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Effect of temperature on the value of the surface potential and the phase state of 4’-n-octyl-4-p-cyanobiphenyl liquid crystal

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Abstract. Liquid crystals are one of the most interesting materials for various applications. The article considers the influence of temperature to the phase change and the value of surface potential of 4’-n-octyl-4-p-cyanobiphenyl liquid crystal Langmuir monolayers. These parameters have a critical role in process of transfer monolayers to the solid substrate and for further using of them. It is shown that with increasing temperature of subphase leads to the monolayer of liquid crystal becomes isotropic and exhibits a gradual decrease in the surface potential in process of compression.

1. Introduction

Liquid crystals (LC) and devices based on them have long been widely used [1, 2]. On the basis of LC are built many types of displays [3, 4], height sensitivity, low power temperature sensors [5] and many other devices [6]. Such popularity of liquid crystals gained through a unique combination of properties. In the normal state in the same time they have the fluid properties and solid state properties and LC exhibit a strong anisotropy of the properties, particularly in optic [7]. It is also well aware of the dependence of the phase state of liquid crystals on the temperature. Possibility of changes phase by the small temperature changes can be crucial in areas where thin films of liquid crystals are used. For example, when we form them using Langmuir-Blodgett technology.

In our work we obtained monolayers of 4’-n-octyl-4-p-cyanobiphenyl (8CB) liquid crystal on the surface of the aqueous subphase by the Langmuir-Blodgett technology. The choice of this material is due by the fact that 8CB molecules are composed of polar and nonpolar part (figure 1). And thus, exhibit amphiphilic properties. In addition, the polar part of the highly long and has a large dipole moment. Thus, if we will be able to control film structure in the process their formation and transfer, we will be able to control the potential relief of the film on the solid substrate.

2. Material and method

The 8CB liquid crystal was purchased from “Sigma-Aldrich and dissolved in chemically pure chloroform (produced by “Vecton”, Russia). The concentration of liquid crystal solution was a...
constant in all experiments $10^{-3}$M. The changing in the surface pressure isotherms and surface potential at air-water interface of 8CB monolayer were investigated by using Langmuir-Blodgett trough (KSV Nima LB Trough Medium KN 1003, Finland) and Surface Potential Sensor (KSV NIMA, Finland) which has sensitivity of $\pm 1$ mV. In all experiments we used like a subphase deionized water with resistance of about 18,2M$\Omega \times$cm.

The 30µl of $10^{-3}$M 8CB solution were spread on the water surface and after 5 min (it is time for chloroform evaporation) the barriers were start compression of the liquid crystal monolayer. The speed of barriers was 10 mm/min. The isotherms were recorded in few series of experiments by various values temperature of subphase - 16°C, 21°C, 33°C and 41°C. Temperature control was realised by using LOIP thermostat (Russia) connected with working trough of Langmuir-Blodgett device.

3. Results and discussion

The molecules of 8CB have polar (CN) group that demonstrate strongly interaction with the water (hydrophilic group). Previous studies demonstrated that the 8CB molecules can form monolayers at air-water interface by using LB-method [8, 9]. The investigation of surface potential $\Delta V$ of liquid crystal monolayer reported previously [10] this parameter can provide us information about molecular organization during gas phase of liquid crystal [11], and the average dipole moment for the monolayer can be presented by Helmholtz equation:

$$\Delta V = \frac{\mu_{\perp}}{A\varepsilon_{1}\varepsilon_{0}}$$

Where $\mu_{\perp}=\mu \cos(\theta)$ ($\theta$ - the angle between the surface and the dipole moment axis), $\mu_{\perp}$ is called the effective dipole moment [12] and $\mu$ is dipole moment, $A$ is the occupied area by molecules on the subphase of water, $\varepsilon_{1}$ and $\varepsilon_{0}$ are the dielectric constant of monolayer and the electric permittivity of vacuum, respectively.

Figure 2a shown the surface pressure isotherm (solid curve) and surface potential dependence (dotted curve) of 8CB monolayer at low temperature of subphase (16°C), obviously we can observe there three regions. The region (I) related to area larger than 168,17 cm$^2$ coexistence of 8CB monolayer gas phase – surface pressure is almost zero and the $\Delta V$ increased gradually to 0,557V at 150,07 cm$^2$. In the region (II) between 168,17 cm$^2$ and 150,12 cm$^2$ the surface pressure increased sharply to the collapse monolayer at 150,12cm$^2$ with $\Delta V$ of 0,642V. At region (III) between 150,12cm$^2$ and 45,07cm$^2$ the formation of liquid crystal multilayers begins [13, 14]. The surface pressure increased slightly up to 6,26mN/m at 45,07cm$^2$ with $\Delta V$ of 0,616V.

The effective dipole moment can be calculated from equation (1), the $\varepsilon_{1}=1$ and the $\mu_{\perp}=1,3D, 1,34D, 0,385D$ for region (I),(II) and (III), respectively. There is a little change in values of surface pressure and $\Delta V$ isotherm between regions (II) and (III). That indicated that the orientation of liquid crystal molecules stay in the same (or near to same) direction.

![Figure 1. Schematic picture of 8CB molecule.](image-url)
Figure 2. Surface pressure isotherms (solid curve) and surface potential ($\Delta V$) (dotted curve) of liquid crystal (8CB) at subphase temperature of 16°C (a), 21°C (b), 33°C (c), 41°C (d).

Figure 2b shown surface pressure isotherm (solid curve) and $\Delta V$ dependence (dotted curve) for 8CB monolayer. Temperature of subphase was 21°C. The region (I) up to 152,64 cm$^2$ shown gas phase with gradually increased surface potential to 0,481V. In this case this region of 8CB monolayer has less molecules concentration than by gas phase at temperature of subphase 16°C (figure 2a). The surface pressure value at region (II) sharply raised from about 0mN/m at 152,64 cm$^2$ till collapse about 5mN/m at 133,89 cm$^2$ (transition region for next phase) and $\Delta V$ was grown to 0,562V. The region (III) presents plateau at area between 133,89 cm$^2$ and 45,28 cm$^2$ and value of surface potential $\Delta V = 0,472V$. We can explain this by process of forming of regular bilayer on the top of monolayer [15]. The effective dipole moment were estimated $\mu_\perp = 1,02D$, 1,04D and 0,298D for region (I), (II) and (III), respectively.

In figure 2a and b the $\Delta V$ value increase slowly with reducing the occupied area in the region (III). It can be assumed that the dipole moment of first 8CB monolayer directed down towards subphase of water [15, 11] at temperature of 16°C and 21°C.

Figure 2c shown typical surface pressure isotherm (solid curve) and $\Delta V$ dependence (dotted curve) for 8CB monolayer on the 33°C water subphase. There are three distinct regions: region (I) presented the gas phase with constant surface pressure up to 148,77 cm$^2$ with decreasing in the $\Delta V$ value to -0,098V. In the next region (II), the surface pressure isotherm sharply rise from 148,77 cm$^2$ to the
collapse point at 128.65 cm$^2$, the $\Delta V$ value slow grown to -0.05 V. In the third region (III) from collapse point to area of 45.55 cm$^2$ the $\Delta V$ value has been minimized to -0.17 V. The effective dipole moment shown values $\mu_{e} = -0.2D$, -0.088D, -0.1D for regions (I), (II) and (III), respectively. The results of surface potential isotherm and effective dipole moment indicated that the molecular orientations changed by increasing the temperature of subphase. Also reason for this is the changing to nematic phase in the 8CB [16, 17].

The surface pressure and $\Delta V$ isotherms at temperature of subphase 41°C presented on figure 2d. The region (I) is a gas phase up to area of 159.41 cm$^2$. In this region the curve of $\Delta V$ clearly shows a significant decrease surface potential to -0.171 V. The $\Delta V$ value increased slightly to -0.126 V in collapse region at 140.7 cm$^2$. In the region III value of surface potential sharply dropped down to -0.448 V at area value of 45.19 cm$^2$.

The 8CB molecules were arranged almost horizontally on the subphase surface and this fact can be confirmed by the results of the surface pressure and $\Delta V$ isotherms [18]. But after barriers start compression, the molecules begin to interact and they lift up from the subphase surface and molecules are arranged parallel to one another [18]. That mean the molecules orientations depends on the surface pressure, this assumption is agreement with the increasing value of $\Delta V$ isotherm and effective dipole moment.

Figure 2c and d show the surface potential value decreasing to the negative value, we can assume that is attributed to the random ordering of the chains of liquid crystal in monolayer. Most probably reason for this is changing in phase by effect of temperature [18]. If the surface potential have negative value the liquid crystal molecules is directed upwards to the air.

Figure 2 shows that the rising temperature and decreasing the occupied area lead to more smooth transition to liquid expanded phase in the region II [17]. The effective dipole moment for 8CB molecule that calculated from equation (1) has higher value at 16°C, with raising temperature of water subphase the effective dipole moment decreasing gradually (figure 2). The changes in the effective dipole moment and $\Delta V$ values are indicating the changing in the direction and orientation angle of 8CB molecules.

4. Conclusion

The formation of 8CB liquid crystal monolayer by Langmuir-Blodgett technique was studied. The surface potential and surface pressure of 8CB monolayers were investigated at various temperature of subphase. The results revealed that the surface potential of 8CB monolayer decrease with the increase the temperature of water subphase. The first monolayer formed at air-water interface and molecules aligned down towards water (from the air to the water) at temperature of subphase 16°C and 21°C. The result revealed formation liquid-expanded phase in region II with increase temperature of subphase (figure 2). The sharp decreases in the value of surface potential of 8CB monolayer at 33°C and 41°C indicating changing the orientation of molecules in monolayers.

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