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Surface potential measurements of Langmuir films of azo dye/liquid crystal mixtures

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ABSTRACT

Two-component films of a non-amphiphilic azo dye and a liquid crystal with strongly polar –CN group were studied at an air–water interface on the basis of the surface potential–mean molecular area dependence recorded simultaneously with the surface pressure–mean molecular area isotherm. Additionally, the morphology of the films was monitored with the aid of Brewster angle microscope. A conventional Langmuir technique was used to form dye/liquid crystal 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 molecules with dipole moments directed from the water to the air with respect to those directed towards water was estimated. The influence of the two components' miscibilities upon the surface potential after addition of the dye to the liquid crystal was determined.

1. Introduction

Azo dyes have found many applications because of providing the whole range of colours from which the most popular are red, orange, brown and yellow. Additionally, they have very high extinction coefficient and give bright, intensive colour by using small concentrations. Thus, more than half the commercial dyes belong to the class of azo dyes. The azo dye molecules exhibit large change in the dipole moment at $\pi \rightarrow \pi^*$ electronic transition from the ground to the excited state (charge transfer transition), the direction of which is mostly parallel to the molecular plane [1]. As a result, they are characterized by high value of the second-order hyperpolarizability and therefore, incorporated into highly oriented matrices, give possibility to obtain the system with nonlinear coefficient (at optical frequencies) much larger than that found in inorganic single crystals [2]. One of the methods used to obtain highly oriented systems is the Langmuir–Blodgett technique [3]. This technique is a unique method which enables to fabricate two-dimensional ordered layers from certain molecules or particles at air–liquid (Langmuir films) and air–solid substrate (Langmuir–Blodgett films) interfaces. From our previous investigations [4–8] it is, however, known that most of the azo dyes are not able to form stable Langmuir and Langmuir–Blodgett films. In such a case it is necessary to use the admixture of a compound that makes stable monolayers at the interfaces and can act as a supporting matrix. Such compounds can be some liquid crystals which are able to form homogeneous Langmuir and Langmuir–Blodgett films [9–12]. On the other hand, it is known that azo dyes dissolve and orient very well in liquid crystals [13,14]. Thus, azo dye/liquid crystal mixtures can be used in guest–host liquid crystal display devices [13,15,16].

In this paper we study Langmuir films formed of azo dyes with strongly polar –NO_2 group mixed with two liquid crystals: 4-octyl-4′-cyanobiphenyl (8CB) and *trans*-4-octyl(4′-cyanophenyl)-cyclohexane (8PCH) using surface potential measurements (SPMs), in addition to surface pressure isotherms and Brewster angle microscopy. SPM is a very convenient method which can be used to deduce information about the molecular organization of polar or charged molecules at the air–water interface [17,18].

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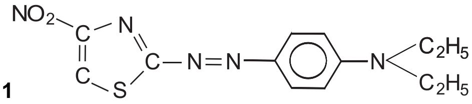
2. Experimental section

The azo dyes with following molecular structure were used: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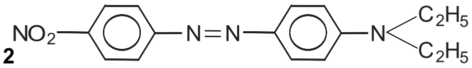
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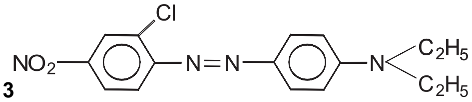
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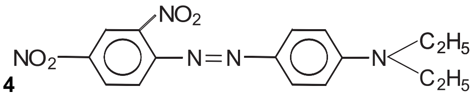
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All of the dyes were synthesized and chromatographically purified in the Institute of Dyes at Łódź University of Technology, Poland. The liquid crystals 4-octyl-4′-cyanobiphenyl (8CB) and *trans*-4-octyl(4′-cyanophenyl)-cyclohexane (8PCH) were purchased from the Dąbrowski Laboratory at the Military University of Technology, Warsaw, Poland and were used without further purification.

The surface pressure (π) and surface potential (ΔV) *versus* the mean molecular area (A) isotherm diagrams for Langmuir films were recorded simultaneously using a Minitrough 2 (KSV Instruments Ltd., Finland). The surface pressure was monitored by a Wilhelmy plate balance with an accuracy of ± 0.1 mN m^{-1}, and the surface potential was measured using the vibrating plate method by means of a SPOT 1 head from KSV with an accuracy of ± 10 mV. Further experimental details about Langmuir films' preparation are given elsewhere [6–8]. All measurements were repeated on fresh subphases three to five times to confirm reproducibility.

The morphology of the films at the air–water interface was visualized by means of a Brewster angle microscope (BAM). The instrument we used is based on Hoenig and Moebius setup [19] and was built in our laboratory. The image features were observed with a lateral resolution of ≈ 5 μm.

3. Results and discussion

3.1. Surface pressure–area and surface potential–area isotherms

The molecules of 8CB and 8PCH consist of strongly polar terminal –CN group, which comes into contact with the water (hydrophilic group), two cyclohexane and/or phenyl rings and hydrophobic alkyl chain, therefore can be treated as amphiphilic molecules. It has been well documented that both liquid crystals can form stable and compressible monolayers at the air–water interface (Langmuir film) [9–12]. Instead, the molecules of azo dyes **1**–**4**, in spite of possessing polar terminal –NO_2 group, are not able to form such a film. After spreading chloroform solution of **1**–**4** at the water surface in the trough, we observed large patches of the dye on the water using Brewster angle microscope (BAM), and the surface pressure did not rise upon the reduction of the available area. However, when **1**–**4** were mixed with 8CB or with 8PCH at appropriate concentrations, compression was possible and we obtained the surface pressure–mean molecular area isotherms

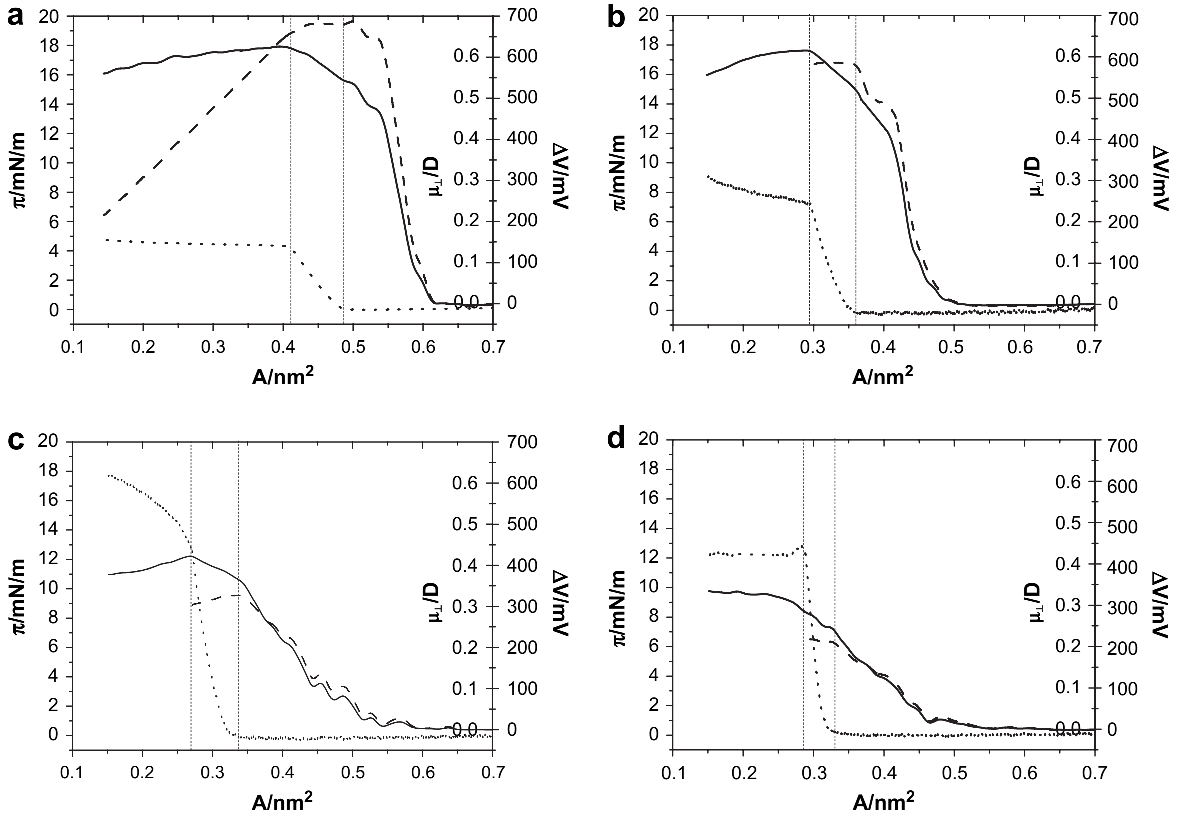


Fig. 1. Surface potential, ΔV (solid curve), surface pressure, π (dotted curve) and effective dipole moment (dashed curve) as a function of the mean molecular area, A for Langmuir film of 8CB (a) and **2**/8CB mixtures at MF equal to 0.1 (b), 0.3 (c) and 0.5 (d).

Table 1
Values of mean molecular area, A_C, surface pressure, π_C, surface potential, ΔV_C, and effective dipole moment, $\mu_\perp$ at the collapse point for Langmuir film of 8CB and dye/8CB mixtures

Compound	A_C/nm^2	π_C/mN m^{-1}	ΔV_C/mV	$\mu_\perp$/D	N_{up}/N_{down}
8CB	0.41	4.8	630	0.67	–
1/8CB					
MF = 0.1	0.29	6.1	626	0.48	0.15
MF = 0.2	0.24	8.5	559	0.36	0.24
MF = 0.3	0.20	19.0	415	0.22	0.34
MF = 0.4	0.18	24.0	362	0.17	0.38
MF = 0.5	0.14	15.7	395	0.15	0.39
2/8CB					
MF = 0.1	0.30	7.2	611	0.49	0.14
MF = 0.2	0.26	8.8	525	0.36	0.23
MF = 0.3	0.27	13.0	422	0.30	0.28
MF = 0.4	0.25	16.4	315	0.21	0.35
MF = 0.5	0.28	12.4	319	0.24	0.32
3/8CB					
MF = 0.1	0.31	6.0	584	0.48	0.15
MF = 0.2	0.24	7.0	489	0.31	0.27
MF = 0.3	0.17	21.0	341	0.15	0.39
MF = 0.4	0.20	22.0	252	0.13	0.40
MF = 0.5	0.20	19.0	251	0.13	0.40
4/8CB					
MF = 0.1	0.35	6.5	595	0.55	0.10
MF = 0.2	–	–	–	–	–
MF = 0.3	0.27	6.5	580	0.42	0.19
MF = 0.4	–	–	–	–	–
MF = 0.5	0.20	5.9	568	0.30	0.28

N_{up}/N_{down} is the ratio of molecules with dipole moment pointing in opposite directions in the monolayer.

[7,8]. On the basis of the π–A isotherm runs we draw conclusions about organization of the dye/liquid crystal mixture molecules in the monolayer at the air–water interface. The surface potential–area isotherm can give further information about molecular organization, particularly at early stages of the film compression when the surface pressure is still zero.

Fig. 1a shows π–A (dotted curve) and simultaneously acquired ΔV–A (solid curve) isotherm diagrams for the Langmuir film of the pure 8CB recorded during the compression process. Both isotherms are quite similar to those reported in literature [9–11,20]. Exemplary results for Langmuir films of **2**/8CB mixtures at the molar fraction (MF) of the dye equal to 0.1, 0.3 and 0.5 are shown in Fig. 1b–d, whereas the values of the area, the surface pressure and the surface potential at the collapse point, A_C, π_C and ΔV_C, respectively, for all the dye/8CB mixtures are presented in Table 1. From the course of π–A isotherms it is seen that the rise of π begins at smaller and smaller values of A as the MF of the dye increases. Moreover, the increase of the π–A isotherm slope is observed. This indicates that the molecules in the Langmuir film of the dye/8CB mixture create the smaller angle with the normal to the water surface in comparison with those in the Langmuir film of the pure 8CB (the detailed results are given in Ref. [7]). As a result, the mixed monolayer is more stable and more densely packed. π_C value rises or remains constant with the increase of MF, while ΔV_C grows smaller with the increase of MF.

Fig. 2a shows π–A (dotted curve) and ΔV–A (solid curve) isotherm diagrams for the Langmuir film of the pure 8PCH recorded during the compression process. To our best knowledge the ΔV–A isotherm for this liquid crystal is presented for the first time. Similarly as for 8CB, the rise of ΔV is observed earlier ($A = 0.68$ nm^2) than the rise of π ($A = 0.56$ nm^2). ΔV increases rapidly to the value

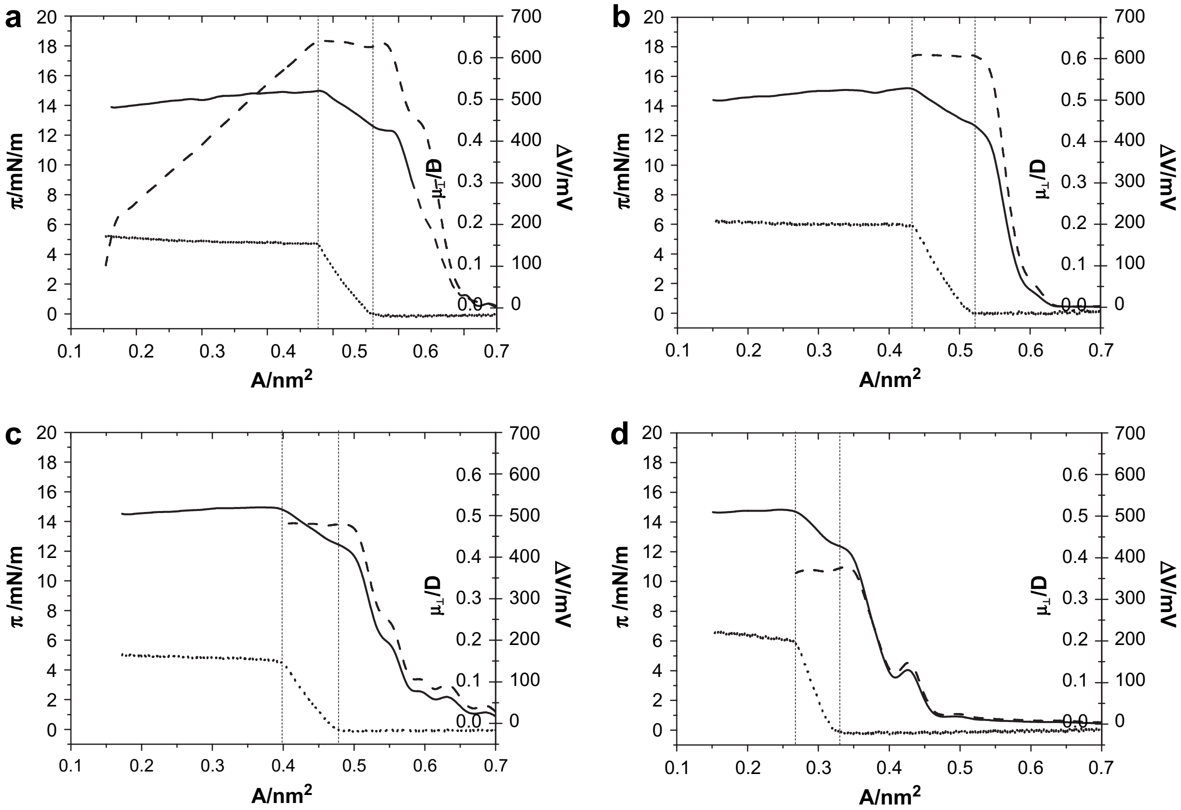


Fig. 2. Surface potential, ΔV (solid curve), surface pressure, π (dotted curve) and effective dipole moment (dashed curve) as a function of the mean molecular area, A for Langmuir film of 8PCH (a) and **4**/8PCH mixtures at MF equal to 0.1 (b), 0.3 (c) and 0.5 (d).

of 425 mV, next increases a little to 435 mV at $A = 0.56\ \mathrm{nm}^2$, and reaches the value of 520 mV at the collapse point. Behind the collapse point both π and ΔV remain constant.

Azo dyes under investigation, added to 8PCH at the appropriate MF, influence the alignment and the packing of the liquid crystal molecules at the air–water interface, similarly as it is observed in the case of 8CB. Upon increasing of MF, the packing density of the molecules and simultaneously the rigidity of the Langmuir film increase, as is confirmed by the rise of the isotherm steepness. The value of π_C increases with MF after addition of dyes **1** and **2** and remains constant for mixtures with dyes **3** and **4**. However, ΔV_C for all the mixtures grows smaller when the dye content increases. The data for the mixtures investigated are gathered in Table 2, whereas Fig. 2b–d shows π–A and ΔV–A isotherm diagrams for the Langmuir film of **4**/8PCH mixtures at MF = 0.1, 0.3 and 0.5, as examples.

The surface potential can be related to an average dipole moment for the monolayer-forming molecules by Helmholtz equation [18,21].

$$\Delta V = \mu_\perp / A\varepsilon_r\varepsilon_0, \qquad (1)$$

where $\mu_\perp = \mu \cos\theta$ (θ is the angle between the surface normal and the dipole axis) is the average vertical component of the molecular dipole moment, A is the mean area per molecule, and ε_r and ε_0 are the dielectric constant of the monolayer and the electric permittivity of the 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 [20,22], *e.g.* local field of methylene group moments, interactions between neighbouring dipoles inducing a mutual depolarization, and the resulting reorientation of water molecules underneath the monolayer. Moreover, one assumes customary that $\varepsilon_r = 1$, although it is known that dipoles in a monolayer may be embedded in media with distinct dielectric constant value, which depends on whether dipoles are at the monolayer–water or monolayer–air interface [23,24]. Therefore, $\mu_\perp$ is often called apparent dipole moment. This value was calculated for 8CB, 8PCH and the dye/liquid crystal mixtures as a function of the mean molecular area. The exemplary $\mu_\perp$–A isotherms are plotted in Figs. 1 and 2 (dashed curves). In Tables 1 and 2 the values of $\mu_\perp$ calculated from ΔV at the collapse point for all the mixtures under investigation are presented.

Table 2
Values of mean molecular area, A_C, surface pressure, π_C, surface potential, ΔV_C, and effective dipole moment, $\mu_\perp$ at the collapse point for Langmuir film of 8PCH and dye/8PCH mixtures

Compound	A_C/nm^2	π_C/mN m^{-1}	ΔV_C/mV	$\mu_\perp$/D	N_{up}/N_{down}
8PCH	0.48	5.3	520	0.64	–
1/8PCH					
MF = 0.1	0.45	6.3	491	0.57	0.05
MF = 0.2	0.31	6.1	481	0.40	0.20
MF = 0.3	0.23	16.0	379	0.23	0.33
MF = 0.4	0.16	16.9	353	0.15	0.38
MF = 0.5	0.17	15.7	298	0.13	0.40
2/8PCH					
MF = 0.1	0.49	6.4	470	0.59	0.04
MF = 0.2	0.39	6.7	409	0.42	0.17
MF = 0.3	0.32	7.9	329	0.28	0.28
MF = 0.4	0.30	10.5	283	0.23	0.32
MF = 0.5	0.25	11.5	270	0.18	0.36
3/8PCH					
MF = 0.1	0.45	6.6	492	0.59	0.04
MF = 0.2	0.37	6.7	461	0.45	0.15
MF = 0.3	0.34	6.0	431	0.39	0.20
MF = 0.4	0.30	6.6	404	0.32	0.25
MF = 0.5	0.27	5.2	364	0.26	0.30
4/8PCH					
MF = 0.1	0.43	5.8	528	0.60	0.03
MF = 0.2	–	–	–	–	–
MF = 0.3	0.40	5.9	513	0.55	0.07
MF = 0.4	–	–	–	–	–
MF = 0.5	0.26	5.9	511	0.35	0.23

N_{up}/N_{down} is the ratio of molecules with dipole moment pointing in opposite directions in the monolayer.

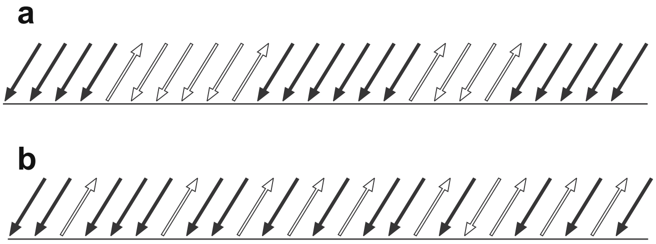


Fig. 3. Schematic representation of the microscopic polar ordering in the Langmuir film of dye/liquid crystal mixture before the collapse point in the case of immiscibility or partial miscibility (a) and good miscibility (b) of both components. Filled and open arrows represent dipole moments of molecules of liquid crystal and dye, respectively.

For the pure liquid crystals the rapid increase of $\mu_\perp$ together with the rise of ΔV is observed, up to the highest value of 0.68 D for 8CB and 0.64 D for 8PCH being reached at the area corresponding to the onset for the surface pressure. Such a value of $\mu_\perp$ remains constant up to the collapse point (the product $\Delta V \cdot A$ is constant in the region between vertical lines in Figs. 1 and 2). Similar behaviour is observed for the dye/liquid crystal mixtures, solely for some mixtures at higher dye concentrations, small diminishing (≤15%) of $\mu_\perp$ is observed (see for example Fig. 1c). The runs of $\mu_\perp$–A isotherms indicate that at large mean molecular area, the liquid crystal and dye molecules lie almost horizontally at the air–water interface. Upon compression, the molecules start to interact and at some critical area the hydrophobic parts of the liquid crystal molecules lift up from the water surface causing their tilted alignment with respect to the horizontal direction. Such orientational changes are confirmed by the significant increase of ΔV and $\mu_\perp$ at this stage. Since $\mu_\perp$ reaches the maximal value at the area where the surface pressure starts to increase and then remains constant up to the collapse point, we suppose that the molecular orientation does not change. This means that the tilt angle of the dye and liquid crystal molecules at the air–water interface are settled already at the beginning of the formation of the condensed monolayer.

The effective dipole moment calculated from Eq. (1) for the dye/liquid crystal mixtures is always smaller than that for the pure liquid crystal and decreases as the MF of the dye rises. This is rather

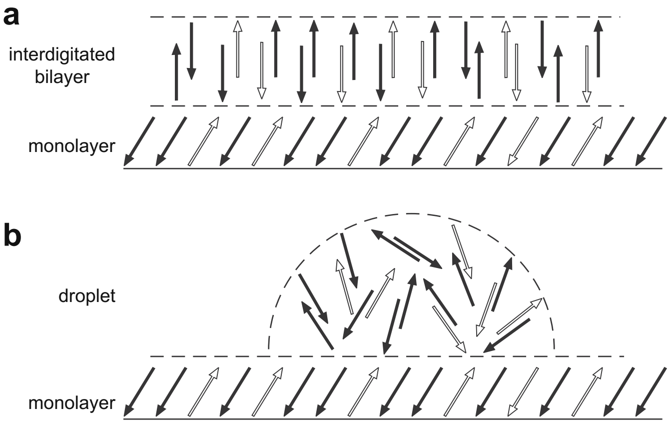


Fig. 4. Schematic representation of the microscopic polar ordering in the Langmuir film of dye/8CB (a) and dye/8PCH (b) mixtures beyond the collapse point. Filled and open arrows represent dipole moments of molecules of liquid crystal and dye, respectively.

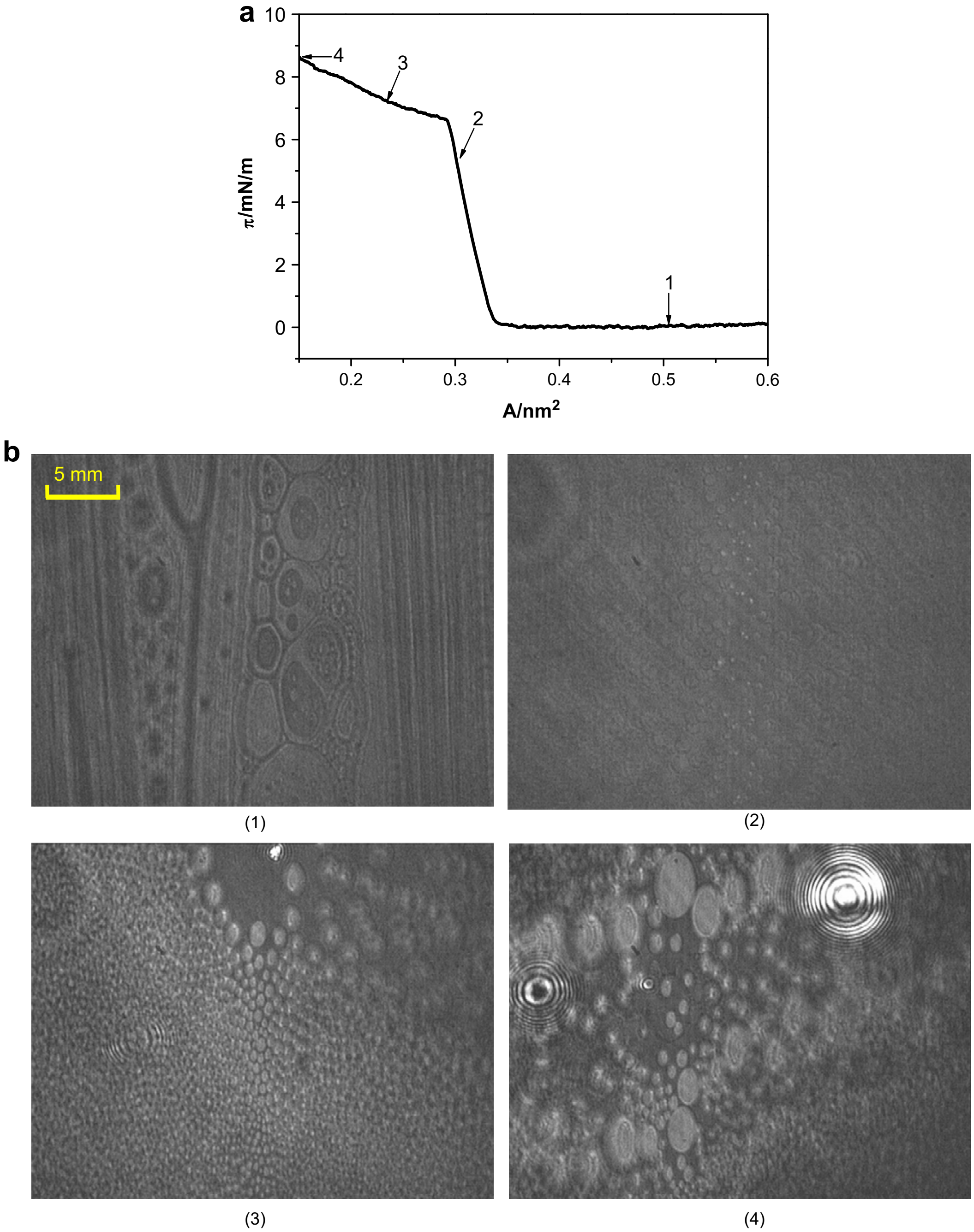


Fig. 5. Surface pressure–mean molecular area isotherms of **1**/8CB mixture (MF = 0.1) in monolayer at the air–water interface (a) and BAM images obtained during the compression (b) at $A = 0.51$ nm^2 (1), 0.32 nm^2 (2), 0.23 nm^2 and 0.16 nm^2. The scale of the images is 0.35×0.30 mm^2.

unexpected result taking into account that the molecules in the Langmuir films formed of the mixtures align more and more perpendicularly to the water surface with the increase of the dye content – in this case $\mu_{\perp}$ value should be higher and higher. Thus, we need to assume that the dye dipoles are aligned mostly opposite to the dipoles of the liquid crystal molecules leading to the diminishing of the total effective dipole moment.

The dipole moments of the liquid crystal molecules in the first monolayer at the air–water interface are directed towards the water (down) giving the effective dipole moment $\mu_{\perp}$. Let us now estimate the number of the molecules in the dye/liquid crystal 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 effective dipole moment $\mu'_{\perp}$, which is smaller than $\mu_{\perp}$. This diminishing is due to the compensation of the resultant dipole moment by pairs of molecules, in which the dipole moments are aligned antiparallel. As the dipole moments of the polar groups –CN and –NO$_2$ differ not significantly ($\mu \approx 4$D), in the first approximation we assume for simplicity that they are the same. Then the ratio of N^{up}/N^{down} can be calculated from the relation

$$\left(N^{down} - 2N^{up}\right)\Big/N^{down} = \mu'_{\perp}/\mu_{\perp}. \qquad (2)$$

The results for various MFs of the dyes in 8CB and 8PCH are presented in Tables 1 and 2, respectively. They indicate the different alignments of the dye molecules in mixtures with both liquid crystals at a low concentration. In the mixtures with 8PCH only

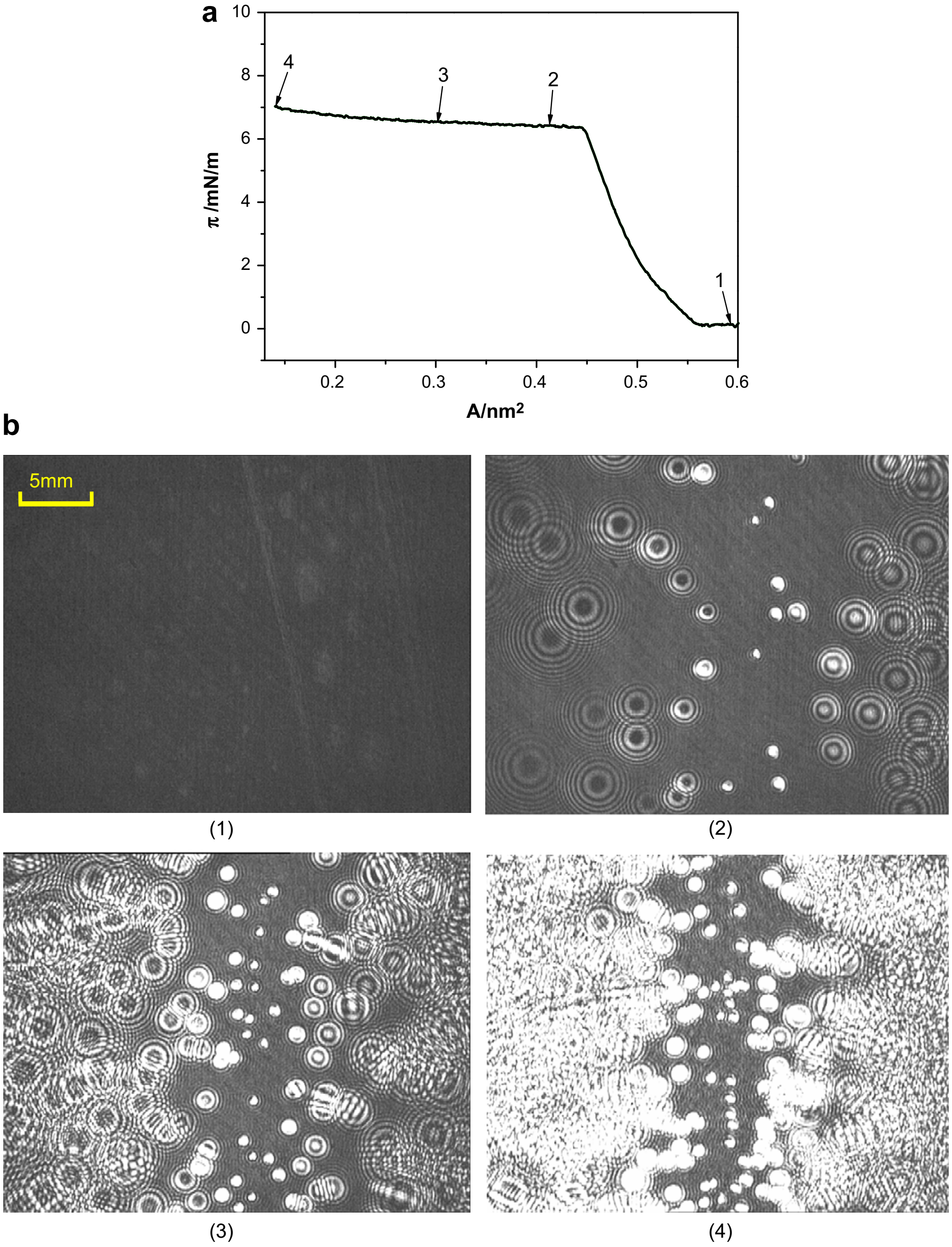
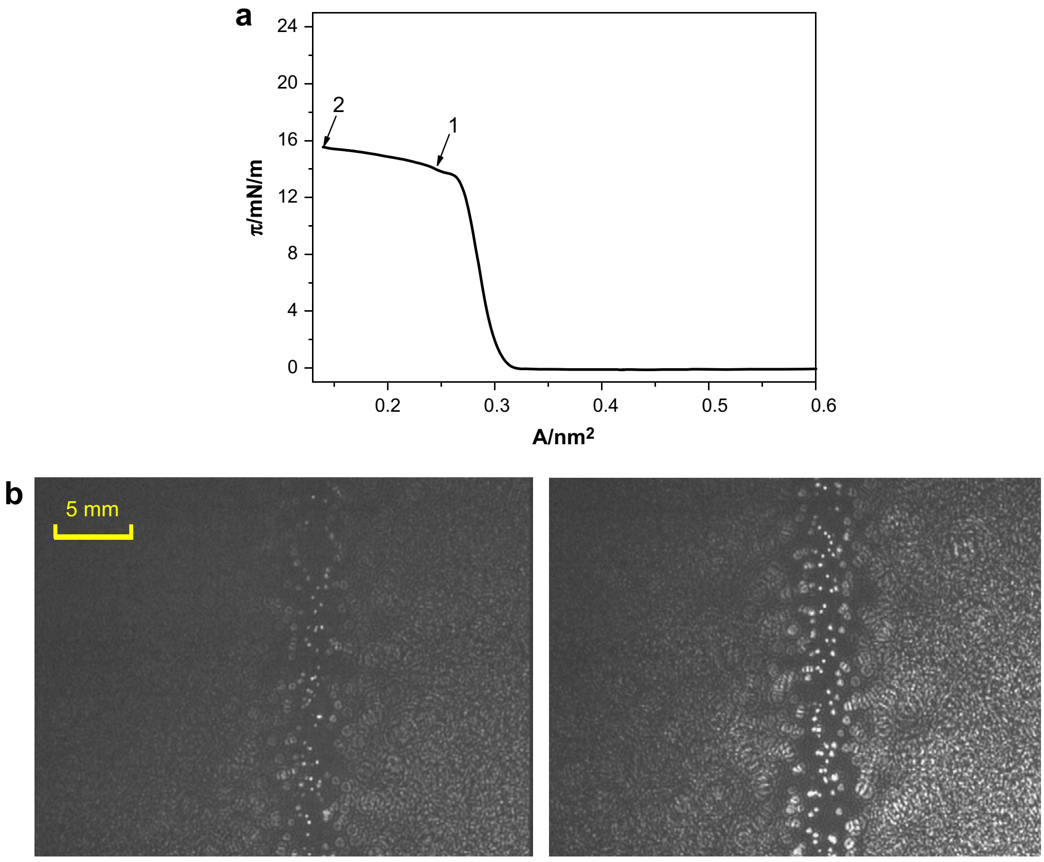


Fig. 6. Surface pressure–mean molecular area isotherms of **1**/8PCH mixture (MF = 0.1) in monolayer at the air–water interface (a) and BAM images obtained during the compression (b) at $A = 0.58$ nm^2 (1), 0.39 nm^2 (2), 0.30 nm^2 and 0.13 nm^2. The scale of the images is 0.35 × 0.30 mm^2.

some part of the dye molecules align with the dipole moment directed from the water to the air. In the mixtures with 8CB it is necessary to assume that not only the dye molecules but also some liquid crystal molecules are directed “up”. When MF rises, the fraction of N^{up} molecules in the mixtures with both liquid crystals becomes similar and at MF > 0.3 it is smaller than the whole number of the dye molecules. However, the alignment of the dye molecules with the dipole moment directed towards the air is further strongly preferred.

It is worthwhile to mention that, as follows from results presented in Tables 1 and 2, there is no correlation between the diminishing of ΔV and $\mu_\perp$ values after the dye addition, on the one hand and the value as well as the direction of the dipole moment of the given dye molecule, on the other. Dyes **1**, **2** and **4** have similar value of the dipole moment, with different directions of it. The value of the dipole moment of dye **3** is smaller because here the –NO$_2$ group is replaced by –Cl group ($\mu \approx 1.5$ D). However, the values of $\mu_\perp$ calculated from Eq. (1) are not associated with these facts. Meanwhile, the smallest changes of ΔV and $\mu_\perp$ appear for **4**/8CB, **3**/8PCH and **4**/8PCH mixtures. It was found previously [7] that in these mixtures the immiscibility or at least partial miscibility of the dye and liquid crystal molecules occurs (π_C remains constant with the change of the mixture composition). In such a case the creation of the antiparallel pairs consisting of the dye and liquid crystal molecules is hindered, which can be confirmed by the small value of the ratio of N^{up}/N^{down} for these mixtures. It is not very easy to propose any reasonable mechanism leading to such situation. In fact, the organization of molecules in Langmuir films of dye/liquid



(1) (2)

Fig. 7. Surface pressure–mean molecular area isotherms of **2**/8CB mixture (MF = 0.3) in monolayer at the air–water interface (a) and BAM images obtained during the compression (b) at $A = 0.23\ \mathrm{nm}^2$ (1) and $0.13\ \mathrm{nm}^2$. The scale of the images is $0.35 \times 0.30\ \mathrm{mm}^2$.

crystal mixtures depends on different intermolecular interactions: repulsive forces between electric dipoles of –CN and/or $-NO_2$ groups, attractive forces between phenyl rings, steric interactions between dye and liquid crystal molecules, as well as interactions of molecules in monolayer with water molecules. It seems that in the case of immiscibility or only partial miscibility, the dye molecules create domains in which the dipolar groups are directed mostly down as a result of attractive interactions with water molecules (the dye molecules have no distinct hydrophobic part). Then, the creation of antiparallel pairs is restricted, ΔV does not change significantly and the monolayer is not stabilized in the presence of dye molecules (π_C remains constant). This is presented schematically in Fig. 3a. However, in the case of good miscibility, individual dye molecules can orient with the dipole moments towards air and create antiparallel dimers with liquid crystal molecules. This leads to diminishing of ΔV and $\mu_\perp$ values and to monolayer stabilization confirmed by an increase of π_C in the presence of a dye (Fig. 3b).

Behind the collapse point, $\mu_\perp$ for the pure 8CB and 8PCH decreases (Figs. 1a and 2a). This is not reasonable, because when the creation of the interdigitated bilayer in the Langmuir film of 8CB is assumed [9,10], $\mu_\perp$ should be constant. In fact, $\mu_\perp$ calculated from Eq. (1) has no physical meaning in this region. The surface potential is contributed further only by the first monolayer coming into contact with the water. Since the dipole density in this layer does not change during reduction of the mean molecular area, ΔV stays constant (Fig. 4a). The detailed analysis of the π–A isotherm shape, supported by BAM images [12], showed that in the case of 8PCH, in contrary to 8CB, no regular bilayer is created on the top of the monolayer. Instead, three-dimensional (3D) droplet-like objects are formed. However, for 8PCH the constant value of ΔV beyond the collapse point is also observed. This leads to the conclusion that 3D domains are created on the top of the homogeneous monolayer in which the dipole density remains constant (Fig. 4b).

The value of $\mu_\perp$ for the dye/liquid crystal mixtures beyond the collapse point is not shown in Figs. 1 and 2. The runs of ΔV indicate, however, that this value is either constant or drops slightly upon reduction of the available area. The decreasing of ΔV is not bigger than 20% and is observed only at $\mathrm{MF} \leq 0.3$ (Fig. 1b and c). At $\mathrm{MF} > 0.3$, ΔV remains constant, which is seen in Fig. 1d. This means that in the layers or the domains created on the top of the first monolayer the antiparallel alignment of the dye and liquid crystal molecules dominates causing that ΔV does not change significantly (Fig. 4). The diminishing of ΔV, observed for some mixtures, could solely suggest the very small excess of the molecules directed with the dipole moment towards the air.

3.2. Brewster angle microscope images

In Figs. 5 and 6 are shown π–A isotherm diagrams for Langmuir films of **1** mixed with 8CB and 8PCH, respectively, at MF = 0.1 with marks of the compression stages at which BAM images, presented below isotherms, were recorded. There are almost no differences between the structures of the pure liquid crystal films described in literature [10,12,25] and those of **1**/liquid crystal mixture films at such low concentration of the dye. Moreover, up to the collapse point BAM images of monolayers with 8CB are very similar to those of monolayers with 8PCH. Before the surface potential and the surface pressure start to rise (Fig. 5a), we observed brighter islands of the molecules on the dark water surface. These islands come together to form a homogeneous film when the surface pressure is still zero but the surface potential already reaches the significant value (*e.g.* Fig. 6a). Further compression makes the film completely homogeneous (Fig. 5b). After the collapse point the phase transition is observed. In the case of the dye/8CB mixtures small regular domains appear, which grow continuously as the monolayer is further compressed (Fig. 5c). The surface pressure increases now (in contrary to the pure 8CB), indicating the presence of the dye molecules in the Langmuir film, which, however, do not perturb the alignment of the 8CB molecules and the liquid crystal domains can join together as the available area is limited (Fig. 5d). The images of **2**/8CB and **3**/8CB mixtures are similar to those of **1**/8CB. The behaviour of **4**/8CB film is slightly different. Already at $\pi = 0$ in the foam-like structure bright shimmer areas with irregular boundaries are seen, which exist also beyond the collapse point (data not shown). This can be the confirmation of the immiscibility of both components in the Langmuir film. For **1**/8PCH and **2**/8PCH at MF = 0.1 we obtained very similar images as for the pure 8PCH beyond the collapse point [12]. In Fig. 6b the appearance of the objects of high brightness surrounded by interference rings is seen very distinctly. The number of these objects rises when the available area on the water surface decreases (Fig. 6c and d). In the case of **3**/8PCH and **4**/8PCH mixtures, we observed, similarly as for **4**/8CB, small perturbations in the obtained BAM images, caused by the phase separation between the dye and liquid crystal molecules. However, at low dye concentration the objects characteristic for pure liquid crystals (flat circular domains in the case of 8CB and 3D droplet-like domains with interference rings in the case of 8PCH) are still recognized.

The contrast between BAM images recorded behind the collapse point for the dye/liquid crystal mixtures and those for the pure liquid crystal grows with increasing MF of the dye. Examples of BAM images for **2**/8CB and **4**/8CB mixtures are presented in Figs. 7 and 8, respectively. When the dye and the liquid crystal are miscible, up to MF = 0.5 it is possible to observe in the Langmuir film the creation of small circular domains. Upon continuous compression, the number of domains increases but their size does not grow. The background monolayer between the interdigitated domains starts to be rough (poorly seen in Fig. 7a). As the available area is further reduced, the domains are very close to one another but do not coalesce. It seems that the rough bottom monolayer prevents the formation of structures bigger in diameter. The mobility of the bilayer created on the rough monolayer is much smaller than that for the pure 8CB in the Langmuir film, where the domains of the interdigitated bilayer coalesce easily. It means that the dye molecules are present both in the monolayer and in the upper part of the Langmuir film. This situation remains almost unchanged to the end of the compression process. When the dye and the liquid crystal are not miscible, as in the case presented in Fig. 8, one notes in BAM images of the mixtures at MF ≥ 0.3 small nonregular patches just after spreading the chloroform solution on the water surface. Upon reduction of the available area after the collapse point, the patches are bigger and bigger but to the end of the compression process the circular domains are further seen. In contrary to the miscible mixtures, the domains grow in size which can be a sign that they contain mostly the liquid crystal molecules. Similar behaviour of the domains we noticed analysing BAM images for the miscible and immiscible Langmuir films of the dye/8PCH mixtures.

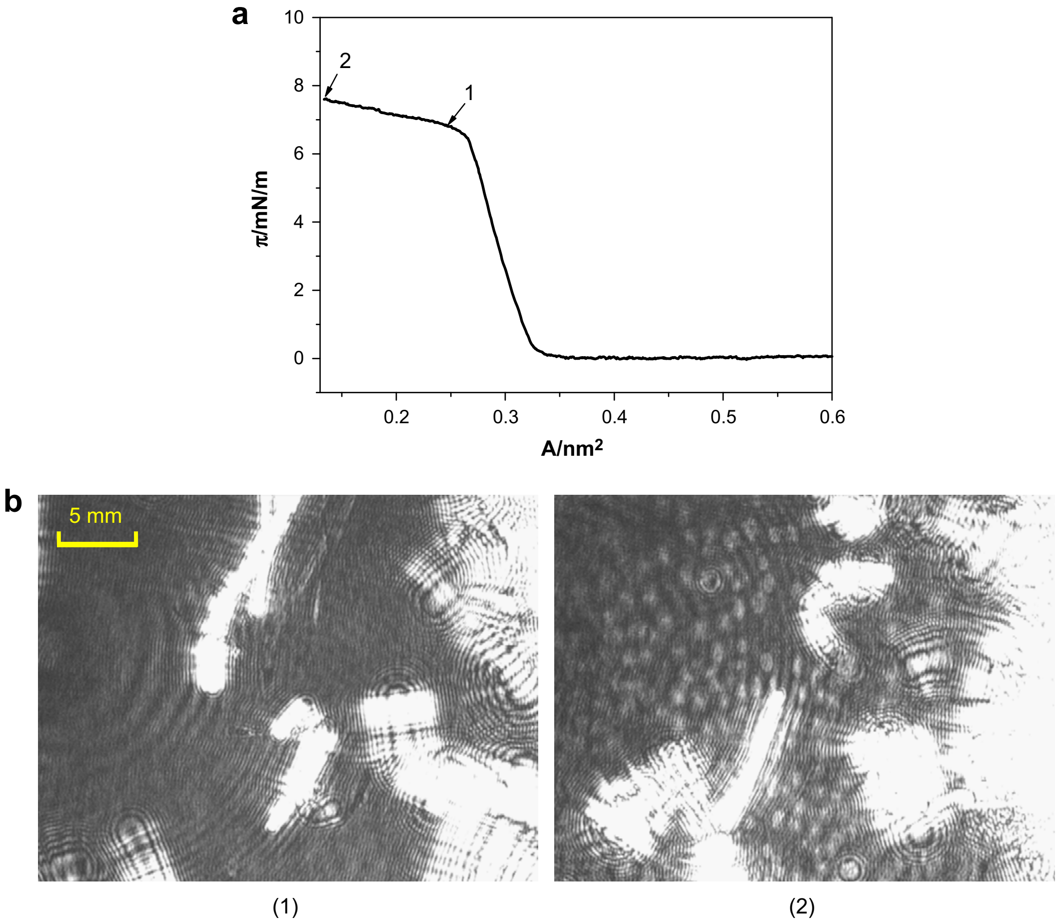


Fig. 8. Surface pressure–mean molecular area isotherms of **4**/8CB mixture (MF = 0.3) in monolayer at the air–water interface (a) and BAM images obtained during the compression (b) at $A = 0.25$ nm^2 (1) and 0.13 nm^2. The scale of the images is 0.35 × 0.30 mm^2.

4. Conclusions

Two-component Langmuir films from the non-amphiphilic azo dye mixed with the liquid crystal 8CB or 8PCH were investigated. The films of various mixture compositions were characterized by recording the surface pressure and the surface potential as a function of the mean molecular area, in addition to Brewster angle microscopy. The results obtained reveal that in the first monolayer formed at the air–water interface the molecules of the dye are aligned with the dipole moment directed mostly opposite to the dipole moment of the liquid crystal molecules, *i.e.* from the water to the air. It is very difficult to correlate the diminishing of the surface potential and effective dipole moment values after the dye addition with the value and the direction of the dipole moment of the given dye molecule. Instead, the influence of miscibility or immiscibility of both components in the Langmuir film on the change of the surface potential was found. During the compression of the monolayer after the collapse point, the objects characteristic for the pure liquid crystals are formed on the top of the monolayer: regular circular domains in the case of the mixtures with 8CB and 3D droplet-like domains in the case of the mixtures with 8PCH. Since the surface potential does not change significantly, we suppose that the molecules in these objects need to be aligned with the dipole moments antiparallel to each other. The detailed analysis of BAM images suggest that in the case of the miscible mixtures the dye molecules are present both in the first monolayer and in the objects formed on the top of it. When in the mixtures the phase separation occurs, the patches of the dye molecules near the domains containing liquid crystal molecules are observed.

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