Molecular Organization in Langmuir Films of a Dichroic Azo Dye-Liquid Crystal Mixture. I. Thermodynamic Data and BAM Observations

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Two-component films of 4-octyl-4'-cyanobiphenyl (8CB) and a nonamphiphilic azo dye on an air-water interface have been studied by means of surface pressure-area (π-A) isotherm measurement, Brewster angle microscopy (BAM), and absorption spectroscopy. Conventional Langmuir technique was used to form **1**/8CB (guest-host) films during compression and expansion of an area occupied by the molecules. The pure dye, spread on the air-water interface, formed irregular three-dimensional structures (3D), visible by the naked eye. In **1**/8CB films the dye was distributed homogeneously only at low mole fraction. At mole fractions higher than 0.3, just after spreading the **1**/8CB solution at the interface part of **1** formed 3D structures. On the basis of π-A isotherm, information about the miscibility of the two components in the **1**/8CB mixtures was obtained by using the area additivity criterion and surface phase rule. BAM images allowed to draw conclusions on the molecular organization of mixed Langmuir films at the air-water interface. The presence of **1**, roughly up to a mole fraction of 0.5, causes the mixed film to be less compressible and more thermodynamically stable (with higher collapse surface pressure). The absorption spectra of the films of **1**/8CB mixtures revealed the formation of dye aggregates.

Key words: Azo Dye; Liquid Crystal; Langmuir Film; Brewster Angle Microscopy; Light Absorption Spectroscopy.

1. Introduction

Molecules consisting of a cyano polar group —CN, two phenyl rings and an alkyl chain belong to thermotropic liquid crystal (LC) materials which possess one (nematic) or two (smectic *A* and nematic) mesophases between the solid and the isotropic liquid, depending on the alkyl chain length [1]. The liquid crystalline properties stem from the inherent ordered bulk structure driven by long-range forces [2]. However, molecular order can also be induced by an interface where amphiphilic properties of molecules, having no inherent order, play the main role in the interaction with substrates [3]. There are many examples of amphiphilic materials, ranging from simple surfactants like fatty acids and alcohols to complex polymeric systems. The ultrathin film formation of such molecules is well known and still widely investigated because it has an impact on industrial applications. Little is known, however, the structure and phase transitions of liquid crystal molecules at the air-water interface. In cyanobiphenyl, compounds the interactions between the phenyl rings induce liquid crystallinity in the bulk, and the strong dipole moment of the cyano-group ($\mu = 13 \times 10^{-30}$ Cm) [4] is responsible for the formation of a monolayer at the air-water interface. Up to now the molecular order in LC films at the interface is known for alkyl-cyanobiphenyl molecules [5 – 14] and three-block-organosiloxanes based on the cyanobiphenyl unit [15 – 17] from investigations using Langmuir technique, and for 4-octyl-4'-cyanobiphenyl (8CB) in freely suspended layers [18, 19]. Such molecules have attracted considerable interest because of the clear and elegant way of the phase transition from the monolayer to the stable multilayer formed upon reducing the area per molecule. A reverse process, i.e. transformation from the multilayer to the monolayer is observed during expansion of the film.

Surface balance measurements [5 – 7, 20], ellipsometry [16], second-harmonic generation [21 – 23], X-ray diffraction [24, 25], atomic force microscopy [12] and Brewster angle microscopy [10, 13, 14, 25] were

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used to investigate the properties of Langmuir films. There are only a few papers discussing the deposition of LC films onto solid substrates by using a Langmuir-Blodgett technique, the anchoring effect and molecular order at a gas-solid interface [12, 24, 26].

Liquid crystals as anisotropic solvents have great ability to orient dissolved guest molecules [27]. This phenomenon, called guest-host (GH) effect, is used in some types of coloured liquid crystal displays (LCDs). For such applications it is important to know whether addition of nonmesogenic materials has a destructive influence on the molecular order or improves it [28–32]. It was found that the addition of a dichroic dye has an effect on the mesophase temperature range, which is critical for applications [29, 30]. Moreover, the short-range orientation of cyanobiphenyl molecules and their association is affected by the presence of some kind of dye molecules, e.g. due to the interaction between the strongly polar —CN and —NO_2 terminal and/or lateral groups [30, 33, 34].

In this work we have studied the behaviour of mixed dye/LC monolayers at the air- water interface. As host we used 8CB, and as guest dichroic azo dye (**1**) which was synthesized for application in GH LCDs. This dye has a high order parameter in LC matrices, reduces only slightly the mesophase and shows good solubility [29, 30, 33, 34]. The **1**/8CB system and other guest-host mixtures were already studied by us in Langmuir and Langmuir-Blodgett films [26, 35, 36], but some questions remained still open. Therefore we have continued the investigation of the **1**/8CB system in Langmuir films. Not only the surface pressure-area isotherms were recorded, but the films were also observed with Brewster angle microscope (BAM). Additionally, the spectral properties of the mixed films were investigated by measuring the absorption spectra at different stages of the films formation.

2. Experimental

8CB was purchased from Merck and used without further purification. The blue dichroic dye **1** was synthesized and purified at the Institute of Dyes, Łódź University of Technology (Poland). The molecular formula and basic parameters of the compounds are shown in Figure 1.

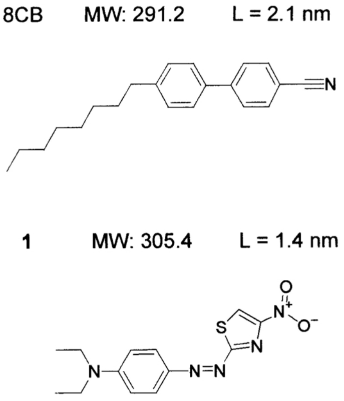

Fig. 1. Molecular structure of dye (**1**) and liquid crystal material 4-octyl-4’-cyanobiphenyl (8CB) studied. MW: molecular weigth, L: length of the molecule calculated on the basis of the space filing model (CPK).

Pure 8CB and its mixtures with **1** solved in were spread chloroform in the required mole fraction (MF) on water from a Milli-Q (Millipore Corp.) water system. The Concentrations of the mixed components were checked spectroscopically. 150 μl of these solutions was spread with a microsyringe on the surface of carefully cleaned water. A commercial KSV-5000 Langmuir-Blodgett system (KSV, Finland), located in a cabinet equipped with a laminar flow air cleaner, was used for symmetrical compression and expansion at a constant barrier – speed of 1.2×10^{-4} nm^2 per molecule and second. The solvent chloroform was allowed to evaporate for 15 min. after spreading. The surface tension was measured with a Wilhelmy platinum plate placed almost in the center of the 43 cm × 15 cm trough. All experiments were performed at 23.5 °C with minimal deviations of the air temperature to prevent capillary convection in the subphase.

A BAM, type NL-EMM 683SS (Nippon Laser Electronics Lab., Japan) based on the standard BAM scheme [37–39], was used to see the structure and phase transitions of the films on compression and expansion. A p-polarized beam of a He-Ne laser was directed at the Brewster angle (53.1°) onto the pure water. One Glan-Thompson polarizer was placed in the incident laser beam. *A* (320×550) μm^2 area of the film was pictured through lenses and an extension tube set attached to the CCD camera. The focal length was 32.5 mm. Images were recorded in an analogous way on videotape via a Quality Image Improver DSV-20 (Hamamatsu, Japan) and printed without correction of the geometrical distortion due to the oblique incident angle associated with the BAM optics on a photoprinter NC-1 (Fujix, Japan). The compact BAM setup allowed to examine different spots on the trough ca. 5 mm from the walls to the center of the trough. In this way we could be sure that we neither missed nor overlooked some structures of the mixed film near the trough borders. Reproducible BAM patterns, typical for the **1**/8CB monolayer morphologies, were only considered. All observations were performed under conditions of continuous compression.

In situ absorption measurements were performed by means of a single beam spectrophotometer MCPD-1000 (Otska Electronics, Japan) equipped with a diode array detector. A fiber optic bundle was used to introduce white light vertically to the water surface. A small aluminum mirror was placed in the bottom of the trough to turn the light back from the trough to a receiver optic fiber. In this way the analyzing light beam travels twice through the film. 256 scans at a wavelength range were accumulated at different stages of the film formation upon compression. The light source was carefully stabilized to prevent a long time light intensity drift and to keep the base line constant during the film compression process.

3. Results and Discussion

3.1. Surface Pressure-area Isotherms

The Langmuir films formed by 8CB as mesogenic host and the nonamphiphilic azo dye **1** as guest were investigated over a wide range of the mole fraction (MF) of **1**. We also tried to make a Langmuir film from pure dye, but we observed, that after spreading 1 mM of the chloroform solution of **1** on the pure water surface, during the evaporation of the chloroform the film becomes more and more uniform. Very slow compression does not cause a rise of the surface pressure. When the surface area is reduced approximately to one half, deeply blue irregular islands, visible by naked eye, arise. At the end of the compression the surface pressure remains still zero, which means that **1** does not form a monolayer on the water surface. Details of the observed film textures will be discussed in the next section.

A basic and widely used technique to characterize Langmuir films is the measurement of the surface pressure (π)-area (A) isotherm, which is a plot of the change in the surface pressure as a function of the area available to each molecule on the water surface (mean molecular area).

Figure 2 presents typical examples of the surface pressure-area isotherms for different concentrations of **1** in an MF range from 0.0 to 0.75. Curve 1 is very similar to that presented in [7,13,14]. Following Xue et al. [7], we can distinguish five regions in the measured area range. If A is greater than 0.5 nm^2, π is almost zero, which indicates submonolayer coverage. Between 0.48 and 0.41 nm^2, the first significant increase in π up to the collapse point occurs at A larger by a factor of two than the theoretical molecular cross-section of 8CB. Xue et al. [7] and de Mul and Mann [13] explained this effect in terms of strong repulsive interactions between the electric dipoles of the cyano groups. As a result of such interactions, the 8CB monolayer is fragile and molecules are not densely packed. It has been found [22] that the average angle between the molecular long axes of 8CB and the normal to the interface is approximately 60°. By further compression of the 8CB film, the plateau region is observed: π remains constant with decreasing A. When the area reaches about 0.11 nm^2, π rises sharply. This value is too small for all the molecules to remain on the water surface, and therefore Xue et al. [7] postulated the existence of an interdigitated bilayer on top of a monolayer (trilayer) adjacent to the interface in this A region. After further compression a second kink and next plateau appear, suggesting the creation of a multilayer.

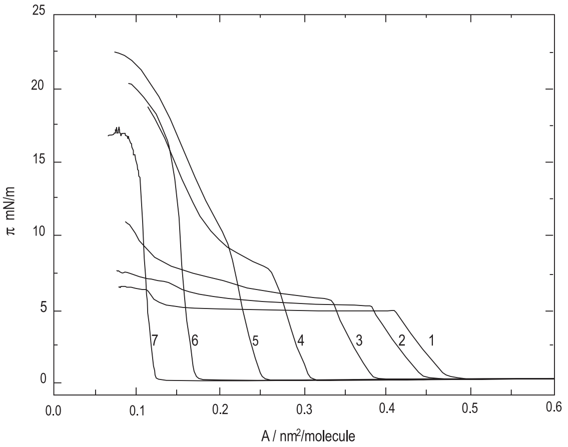

Fig. 2. Surface pressure (π) vs. area (A) isotherms of pure 8CB: 1, and **1**/8CB films with the following MF's of **1**; 0.05: 2, 0.10: 3, 0.25: 4, 0.35: 5, 0.55: 6, 0.75: 7.

Only the isotherms for relatively low concentration of **1** (MF < 0.1) have kinks which can be ascribed to the corresponding kinks in pure 8CB. This suggests that a successive multilayer formation as observed for cyanobiphenyls [5–14] and organosiloxane smectogens [15–17], can also take place in Langmuir films of **1**/8CB mixtures. When the concentration of **1** in the film increases, the rise of surface pressure upon the film compression starts to appear at smaller and smaller A. Additionally, the kinks of the isotherms are observed at higher and higher pressure – the collapse surface pressure π_c increases with the dye concentration. The shape of the isotherms of the highly concentrated mixed film reveals that the surface pressure above π_c rises monotonically instead of creating the plateau region characteristic for pure 8CB. This fact, together with the observed increase of the isotherm slope with the rise of the MF of **1** indicates the enhancement of the mixed film molecular packing and stability. However, at MF = 0.75 the surface pressure starts to increase at $A \approx 0.12$ nm^2. This value is too small for even the most dense packing of the molecules on the water, and therefore we should suppose that at such a high content of **1** in 8CB the formation of a defined monolayer is no longer possible.

The knowledge of a very complex process of miscibility is up to now not sufficient, and one can find only a few papers discussing this deeply. Mostly complete immiscibility and phase separation are reported in [40–46]. One can discuss this problem in terms of the excess area additivity criterion and surface phase rule [40, 47, 48]. The surface phase rule states that if the equilibrium spreading pressure (ESP) of the mixed film is dependent on the mixture composition, then the components are miscible; when the ESP is independent of the composition, the components are immiscible. In **1**/8CB mixtures π_c is well pronounced, at least up to MF = 0.5, and therefore π_c can be used instead of the ESP [47]. As can be seen from the results presented in Fig. 3, π_c rises over the whole range of composition investigated. Only at higher concentrations the increase of π_c is lower and shows the tendency to stay constant.

According to the area additivity criterion, if components in a binary mixture are immiscible, they act independently and A in the mixed monolayer follows the rule [47]

$$A_{12} = x_1 A_1 + x_2 A_2, \tag{1}$$

where A_{12} is mean molecular area of the mixed film, $x_i (i = 1, 2)$ are the mole fractions of the components, and A_i are the molecular areas in one-component films at the same surface pressure. In Fig. 3 a plot of A for **1**/8CB mixtures versus the MF of **1** at an surface pressure of 3 mN $\times$ m^{-1} is presented. The experimental points (crosses) lie below a straight line (dashed line) connecting A of pure the components following the additiving rule. This small negative deviation suggests some weak attractive interaction between **1** and the 8CB molecules and, together with the change of π_c with the mixture composition, indicates at least partial miscibility of the two components.

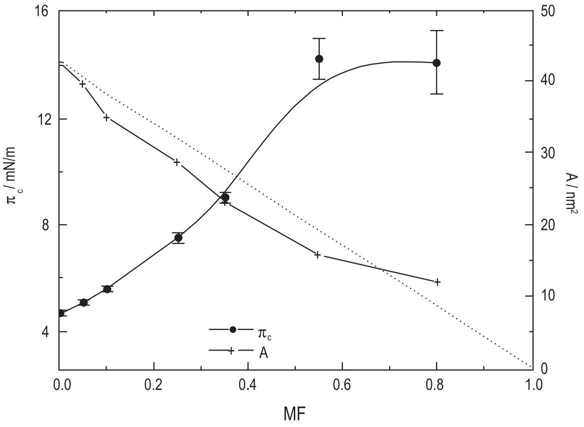

Fig. 3. Thermodynamic criteria of miscibility. Average area per molecule (A) at 3 mN/m of **1**/8CB mixtures: measuring points (crosses) and the additivity rule (dashed line) as well as collapse pressure π_c versus mole fraction (MF) of **1** (filled circles). Solid lines are visual guides. Data come from the isotherms presented in Figure 2.

The expansion isotherm of the binary film shows, under the experimental conditions, a very slight hysteresis with respect to the compression isotherm when MF of **1** is below 0.3. This is shown in Fig. 4 for **1**/8CB at MF = 0.25. For higher MF of the dye, a stronger hysteresis is observed and the films are compressible to the minimum of the available surface area. This could be explained by the fact that some part of the spread material settles on the borders of Teflon trough barriers and the Wilhelmy plate as well. When the MF is higher than 0.4, the stability of the film decreases at high surface pressure. The films can be still formed, but the expansion following first compression shows a significant hysteresis (data not shown).

3.2. Brewster Angle Images

The Brewster angle microscopy is known as a very powerful technique for imaging monomolecular films *in situ*, which greatly helps in recognizing the morphology and understanding the phase behaviour of monolayers [16, 37, 49].

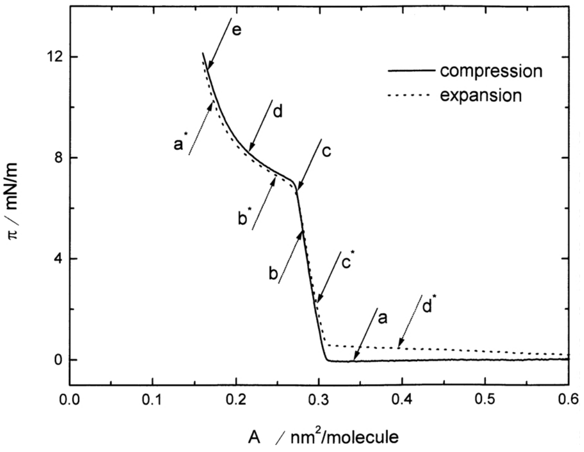

Fig. 4. Compression and expansion isotherms of **1**/8CB mixture at MF = 0.25 recorded at 23.5 °C. Arrows with the Roman letters indicate the states at which the corresponding BAM images in Fig. 5 and Fig. 6 were recorded.

Pure 8CB, pure **1** and mixed **1**/8CB films with very low dye concentration

The BAM images of the pure 8CB in all Langmuir film states were similar to those presented in [13, 14], whereas the BAM image of pure **1** showed thick irregular patches (Figure 5f). This confirms the conclusion drawn from the lack of the π rise at the compression process (Sect. 3.1), that **1** does not form a compressible monolayer at the air-water interface.

There were almost no differences between the structures of the pure 8CB film and the mixed films at MF's in range from 0.01 and 0.05 (data not shown). All phase transitions of the film from the gas state of the molecules at the interface to the monolayer and than multilayer systems were observed and can be interpreted in the same way as for the pure 8CB. In the isotherm plateau region we observed bright disc-like domains, very regular in size and shape. Under further compression these disc-like domains grow in the size and numbers. Some inhomogeneous distribution of these structures is notified, which had also been observed earlier for pure 8CB [13].

1/8CB film at MF = 0.25 on compression

As a typical example of the mixed film transformation on compression, the BAM images of a binary mixture of **1**/8CB for the dye with MF = 0.25 are presented in Figures 5a – e. Each image, signed by a Roman letter, corresponds to the appropriate point on the compression isotherm, as indicated by an arrow and the Roman letter in Figure 4.

For zero surface pressure at an open trough area a uniform background is observed. When A is ≈ 0.70 nm^2, a gas phase in coexistence with a liquid phase in form of the distorted circular patterns, followed by big liquid islands is seen (Figure 5a). These textures appear near the Teflon wall of the Langmuir trough. Before the surface pressure starts to rise at A near 0.50 nm^2, a uniform film almost completely covers the water surface. Only a small number of disclination lines can be identified. Further compression makes the film completely homogenous and brighter (Fig. 5b) because of the increase of the effective refractive index of the film due to the rise of the molecular packing. Just before the collapse point, a new form of texture appears (Figure 5c). One observes bright shimmer areas with irregular boundaries, which exist also just beyond the collapse point. A similar texture was observed by Ibn-Elhaj et al. [24] (see the Figs. 4b and 4d) for a three-block organosiloxane, based on the pentyloxy-cyanobiphenyl unit. At further compression one can see the first signs of the second layer formation in the form of bright small circular domains due to the nucleation. At the same time, the shimmer areas disappear. We strongly believe that the bright circular domains consist of three layers, which suggests their homogenous reflectivity. Upon continuous compression the number of domains increases, but their size grows not so fast as in the pure 8CB film. The background monolayer between the interdigitated domains start to be rough (poorly seen in Fig. 5d because masked by diffraction patterns). It seems that the concentration of **1** in the bottom part of the film increases when the bilayer is formed. We assume that some part of the dye molecules is present in the upper bilayer, but the concentration of the dye is lower than in the monolayer. This assumption was confirmed by surface potential measurements (data not presented). A detailed and systematic study and discussions will be given in [50]. Upon reduction of the trough surface, the domains are very close to one another, but do not coalesce. It seams that the rough bottom monolayer prevents the formation of structures bigger in the diameter. The mobility of the bilayer created on the rough monolayer is much smaller than for pure 8CB system where interdigitated bilayer domains coalesce easily. The line tension must also be lower than for pure 8CB bilayers. This situation remains almost unchanged to the end of the compression process. Near to the end of the compression

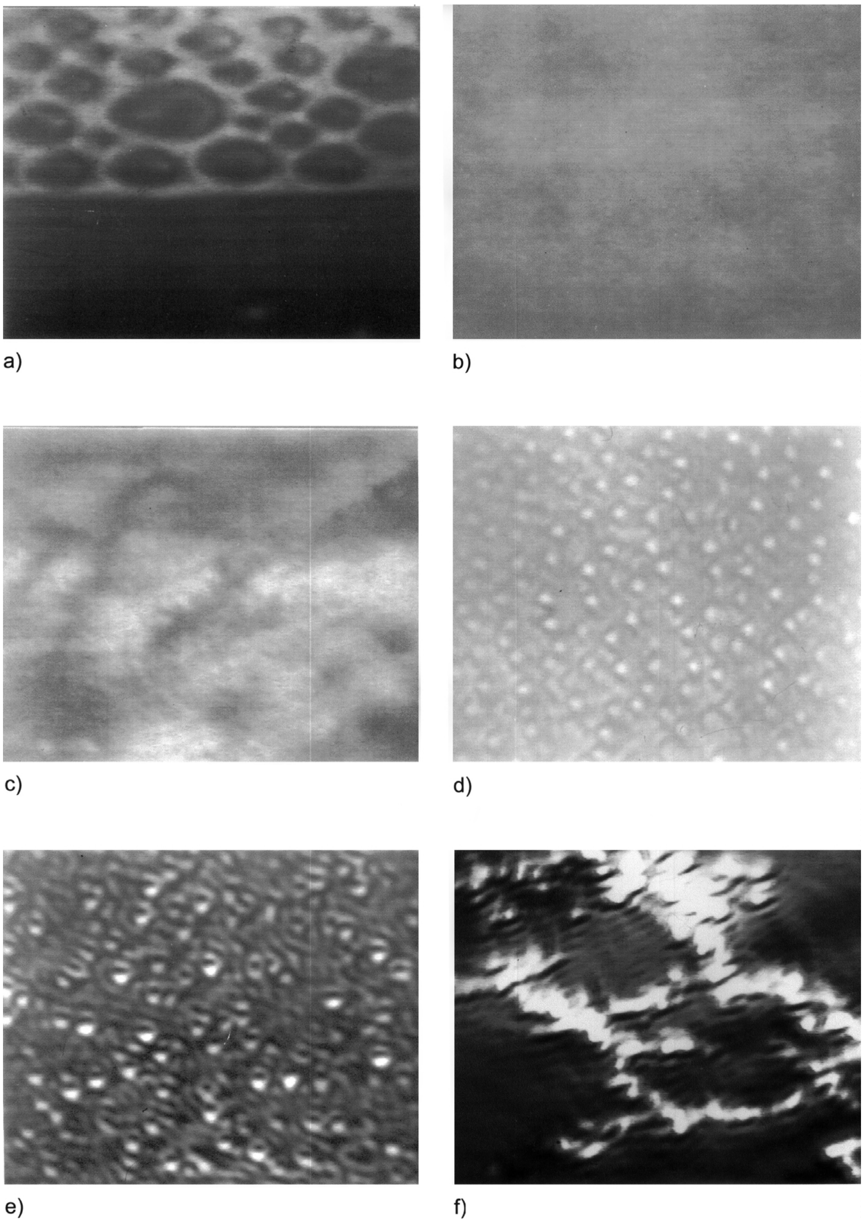

Fig. 5. Brewster angle microscope images of the **1**/8CB film formation and collapse during continuous compression (a – e). Aggregates of **1** after spreading pure dye chloroform solution at the air-water interface (f). The conditions of the films are indicated by the arrows and Roman letters in Figure 4. Dark areas correspond to the monolayer and light ones to multilayer structures. Images were taken without analyzer.

a big number of discs, close to each other, can be observed, and simultaneously a small number of brighter domains appears (Figure 5e). These most bright domains should be interpreted as the formation of the next interdigitated bilayer on top of the previous one, which was observed for the pure 8CB films at a corresponding trough area. At the area of about 0.1 nm^2 some of circular domains coalesce, making elongated structures. We want to emphasize that we did not detect any other form of the dye in the film at MF = 0.25. Our BAM setup allows us to control different spots across the trough width. We did not record any bright thick forms, which could be similar to the 3D associates presented in Fig. 5f for pure **1**. We also exclude the multilayers stacking below the air-water interface (as it was shown e.g. by Frey et al. [45] small protein crystals attached to the lipid bilayer are visible by BAM even if they are located below a lipid monolayer, and the difference in refractive index between the layers is lower than 0.05). This allows us to suppose that in our films we do not have the dye in form of slabs neither on the top of the **1**/8CB film facing the air nor at the bottom of the film, facing the water.

1/8CB film at MF = 0.25 on expansion

Images of the film observed upon continuous expansion, 10 min. after the end of the compression process, are presented in Figure 6. Each picture corresponds to the state of the film on the trough indicated by arrows and Roman letters with asterisk in the expansion isotherm shown in Figure 4. All the microphotographs present typical types of the film structure across the Langmuir trough. The description of the **1**/8CB film textures is compared with appropriate observations for pure 8CB. In our experiments, the pure 8CB film at the expansion process has the same structures as it was observed by Friedenberg et al. [14]. Starting from a maximally compressed film, the BAM images show separated disc-like domains. As the film expands to the wider area at the lower surface pressure, first the most bright domains quickly vanish and are replaced by disc domains, and than the distance between bilayer domains increases (Figure 6a). At continuous expansion, the bottom monolayer becomes perfectly homogenous. Next, the size of the domains decreases. The domains are distributed randomly on the trough area, even near the Teflon walls. When only small dots of vanishing domains remain, the film starts to shine, and fluctuations in intensity of the shadows with irregular shapes and without sharp borders appear, as it is shown in Figure 6b. Similar observations were made during compression almost in the same region of *A*. This takes place just before a fast decrease in the surface pressure when the film transfers to the extended liquid state. The fluctuating stables vanish at the same time as the rest of the domains disappears. From that state, upon further expansion when π steeply decreases, the film images are like those for an uniform monolayer which is shown in Figure 6c. We do not observe even small changes in the film intensity across the trough at this state of the Langmuir film. Moving the BAM head over the film we have recorded perfectly uniform images of the expanded liquid state, very similar to the images presented in Figure 5b. At the area near 0.5 nm^2 the monolayer suddenly brakes at many places, and a two-dimensional (2D) foam appears (Figure 6d). In this way the images of the **1**/8CB film below the collapse point look like those for a pure 8CB film.

1/8CB film at higher MF

At MF of **1** higher than 0.4, the BAM images show small non-regular thick patches just after spreading the chloroform solution of **1**/8CB at the interface. Sizes of these patches are almost the same in different places on the trough and are invariable under compression. Only the small number of the patches in the viewing field increases. Upon reduction of the available trough area the patches do not coalesce making bier structures, and the rest of the film behaves as for low MF. Still the homogenous film appears between the dye patches at first steep increase of the surface pressure. The lateral resolution of the BAM is only a few micrometers ($\approx 5\ \mu$m) and in that way we could not rule out, however, that some small crystallites or nanometer size clusters exist in this phase, even for very low MF. Required scale resolution can be reached by atom force microscopy (AFM) and similar techniques, but this is applicable to films on solid substrates only. For example, small grains of about 250 molecules of 8CB were observed in a monolayer transferred onto a mica substrate by using AFM, which reflects the scale of the orientation order in 8CB [12].

3.3. Spectral Analysis

Absorption spectra of a monolayer at the air-water interface were recorded at different stages of the film formation upon compression and expansion in the whole MF range investigated. Figure 7 presents representative spectra of **1** in a binary film with 8CB at a dye MF of to 0.1 before and after the collapse point, and for comparison the spectrum of **1** in ethanol ($c = 10^{-5}$M/l) which has dielectric properties similar to those of the air-water interface. There were no differences in the spectra of the Langmuir film for MF of **1** in 8CB up to 0.3. Moreover, there is a significant difference in the absorbance spectra of the film at the interface and those for **1** dissolved in ethanol. Even without Gaussian decomposition it is easy to designate that **1** has two peaks at about 580 nm and 620 nm, instead of one at 580 nm seen in ethanol. Moreover, a small but noticeble increase on short-wavelength side of the absorption spectrum is observed with increase of the surface pressure. This tendency is similar in the whole range of MF. We can suppose that **1** is in another form

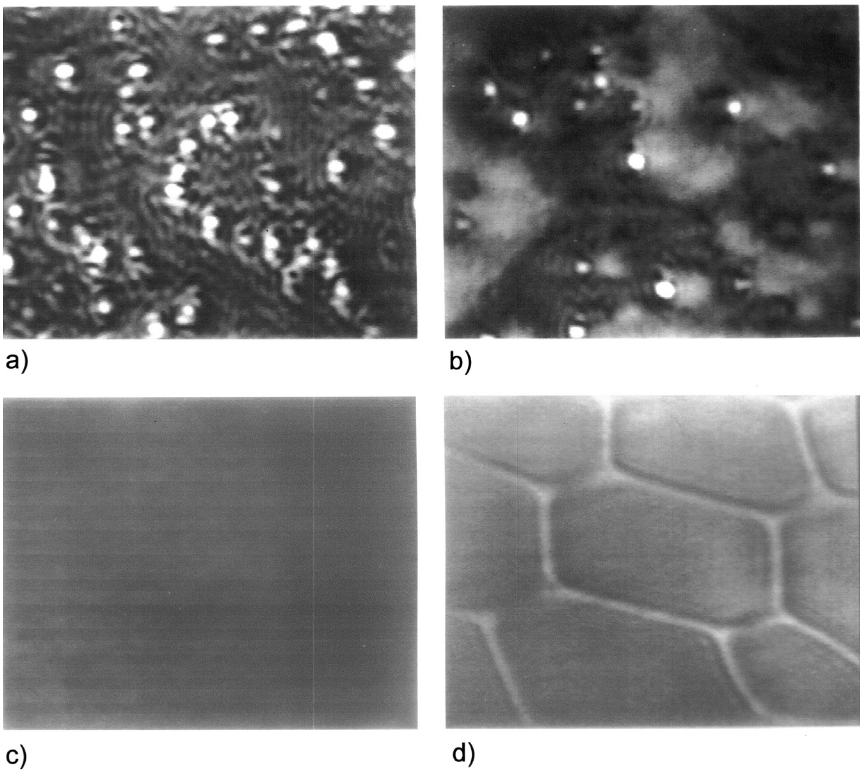

Fig. 6. Brewster angle microscope images of the film formation under expansion, 10 minutes relaxation time after compression. Dark areas represent monolayers; light areas correspond to the multilayer structures. The conditions of the films are indicated by the arrows and Roman letters with asterisk in Figure 4. Images were taken without analyzer.

in the low concentration ethanol solution than in the monolayer at the air-water interface. The same statement was made on the basis of the absorption spectra of **1**/8CB films deposited onto hydrophilic quartz substrates by the Langmuir-Blodgett method [26], where the films were investigated by polarized absorption spectroscopy at angular incidence. A strong increase at the short-wavelength side of s-polarized (perpendicular to the light incidence plane) absorption spectra was observed for films deposited at high surface pressure and high MF. We postulated that this effect can be explained in terms of the aggregate form of **1**.

4. Conclusions

Two-components monolayers at the air-water interface (Langmuir films) formed from the nonamphiphilic azo dye-liquid crystal 8CB mixtures were investigated. Langmuir films of pure 8CB are very well described in the literature, and we discuss the influence of the dichroic dye on the molecular organization in an ultrathin 8CB layer. The dye itself spread from the chloroform solution at the air-water interface does not produce a stable and compressible monolayer. However, when **1** is mixed with 8CB it is possible to obtain a compressible Langmuir film on the water surface, even at the MF of **1** greater than 0.5. The thermodynamic study reveals that addition of **1** to 8CB causes the increase of the packing density and the stability of the

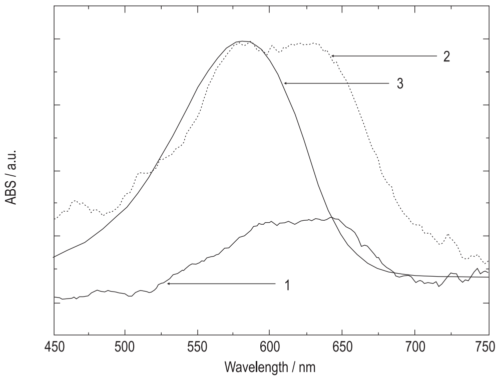

Fig. 7. Absorption spectra of **1** in mixed **1**/8CB Langmuir film at MF = 0.1 upon continuous compression: 1) π = 5.0 mN/m (before collapse), 2) π = 6.0 mN/m (after collapse) and 3) **1** in ethanol.

liquid crystal monolayer. Variation of the collapse surface pressure with the mixture composition as well as a small negative deviation of the average molecular area from the additivity rule indicate that in the **1**/8CB system the molecules of the two components are at least partially miscible. BAM images analysis confirms this statement. Moreover, on the basis of BAM observations we postulate that the phase separation takes place during a collapse process when, as we believe, an upper interdigitated bilayer is formed. This bilayer contains a much smaller number of **1** molecules than the monolayer. The *in situ* absorption spectra of **1** taken under compression reveal that the same aggregates of the dye exist in the Langmuir film even at a relatively low MF.

Finally, it should be notified that a definitive answer on the questions about the miscibility and aggregation of azo and other dichroic dyes in cyanobiphenyl liquid crystal films at an air-water interface would be only possible by vigorous experimental investigations with molecules well characterized from a spectroscopic point of view. Further studies using other methods, such as X-ray diffraction, AFM/STM, polarized absorption and fluorescence of the dye and cyanobiphenyl liquid crystals as well seem to be necessary to clarify and understanding the phase behaviour of binary mixtures the in monomolecular scale.

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