Effect of the composition and temperature of the subphase on the surface potential of the Langmuir monolayer of 8CB liquid crystal

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Abstract. The effect of the composition and temperature of the subphase on the effective dipole moment of the Langmuir monolayers of a liquid crystal 4-n-octyl-4′-cyanobiphenyl on the surface of pure water and an aqueous solution containing copper nanoparticles was studied. It is shown that the presence of nanoparticles in the subphase leads to increase of the area occupied by the monolayer in the condensed state, increase of the collapse pressure, and reduction of the surface potential at the end of monolayer compression. The effective dipole moments of liquid crystal molecules were calculated for monolayers formed under various conditions.

1. Introduction

Liquid crystal (LC) materials have always been given great attention due to the broad prospects for many practical applications, such as nanosensors and devices for chemical analysis, displays and devices with active media for optical information processing, etc. \cite{1}. The features of their molecular structure lead to many variations in the rearrangements of the structure, which strongly depends on many external factors, such as electrical and magnetic fields, light stimulation, microrelief on substrate surface and other. And the temperature acts especially strongly, affecting the short and long range order of molecules \cite{2,3}. The competition of two factors – temperature and the presence of the air-water interface, significantly complicates the ordering conditions, and this gives a greater variety of ways for the transforming of the liquid crystals structure (in particular for lyotropic LC) \cite{4,5}.

Currently, there are many papers on the influence of temperature on the ordering of simple molecules of LC such as 4-n-octyl-4′-cyanobiphenyl (8CB). Authors \cite{6} studied two-component films of a non-amphiphilic azo dye and a liquid crystal at an air-water interface and at a subphase temperature of 20-21 °C. They calculated the effective dipole moment in the first monolayer formed on the water from the surface potential–mean molecular area dependence, and estimated the number of molecules with dipole moments directed from the water to the air with respect to those directed towards water. They also showed that in the first monolayer formed at the air-water interface the dipole moment of the liquid crystal molecules directed mostly from the air to the water. At the same time the dipole moment of the dye molecules are aligned in the opposite direction \cite{6}. As a rule, the
effect of temperature on the orientation of molecules and the rheological properties of LC materials was studied only for bulk samples [7]. A study of the influence of temperature on the dipole moment of molecules in Langmuir monolayer (2D system) was practically not carried out.

This article presents data on the effect of temperature on the surface potential–area per molecule dependences for the Langmuir monolayer of 8CB liquid crystal molecules. We chose 8CB liquid crystal as a typical representative of nematic liquid crystals, which is well studied and has the simplest molecular structure. The presence of a polar CN-group provides reliable anchoring of the LC molecule to the surface of the aqueous subphase. But this does not interfere with rearrangements of the LC molecules during the compression of the monolayer by moving barriers and with phase transitions in the two-dimensional system in case of changes in subphase temperature [6, 8, 9].

There are many works devoted to the study of complex nanocomposite systems in which there is a very large difference in the properties of the components. Systems such as nanoparticles in various organic matrices are “on top” of the interests of many researchers. There is every reason to expect the mutual synergistic influence of both components [5, 10-12], which will be very useful for the synthesis of new materials with improved or unexpected properties [13, 14].

We already reported earlier about the wavelength shift of the luminescent peak of semiconductor nanoparticles (NPs), which depended on the dipole moment of the organic molecules surrounding the nanoparticles [11, 15, 16].

In this work, we investigated the features of the formation of a 4-n-octyl-4’-cyanobiphenyl monolayer on the surface of aqueous solutions of copper nanoparticles at various temperatures. This is the next stage of the work that we started earlier [9]. One of the key questions of this work: what will be the mutual influence of the components – NP (from the subphase) and LC (from the monolayer) for the case of a 2D-system.

2. Materials and Methods

The molecular structure of the compounds investigated is given in Figure 1. The liquid crystal 4-n-octyl-4’-cyanobiphenyl (Sigma-Aldrich) was dissolved in chloroform (Vecton, Russia) to obtain a concentration of \(10^{-3}\) M. 50 µl of this solution was spread on the surface of ultrapure water (18,2 Ω×cm from Smart2Pure (Thermo Scientific)) and an aqueous solution of copper nanoparticles (Cu NPs) stabilized by sodium dodecyl sulfate (SDS) surfactant to form monolayers. The subphase with Cu NPs was prepared by adding 50 µl of a colloidal solution of Cu NPs stabilized by SDS surfactant into ultrapure water. A colloidal solution of Cu NPs was obtained by the method described in [17-19]. According to the dynamic light scattering (DLS) method the average nanoparticles size was 32.7 nm, and the polydispersity was 48.5 %. In the control experiment an aqueous SDS solution was used as a subphase by adding 50 µl of a 0.01 M SDS surfactant solution to the ultrapure subphase. The subphase volume was 150 ml.

![Figure 1. Molecular structure of 8CB liquid crystal (a) and SDS surfactant (b).](image)

After applying the 8CB solution onto the subphase a monolayer was equilibrated for 5 minutes to allow chloroform to evaporate. Then the monolayer was compressed symmetrically from both sides at a barrier motion speed of 15 mm/min. The study of monolayers was carried out by measuring the dependence of surface pressure and surface potential on the area occupied by the monolayer using the Langmuir-Blodgett method on the KSV NIMA LB Trough Medium KN 2002 (KSV Instruments Ltd., Finland) with the KSV NIMA Surface Potential Sensor for measuring surface potential. A subphase...
temperature was kept constant by a LOIP LT-205a circulation thermostat (Russia) at 23 °C and 37 °C. The accuracy of maintaining the desired temperature was 0,1 °C. The surface tension was measured by weighing the Wilhelmy plate with an accuracy of 0,1 mN/m.

3. Results and discussion

Figure 2 shows the compression isotherms of 8CB monolayer on the surface of pure water and an aqueous solution of SDS surfactant obtained at a subphase temperature of 23 °C. The compression isotherms to the collapse point πc coincide completely with each other. The difference is that for the 8CB monolayer obtained on the surface of the SDS surfactant solution, the collapse occurs later relative to the monolayer formed on pure water. It is known that SDS surfactant does not significantly change of the surface pressure value [20]. Therefore, the mean monolayer area of 8CB in the condensed state (specific area per monolayer) in both cases is approximately 180 cm².

![Figure 2](image)

Figure 2. Surface pressure–mean monolayer area (π-A) isotherm for 8CB monolayer on the surface of pure water (black line) and an aqueous solution of SDS surfactant (red line) at a subphase temperature of 23 °C.

Figure 3 presents π-A (black lines) and ΔV-A (blue lines) isotherms for 8CB on the surface of pure water and an aqueous solution of Cu NPs stabilized by SDS surfactant at a subphase temperatures of 23 °C and 37 °C. Three regions corresponding to different phase states and the structure of 8CB monolayer can be distinguished on the isotherms of Figure 3, a. For region (I), up to area 170 cm² per monolayer there is no significant increase of the surface pressure due to the large intermolecular distance (gas phase). An increase of the surface potential up to 0,05 V at 170 cm² occurs earlier than the increase of the surface pressure. In region (II), between 170 cm² and 138 cm² due to compaction of 8CB molecules in a monolayer the surface pressure increases linearly up to 4,6 mN/m. This point corresponds to the collapse of the monolayer. Surface potential rises up to 0,51 V. In region (III), after the collapse point a three-dimensional structure is formed [6, 8]. On further compression, with increasing of the surface pressure the surface potential at first remains almost constant but at the end of compression it decreases slightly. This is explained by the transition of the monolayer into a multilayer structure. In such a structure the surface potential is determined by the dipoles of the monolayer adjacent to the air-water interface because the upper bilayer is nonpolar.

Then, the 8CB monolayer was formed at a subphase temperature of 37 °C. Figure 3, b shows that the behavior of the isotherm of 8CB monolayer changed relative to a subphase temperature of 23 °C. In region (I), up to area 178 cm² per monolayer, the surface pressure also changes slightly. In region (II), between 178 cm² and 148 cm², the surface pressure increases up to 4,5 mN/m. The surface potential rises up to 0,065 V. In this case, the sign of the surface potential changes. At the end of region, the collapse point almost disappears. Upon transition to region (III), the surface pressure changes more smoothly compared to room temperature. The surface potential is significantly reduced.
Figure 3. $\pi$-A (black line) and $\Delta V$-A (blue line) isotherm for 8CB monolayer on the surface of pure water at a subphase temperatures of 23 °C (a) and 37 °C (b) and an aqueous solution of Cu NPs stabilized by SDS surfactant at 23 °C (c) and at 37 °C (d).

A similar behavior of the compression isotherms is observed for 8CB monolayer on the surface of an aqueous solution of Cu NPs stabilized by SDS surfactant at a subphase temperature of 23 °C (Figure 3, c). In area (I), up to area 180 cm$^2$ per monolayer, the surface pressure is about zero due to the large distance between 8CB molecules and the SDS surfactant monomers with Cu NPs adsorbed to the monolayer. An increase of the surface potential up to 0,247 V compared with a change of the surface pressure (in this case) and relative of the surface potential obtained during the formation of 8CB monolayer on the water surface at 23 °C is explained by the adsorption of Cu NPs onto the air-water interface. Therefore, the compression isotherm shifts toward the large specific areas per monolayer. In region (II), between 180 cm$^2$ and 135 cm$^2$ due to the densification of the surfactant molecules in the monolayer, there is a sharp almost linear increase of the surface pressure up to 5,6 mN/m. At the end of this region a collapse point is observed. Moreover, with an increase of the surface pressure the surface potential increases up to 0,506 V. This is due to the densification of the arrangement of surfactant molecules upon compression of the monolayer, which leads to the increase of the interaction between them and to changes the surfactant molecules orientation on the subphase surface. As a result, the surface potential changes. In region (III), during the formation of a three-dimensional structure of 8CB the surface pressure and surface potential change smoothly.

The experiment was repeated at a subphase temperature of 37 °C. Figure 3, d shows that the behavior of the isotherms of 8CB monolayer with adsorbed Cu NPs changed relative to a temperature of 23 °C. In region (I), up to area 176 cm$^2$ per monolayer, the surface pressure also changes insignificantly as it was shown earlier. Compared to the subphase temperature of 23 °C there is no sharp increase of the surface potential. In region (II), as in the previous experiment, there is a sharp increase of the surface pressure up to 5,1 mN/m. This point corresponds to the area of 140 cm$^2$ per
monolayer. Compared to a room temperature the sign of the surface potential changes. In the transition from the region (II) to the region (III) the collapse point almost disappears. The change of the surface pressure and the surface potential occurs more smoothly than subphase temperature of 23 °C.

The surface potential can be related to an average effective dipole moment for the monolayer-forming molecules by the Helmholtz equation (1):

$$\Delta V = \frac{\mu_{\perp}}{A \varepsilon \varepsilon_0}$$

where $\mu_{\perp}$ is effective dipole moment ($\mu_{\perp} = \mu \cos \theta$, $\theta$ is the angle between the surface normal and the dipole axis, $\mu$ is dipole moment), $A$ is the mean area per monolayer, $\varepsilon_r$ and $\varepsilon_0$ are the dielectric constant of the monolayer and the electric permittivity of the free space ($\varepsilon_0 = 8,85 \times 10^{-12}$ F/m), respectively [6, 8].

From the isotherms shown in Figure 3 the main parameters of 8CB monolayers at the collapse point were determined for various temperatures and composition of subphase (Table 1).

**Table 1.** Values of the mean monolayer area ($A_c$), surface pressure $\pi_c$, surface potential $\Delta V_c$ and effective dipole moment $\mu_{\perp}$ at the collapse point of 8CB monolayer on the surface of pure water and an aqueous solution of Cu NPs stabilized by SDS surfactant.

| Monolayer/subphase | Subphase temperature, °C | $A_c$, cm$^2$ | $\pi_c$, mN/m | $\Delta V_c$, V | $\mu_{\perp}$, D |
|--------------------|---------------------------|---------------|----------------|----------------|-----------------|
| 8CB/H$_2$O         | 23                        | 138           | 4,6            | 0,510          | 0,623           |
|                    | 37                        | 148           | 4,5            | 0,065          | 0,085           |
| 8CB/H$_2$O+Cu NPs  | 23                        | 135           | 5,6            | 0,506          | 0,606           |
|                    | 37                        | 140           | 5,1            | 0,080          | 0,099           |

It was found that an increase of the subphase temperature leads to increase of the specific monolayer area of 8CB on the surface of pure water by 18 %. In this case, $\mu_{\perp}$ reduces by 13 times, and $\pi_c$ reduces by 1,1 times. The change of the specific monolayer area is associated, firstly, with an increase of the length of hydrogen bonds between water molecules due to thermal expansion of the liquid. Secondly, this is due to phase transitions in which the ordering of the molecules and the structure of 8CB monolayer change [7, 11, 21, 22].

With increasing of the subphase temperature an increase of the surface pressure should be expected. However, this does not occur due to an increase of the disorder of molecules at the air-water interface. Therefore, $\mu_{\perp}$ of molecules in the monolayer reduces, and an early transition to the formation of a three-dimensional structure occurs.

For 8CB monolayer on the surface of aqueous solution with Cu NPs an increase of the subphase temperature also leads to increase of the specific area per monolayer by 8 %. In addition to these factors, the adsorption of SDS surfactant molecules with Cu NPs is added. As a result, the compression isotherms shift towards the large specific areas per monolayer. In this case, $\mu_{\perp}$ and $\pi_c$ reduce by 15 and 1,2 times, respectively.

It was found that the presence of Cu NPs stabilized by the SDS surfactant in water, regardless of its temperature, leads to an increase of $\pi_c$. This is due to increase of the surfactant molecules concentration during the adsorption of SDS with Cu NPs on the subphase surface. After the monolayer collapse point decrease of the surface potential is observed. At the end of the monolayer compression, the surface potential is lower for the Cu NPs aqueous solution subphase in comparison with the pure water subphase. This may be due to the displacement of 8CB molecules from the mixed monolayer into the upper bilayer [21].

4. Conclusions

The mesogenic cyanobiphenyl 8CB was studied as Langmuir monolayer. The effect of the temperature and subphase composition showed that it is possible to control the process of monolayer formation at the air-water interface. The influence of these parameters leads to the following effects: an increase of the specific area of 8CB monolayer, decrease of the effective dipole moment of the molecules in the monolayer, and the appearance of an early transition to the formation of a three-dimensional structure.
The impact of the subphase temperature is based on the thermal expansion of the monolayer and subphase, as well as a change of the phase state of the liquid crystal. The effect of the subphase composition is due to the adsorption of surfactants with Cu NPs at the air-water interface. The results obtained indicate that the temperature and composition of the subphase are important parameters for controlling the phase states, structure, degree of ordering, and monolayer properties.

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References
[1] Pasechnik S V, Chigrinov V G and Shmeliova D V 2009 Liquid Crystals: Viscous and Elastic Properties in Theory and Applications (John Wiley & Sons) p 436
[2] de Gennes P G, Prost J 1993 The Physics of Liquid Crystals (Clarendon Press, Oxford)
[3] Singh S and Dunmur D A 2002 Liquid Crystals: Fundamentals (World Scientific) p 531
[4] Hamelinck P J and Huck W T S 2005 J. Mater. Chem. 15 381
[5] Chumakov A S, Al-Alwani A J K, Gorbachev I A, Ermakov A, Shinkarenko O A, Begletsova N, Kolesnikova A, Glukhovskoy E 2017 J. Phys.: Conf. Ser. 917 092002
[6] Inglot K, Martyński T, Bauman D 2009 Dyes and Pigments 80 106
[7] Porter D, Savage J R, Cohen I 2012 Phys. Rev. E. 85 041701
[8] Schmitz P, Gruler H 1995 Europhys. Lett. 29 451
[9] Chumakov A S, Al-Alwani A J K, Gorbachev I A, Glukhovskoy E G, Usoltseva N V 2017 J. Phys.: Conf. Ser. 929 012044
[10] Al-Alwani A J, Chumakov A S, Begletsova N N, Shinkarenko O A, Markin A V, Gorbachev I A, Bratashov D N, Gavrikov M V, Venig S B, Glukhovskoy E G 2018 Mater. Res. Express 5 045050
[11] Al-Alwani A J K, Kosolapova K I, Chumakov A S, Lukyanova V O, Gorbachev I A, Kazak A V, Smirnova A I, Shtykov S N, Usol’tseva N V, Glukhovskoy E G 2018 BioNanoSci. 8 1081
[12] Chumakov A S, Al-Alwani A J K., Gorbachev I A., Ermakov A V, Kletsov A A, Glukhovskoy E G, Kazak A V, Usol’tseva N V, Shtykov S N 2017 BioNanoSci. 7 666
[13] Stamatoiu O, Mirzaei J, Feng X, Hegmann T 2011 Top. Curr. Chem. 318 331
[14] Matsuyama A 2009 J. Chem. Phys. 131 204904
[15] Al-Alwani A J K, Shinkarenko O A, Chumakov A S, Pozharov M V, Begletsova N N, Kolesnikova A S, Sevostyanov V P, Glukhovskoy E G 2019 Mater. Sci. and Technol. 35 1053
[16] Al-Alwani A J K, Chumakov A S, Gorbachev I A, Kuznetsov N O, Kletsov A A, Glukhovskoy E G 2017 BioNanoSci. 7 496
[17] Mirgorod Ju A, Borshch N A Method of producing nanoparticles of metals or hybrides of nanoparticles of metals. Pat. RU 2369466; Date of publication: 10.10.2009. Bull. 28.
[18] Vaseem M, Lee D, Hahn Y 2011 Mater. Chem. Phys. 125 334
[19] Begletsova N N, Selifonova E I, Zakharievich A M, Chernova R K, Sevostyanov V P, Glukhovskoy E G 2019 Moscow University Chem. Bull. 74 79
[20] Tah B, Pal P, Mahato M, Talapatra G B, 2011 J. Phys. Chem. B. 115 8493
[21] Modlińska A, Bauman D 2011 Int. J. Mol. Sci. 12 4923
[22] Collins J, Funfschilling D, Dennin M 2006 Thin Solid Films 496 601