Molecular Organization in Langmuir Films of Dichroic Azo DyeLiquid Crystal Mixtures.
II. Surface Potential Measurements

T. Martyński, A. Biadasz, and D. Bauman

Faculty of Technical Physics, Poznań University of Technology,
Nieszawska 13A, 60-965 Poznań, Poland

Reprint requests to Dr. T.M.; Fax: 0048-61-665-3201, e-mail: martyns@phys.put.poznan.pl

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Two-component films of 4-octyl-4’-cyanobifenyl (8CB) and non-amphiphilic azo dye (**1**) at different molar fractions were studied at the air-water interface on the basis of the surface potential-mean molecular area dependence recorded simultaneously with the surface pressure-mean molecular area isotherm. Conventional Langmuir technique was used to form **1**/8CB (guest-host) films during reduction and expansion of an area occupied by the molecules. From the surface potential value the effective dipole moment in the first monolayer formed on the water was calculated. Moreover, the number of dipole moments directed to the air with respect to those directed towards the water was estimated. A model of the microscopic polar ordering of the molecules in **1**/8CB films at the air-water interface is proposed.

Key words: Azo Dye; Liquid Crystal; Langmuir Film; Surface Pressure-Area Isotherm; Surface Potential.

1. Introduction

One of the possibilities to realize coloured liquid crystal displays (LCDs) is utilization of the guest-host (GH) effect [1]. In GH LCDs a small amount of a dichroic dye (guest) is dissolved in a liquid crystalline host which acts as a matrix to orient the guest molecules. The electric field applied to the display reorients the liquid crystal and dye molecules along the field direction and induces a change in the selective absorption of the dichroic dye. In order to obtain LCDs with the required parameters it is necessary to choose an appropriate dye for a given liquid crystal matrix, and therefore knowledge of the interactions between guest and host molecules is of primary importance. Very simple systems, in which the intermolecular interactions can be easily determined, are gas-liquid or gas-solid interfaces that provide us with a unique method for studying matter in the form of one molecule thick layers [2 – 4]. Using such a method for liquid crystals it is possible to obtain information about the molecular orientation in the first few monolayers at the surface, and about how the interfacial interactions affect the macroscopic molecular alignment in the bulk [5 – 7]. Recently, the study of binary liquid crystal mixtures [8, 9] and dichroic dye-liquid crystal mixtures [10 – 13] at air-water (Langmuir films) and air-solid substrate (Langmuir-Blodgett films) interfaces were undertaken. Thermodynamic and Brewster angle microscopy studies of Langmuir films as well as polarized absorption and fluorescence measurements on Langmuir-Blodgett films [10 – 13] were carried out. However, up to now a clear picture of the dye molecules alignment with respect to the liquid crystal molecules in surface monolayers has not been obtained. In order to obtain insight into the molecular organization of a liquid crystal doped with a dichroic dye in a Langmuir film, surface potential measurement (SPM) should be made. SPM is a very convenient method that allows to determine the orientation of polar or charged molecules at the air-water interface [14]. This method has been

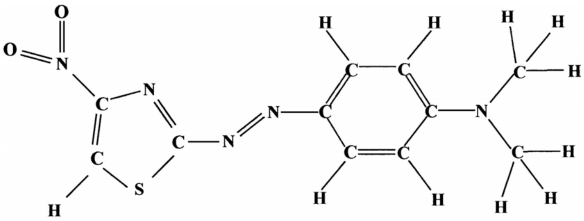

Fig. 1. Molecular structure of the azo dye molecule **1**.

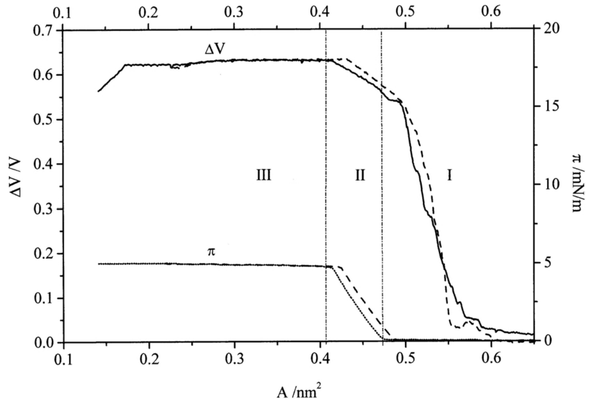

Fig. 2. Surface potential ΔV (solid curve) and surface pressure π (dotted curve) as functions of the mean area A per molecule for 8CB in a Langmuir film during compression process. Dashed curves present ΔV and π during expansion.

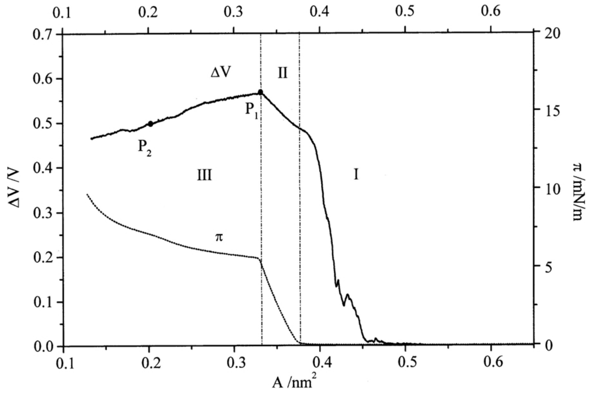

Fig. 3. Surface potential ΔV (solid curve) and surface pressure π (dotted curve) as functions of the mean area A per molecule for **1**/8CB in a Langmuir film with a mole fraction 0.1 of **1**.

used in this work to study the polar ordering in a mixture of 4-octyl-4'-cyanobiphenyl (8CB) with an of azo dye having a strongly polar —NO_2 group. The results presented here are complementary to those presented in [13]. SPMs on mixtures with various compositions were carried out, and a model of the dye and liquid crystal molecules alignment at the air-water interface has been proposed.

2. Experimental Section

The liquid crystal 4-octyl-4'-cyanobiphenyl (8CB) was purchased from E. Merck (Germany) and was used without further purification. The molecular structure of the azo dye (**1**) is presented in Figure 1. It was synthesized and chromatographically purified in the Institute of Dyes at the Łódź University of Technology.

Spectroscopic grade chloroform was used to prepare the spreading solutions. The dye and the liquid crystal solutions were made at a constant concentration of 8CB (1 mM), and appropriate amounts were mixed to obtain mole fractions of the dye in the whole range of concentrations. The guest-host mixtures were then spread from chloroform solutions onto deionized water, and the solvent was allowed to evaporate for 15 min.

The surface pressure-area isotherms and surface potential-area dependences were recorded by a commercial Minitrough 2 Langmuir-Blodgett system (KSV Instruments Ltd., Finland). A Wilhelmy platinum plate was used to measure the surface pressure (π), and the vibrating plate method (SPM head, KSV) was applied for determining the surface potential (ΔV). Accuracies of 0.1 mN/m and 1.0 mV were characteristic for the two measurements. All experiments were performed at a subphase temperature of 23.5 °C and kept constant within ±0.5 °C.

3. Results and Discussion

The molecules of 8CB have a strongly polar terminal —CN group which comes into contact with the water (hydrophilic group), two phenyl rings and hydrophobic alkyl chain. They therefore can be treated as amphiphilic molecules. It has been well documented that 8CB molecules can form a stable and compressible monolayer at the air-water interface (Langmuir film) [5–8]. The molecules of the azo dye **1**, however, inspite of possessing a polar terminal —NO_2 group, are not able to form such a film. After spreading a chloroform solution of **1** at the air-water interface, we observed by means of a Brewster angle microscope (BAM) [13] large patches of the dye on the water, and the surface pressure did not rise upon reduction of the available area. However, when **1** was mixed with 8CB at appropriate concentrations, compression was possible and we obtained surface pressure-mean molecular area ($\pi - A$) isotherms [13].

The surface potential ΔV of a floating monolayer is defined as the difference in a potential between a monolayer-covered surface and a clean water surface and can be related to an average dipole moment for the monolayer-forming molecules by the Helmholtz equation [15]

$$\Delta V = \frac{\mu_\perp}{A\varepsilon_r\varepsilon_0}, \tag{1}$$

where $\mu_\perp = \mu\cos\theta$ (θ = the angle between the surface normal and the dipole axis) is the average component of the molecular dipole moment normal to the plane of the monolayer, A is the mean area per molecule, and ε_r and ε_0 are the dielectric constants of the monolayer and the electric permittivity of free space, respectively.

The quantity $\mu_\perp$ is the so-called effective dipole moment and should not be mistaken for the dipole moment of an isolated molecule, because it is influenced by several dipole fields [16], e.g. the local field of the methylene group moments and the polarizable surrounding.

Figure 2 shows the $\pi - A$ isotherm (dotted curve) and simultaneously the acquired ΔV versus A (curve solid) for pure 8CB during compression. These results are very similar to those reported in [5–8,17]. Additionally, in Fig. 2 the surface pressure and the surface potential as a function of A during expansion process (dashed curves) are presented. Both π and ΔV reveal almost identical runs during expansion and compression, which confirms that the system is at equilibrium.

Following Xue *et al.* [5], we can distinguished three regions in the measured region of A presented in Figure 2. In region I, where A is larger than 0.48 nm^2, coexistence of gas and liquid exists and π is constant and near by zero. ΔV rises rapidly to about 530 mV in the area a little over 0.5 nm^2 and then increases slowly to 540 mV at A = 0.48 nm^2. In region II, between 0.48 nm^2 and 0.41 nm^2, the increase of π up to the collapse point at π_C = 4.8 mN/m is observed, indicating the creation of the homogeneous monolayer. ΔV rises too, but more steeply during the whole region II and at the collapse point reaches the value of 630 mV. Taking ε_r = 1 in (1), we calculated that this equals to an effective dipole moment $\mu_\perp$ = 0.68 D. Such a value of $\mu_\perp$ can be obtained within the whole region II, the product $\Delta V \cdot A$ remains constant and is equal to 0.258 Vnm^2. According to Schmitz and Gruler [17] this indicates that the polar ordering (defined as molecules aligned with polar heads pointing in the same direction) of 8CB molecules does not change, only their density on the surface increases. In region III we observe a plateau both for π and ΔV. The constant value of π means the creation of the next layer (or layers) on top of the monolayer, which was also confirmed by BAM observations [6]. Xue *et al.* [5] postulated that the upper layer is in fact an interdigitated bilayer in which the 8CB molecules are aligned antiparallel. As a result of such an alignment, the dipole moments are compensated and do not contribute to $\mu_\perp$. Therefore, ΔV remains constant in region III at least to the value of A = 0.17 nm^2. At this point ΔV starts to decrease slowly. The surface pressure, however, remains still constant and a transition to the multilayer cannot be supposed. A similar effect was observed by Schmitz and Gruler [17], who explained it in terms of the coexistence between monolayer and trilayer domains being in touch with each other in this region (between 0.17 nm^2 and 0.11 nm^2). Below 0.11 nm^2 the transition to the multilayer occurs [5–7].

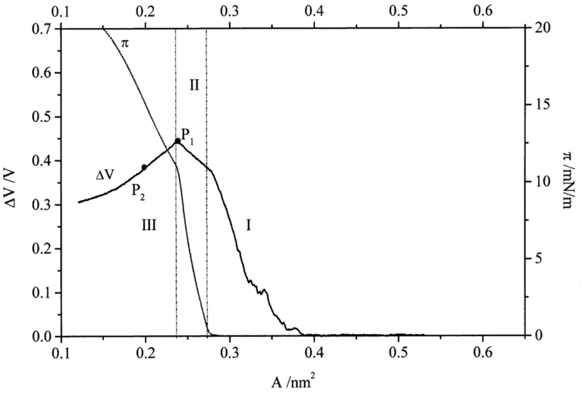

Fig. 4. Surface potential ΔV (solid curve) and surface pressure π (dotted curve) as functions of the mean area A per molecule for **1**/8CB in a Langmuir film with a mole fraction 0.3 of **1**.

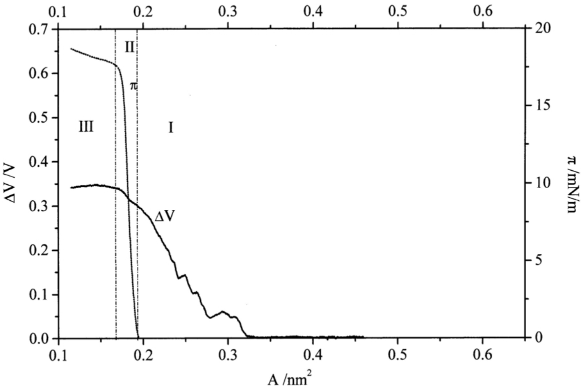

Fig. 5. Surface potential ΔV (solid curve) and surface pressure π (dotted curve) as function of mean molecular area, A for **1**/8CB in Langmuir film with a mole fraction 0.5 of **1**.

Another situation is observed when dye **1** is added to 8CB. This is presented in Figs. 3–5 for three chosen MF's of **1**. First of all, from the course of the $\pi - A$

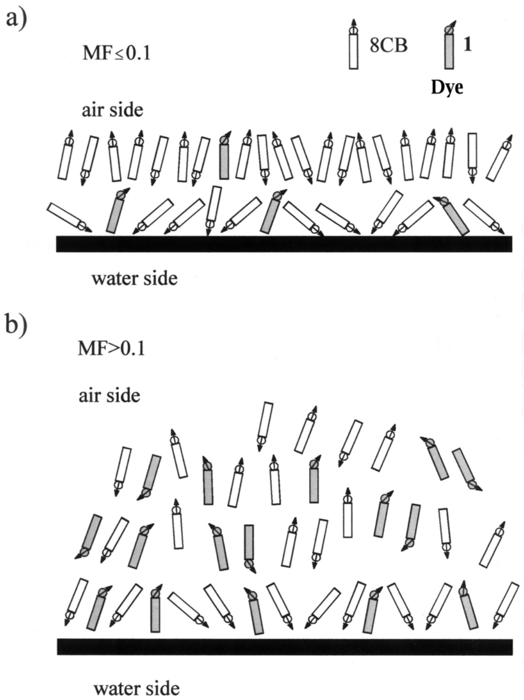

Fig. 6. Schematic representation of the microscopic polar ordering in the Langmuir film of **1**/8CB at small (a) and high (b) dye concentration. MF = Mole fraction of the dye.

Table 1. Ration of dipoles pointing in opposite directions $N^{\mathrm{up}}/N^{\mathrm{down}}$ in a monolayer of the **1**/8CB mixture at the air-water interface.

MF of **1**	$\Delta V'$/mV	$N^{\mathrm{up}}/N^{\mathrm{down}}$
0.1	560	0.11
0.3	440	0.30
0.5	330	0.48

isotherm it is seen that region II begins at smaller and smaller values when the MF rises. Moreover, an increase of the $\pi - A$ isotherm slope is observed. This indicates that the molecules in the Langmuir film of **1**/8CB create a smaller angle with the normal to the water surface in comparison to those in the Langmuir film of pure 8CB. As a result, the mixed film is more stable and more densely packed. ΔV becomes smaller from the collapse point with the increase of **1** concentration. The effective dipole moment calculated from (1) is 0.50 D for MF = 0.1, 0.29 D for MF = 0.3, 0.13 D for MF = 0.5 and 0.08 D (the approximated value) for MF = 0.7. These are rather unexpected results, taking into account that the molecules in **1**/8CB mixtures align more and more perpendicularly to the water surface with the rise of the dye content; in this case $\mu_\perp$ should increase. Therefore we must assume that the dye dipoles are aligned mostly opposite to the dipoles of the 8CB molecules, leading to the diminishing of the total effective dipole moment.

The 8CB dipole moments in the first monolayer are directed towards water (down) giving the surface potential ΔV = 630 mV. Let us now calculate the number of molecules in **1**/8CB mixtures with the dipole moments pointing in the opposite direction (up). We assume that at the water surface there exists a monolayer with N^{up} and N^{down} molecules, giving the surface potential $\Delta V'$, which is smaller than ΔV. This diminishing is due to the molecules directed up, and we can determine ΔV^{up} as

$$\Delta V^{\mathrm{up}} = \Delta V - \Delta V'. \qquad (2)$$

Thus the fraction of N^{up} molecules can be calculated from the relation

$$\frac{\left(N^{\mathrm{up}} + N^{\mathrm{down}}\right)}{N^{\mathrm{up}}} = \frac{\Delta V'}{\Delta V^{\mathrm{up}}}. \qquad (3)$$

The results for three MF's of **1** in 8CB are presented in Table 1. They confirm our earlier conclusion that almost all the molecules of **1** in the monolayer are directed from the water to the air.

In region III of the Langmuir film of **1**/8CB mixtures the plateau region of the $\pi - A$ isotherm can be distinguished only for small MF's of **1** (Fig. 3), and we suppose that in this case the creation of the regular bilayer on top of the monolayer takes still place. When the concentration of **1** in the film increases, the collapse occurs at higher and higher pressure, and no distinct plateau after the collapse point is seen. The former observation allows to assume that the Langmuir film becomes more and more stable and rigid, which leads to the conclusion that the formation of any regular bilayer or multilayer does not occur. ΔV in region III grows smaller with the reduction of the available area, which is distinctly seen at least to MF = 0.3. The diminishing of ΔV indicates that during the compression in the Langmuir film of **1**/8CB mixtures an excess of dipoles directed up increases. We are able to estimate the number of molecules in region III of the Langmuir film with dipole moment pointing opposite to the monolayer resultant dipole moment in the similar way as previously. Let us now denote the surface potential of the incompressible monolayer (i.e. at point P_1 at Figs. 3 and 4) containing N_{mono} dipoles as ΔV_{mono}. The surface potential at point P_2, which corresponds to the first inflection point on the $\pi - A$ isotherm (we suppose that from this moment the multilayer is formed), can be marked as ΔV_L. We obtain the difference $\Delta V_{mono} - \Delta V_L$ which is connected with the number of dipoles pointing up in the whole Langmuir film. The latter value can be calculated by the equation

$$\frac{N_L^{up}}{N_{mono}} = \frac{(\Delta V_{mono} - \Delta V_L)}{\Delta V_{mono}}. \quad (4)$$

A reliable value can only be obtained for MF = 0.1, and it is $N_L^{up} = 0.12\ N_{mono}$. Previously we have ascertained that at such small dye concentrations almost all the dye molecules are placed in monolayer. This value suggests therefore that in the bilayer occur mostly the 8CB molecules, with the excess of dipoles pointing up. Similarly, Harke et al. [18] found that the bilayer formed on top of the monolayer for some triblock organosiloxane smectogens with a terminal —CN group contains an excess of dipoles, which does not lead to the compensation of the effective dipole moments in the plateau region of π. However, the fact that the bilayer of a **1**/8CB Langmuir film at small MF of the dye contains first of all the liquid crystal molecules was confirmed by BAM observations described in details in [13].

For MF = 0.3 (Fig. 4) it is difficult to observe a distinct inflection point in the $\pi - A$ isotherm. Therefore the point P_2 was marked at $A = 0.2$ nm^2, which corresponds approximately to the cross section of both the 8CB and **1** molecules. We found N_L^{up}/N_{mono} to be 0.15 in this case. This value is about two times smaller than N^{up}/N^{down} in the monolayer, which suggests that in this case during the compression the excess of dipoles pointing up in the whole Langmuir film decreases. It seems that in the multilayer the "up" and "down" directions of the effective dipole moments become equal by probable. This is confirmed by the lack of the ΔV-change in region III for MF = 0.5 (Figure 5).

The microscopic polar ordering in the **1**/8CB Langmuir film proposed by us on the basis of BAM observations and $\pi - A$ isotherm runs, which are described in detail in [13] as well as by the ΔV behaviour, is illustrated in Figure 6.

4. Conclusions

Two-component Langmuir films formed by non-amphiphilic azo dye-liquid crystal 8CB mixtures were investigated. The surface potential as a function of the mean molecular area was recorded for various mixture compositions. The results revealed that in the first monolayer formed at the air-water interface the molecules of the dye are aligned with the dipole moment directed opposite to the dipole moment of the 8CB molecules, i.e. from the water to the air. During the compression process, as the next layers are formed, first 8CB molecules "jump out" on the top of the monolayer and create a bilayer at small dye concentration. The effective dipole moments in this bilayer are, however, not compensated. With rise of the dye molecule-content both 8CB and dye molecules can be present in the multilayer, but rather with the dipoles aligned antiparallel to each other.

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