physical properties of solid substrates, as well as the properties of biological tissues [10]. Since the role of the surface tension in these processes is very significant, we review the specifics of the surface tension and solubility of surfactants, which were used in our experiments.

To evaluate a physical property, such as surface tension, it is important to turn our attention to the indicator of hydrophilic-lipophilic balance (HLB). HLB is determined by the mass ratio of the hydrophilic and lipophilic parts of the hydrocarbon radical. HLB was proposed by Griffin in 1949 [10].

The HLB value is determined by evaluating the surfactant's potential for emulsion stabilization. A value of $HLB = 1$ is assigned to oleic acid as a definition in the HLB scale. The higher the hydrophilicity is, the larger is the HLB value (the scale varies from 1 to 40). In this scale the SDS molecule has the highest HLB value of 40 since it is the most hydrophobic, while Triton X-100 is characterized by HLB value of 13. It is important to note that Triton X-100 is classified as an emulsifier agent and SDS is classified as a solubilizing agent [11].

The highest hydrophilicity of SDS ensures the highest decrease of surface tension, since water expels the carbohydrate chains in an attempt of preserving its hydrogen bonding structure. It is possible, that in our case the aliphatic chains of the surfactant molecules penetrate [13, 14] into the LC at the LC/water interface as depicted in Fig. 10.

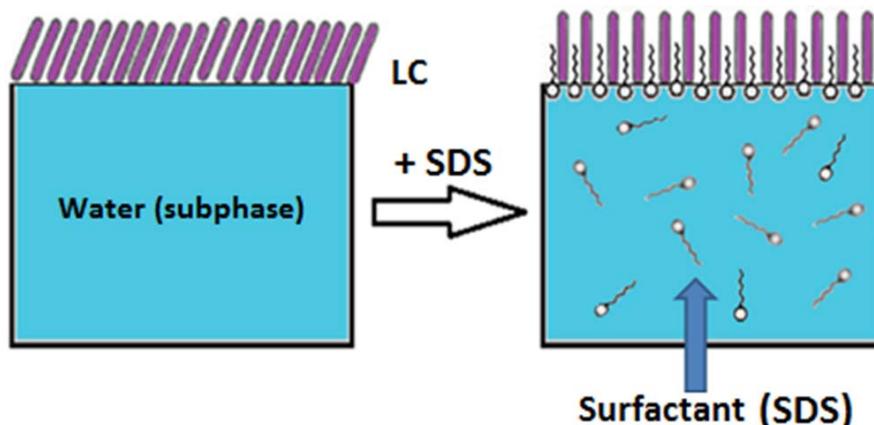


Fig. 10. Schematics of LC layer reorientation in the vicinity of the subphase, which contains SDS

The surfactant not only reduces the surface tension of the subphase, but also the additional hydrophobic intermolecular interaction of 5CB and SDS facilitates further to the hybrid-to-homeotropic transition.

In the case of Triton X-100, which is characterized by a lower value of HLB and thus has a lower effect on surface tension reduction of the subphase, the penetration into the LC should likely proceed in two steps (Fig. 11). During the first step of

the surfactant addition, the reduction of surface tension is significantly smaller as compared to the case with SDS, which does not facilitate to the formation of homeotropic orientation of the LC. After achieving a certain concentration of surfactant in the subphase, the mixing of Triton X-100 in the LC due to aliphatic tail penetration becomes excessive and a rupture of the sensing film occurs, which proceeds with a formation of an oil (LC)/water emulsion in a form of spherical colloids (Fig. 8 and Fig. 11).

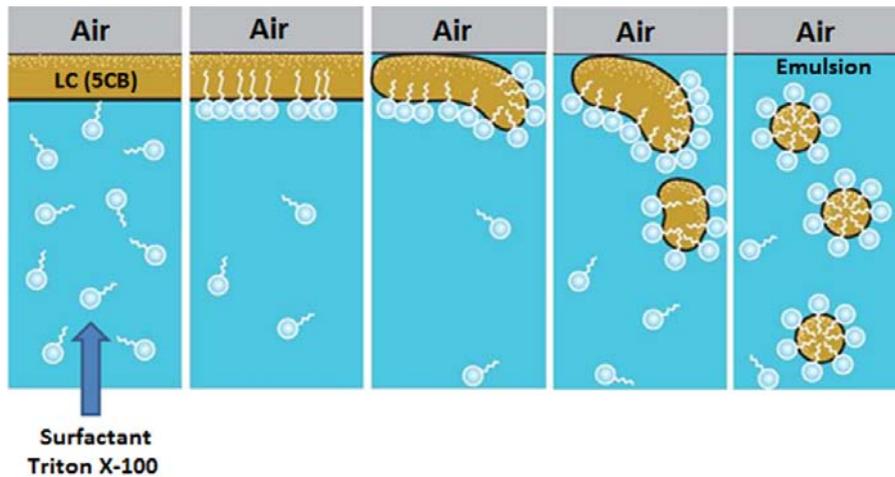


Fig. 11. Schematics of the influence of non-ionic surfactant Triton X-100 on the 5CB LC film.
Formation of an emulsion of oil-in-water type

It is important to notice, that the reduction of the subphase's surface tension happens before the achievement of the critical micelle concentration (CMC), which for ionic surfactants depends strongly on the aliphatic tail length of the radicals. The surface tension remains constant beyond achieving the CMC level. In case of non-ionic surfactants, the CMC values are typically two orders of magnitude lower as compared to ionic surfactants with similar hydrophobic tail lengths. The combination of these factors leads to the lack of hybrid-to-homeotropic molecular alignment transition of the LC when non-ionic surfactants are present.

An interesting fact is that the decrement in the pH of the solution leads to a hybrid-to-homeotropic transition occurring at lower minimum effective surfactant concentration and the increment of the pH leads to higher minimum surfactant concentration according to our experimental results which were described above. Perhaps, under lower pH values, which are accompanied by a lower CMC values [15], the smaller surfactant concentrations facilitate the formation of saturated adsorbed layer at the LC/water interface and this leads to a fast growth of the difference between surface tensions of the LC and the subphase, which in turn leads to formation of the optimal homeotropic alignment of LC molecules at lower (as compared to the concentration in the aqueous solution) concentrations of SDS. In contrast, the basic environment diminishes the dissociation of the polar group and lowers (similar to non-ionic surfactants) the adsorption of surfactants at the

interface. Thus, the ionic SDS concentration, which causes the LC to transition to homeotropic alignment state, becomes somewhat increased. At high $\text{pH} > 11.8$, the SDS causes the LC film to rupture (similar to the case with Triton X-100) instead of facilitating the hybrid-to-homeotropic transition.

Conclusions

We have analyzed the possibilities of developing new approaches for determination of low concentrations of ionic and non-ionic surfactants using sensing films of nematic and chiral-nematic types by varying the pH of the subphase and determining the minimum effective concentration of the surfactants, which is required to reorient the LC molecules from hybrid to homeotropic alignment or to a collapse of the film.

It was shown, that at lower pH of the environment the sensitivity of the LC to SDS increases, which leads to hybrid-to-homeotropic reorientation at lower SDS concentrations as compared to neutral pH values. When the pH is increased, the sensitivity to SDS is diminished and at $\text{pH} > 11.8$ the LC films tend to rupture instead of changing molecular alignment. Thus, acidification of the subphase can help in identification of SDS at lower concentrations.

We have established that chiral-nematic films do not change their alignment when in contact with aqueous solutions of surfactants, but the increasing concentration of SDS causes the finger-print domains

to join and increases the helical pitch of the cholesteric phase. For the first time the cholesteric pitch of the finger-print texture was measured on chiral-nematic LC films that are in contact with subphases containing surface active agents. Our calculations may serve as a foundation to methods of quantitative determination of surfactants present in aqueous solutions by measuring the pitch of the finger-print texture.

In presence of non-ionic surface active Triton X-100 in the subphase, the 5CB film does not change its molecular alignment. Moreover, the film collapses at high enough concentration of Triton X-100, similar to the rupturing taking place when SDS is introduced at high pH values (more than 11.8). In neutral conditions of the subphase the LC film is less sensitive to the presence of Triton X-100 in comparison to the presence of SDS as determined by the method of the *minimum effective concentration of surfactants*.

The lack of hybrid-to-homeotropic transition of LC molecules is explained for the first time by noticing the difference of the hydrophilic-lipophilic balance of SDS and Triton X-100 (40 and 13, respectively). In case of Triton X-100 the surfactant is penetrating into the LC film producing a mixed layer, which enables the formation of oil/water emulsion and causes the sensing film to collapse. In contrast to this, the SDS compound as one of the most hydrophilic surfactants is decreasing the surface tension of the subphase enough to reorient the 5CB liquid crystal molecules into homeotropic alignment.

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Поступила в редакцию 25.01.2017 г.
Received 25 January 2017