Alignment of liquid crystal and dichroic dye molecules in mixed Langmuir and Langmuir-Blodgett films

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Alignment of liquid crystal and dichroic dye molecules in mixed Langmuir and Langmuir–Blodgett films

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A study of dichroic dye–liquid crystal mixtures (guest–host systems) in monolayers formed at a gas–liquid interface (Langmuir films) and at a solid surface (Langmuir–Blodgett films) has been made. As a host 4-*n*-octyl-4′-cyanobiphenyl (8CB) or 4-*n*-pentyl-4″-cyano-*p*-terphenyl (5CT) were chosen, while three dichroic azo dyes with various molecular structures were used as guest species. The dyes were added to the liquid crystal matrices at a concentration corresponding to the whole range of molar fractions and the surface pressure–mean molecular area isotherms for Langmuir films were recorded. On the basis of the isotherms, conclusions about the molecular organization and the miscibility of the components in the ultrathin films were drawn. The Langmuir films were transferred onto the quartz plates at surface pressures below the collapse point. The polarized absorption spectra of the Langmuir–Blodgett films were recorded and information about the alignment and intermolecular interactions in the mixtures of the non-amphiphilic dichroic dyes and the liquid crystals with strongly polar terminal groups were obtained.

1. Introduction

As is known, liquid crystal molecules are able to orient dissolved dichroic dye molecules parallel to their long axes. This phenomenon was found by Heilmeier *et al.* [1, 2] and is called the 'guest–host' effect. It has found applications both in science and technology. Investigations of dichroic dye–liquid crystal mixtures are very useful in two important scientific areas: optical spectroscopy and the physics of liquid crystals. In the former area, such investigations give information concerning the electronic spectra of the dyes [3–9], and in the latter they enable a better understanding of the intermolecular forces in anisotropic media. In technology, the guest–host (GH) effect is utilized in the construction of electro-optical liquid crystal display (LCD) devices working in both passive and active modes [10–12]. GH LCDs in comparison with conventional twisted nematic (TN) LCDs have advantages such as wider viewing angle and higher image brightness.

The addition of a dye to a liquid crystalline host affects some parameters of the host, e.g. the refractive index [13], the dielectric constant [14], the orientational order [13, 15], the phase transition temperatures [13–15] and the molecular association [14, 16, 17]. The reason for these effects is the strong microscopic mutual interactions among the dye and liquid crystal molecules,

which, despite very intense studies of guest–host systems, continue to be the subject of speculation. Therefore, in order to have better insights into the intermolecular interactions in such systems, one of us has recently undertaken investigations of dichroic dye–liquid crystal mixtures in two-dimensional layers formed at the air–water interface (Langmuir films) and at solid surfaces (Langmuir–Blodgett films) [18, 19]. As a host, 4-octyl-4′-cyanobiphenyl (8CB) was chosen, while two dichroic dyes: a blue azo dye [18, 19] and a yellow naphthalene-benzimidazole derivative with excellent fluorescent properties [18] were used as guest species.

In this paper we have extended such investigations to dyes with various molecular sizes and shapes. We chose three azo dyes, which are known as compounds with high order parameters in liquid crystals [15, 20], giving them the potential to be applied in GH LCDs. As a host we used 8CB or 4-pentyl-4″-cyano-*p*-terphenyl (5CT). These two liquid crystals are able to form homogeneous Langmuir (L) and Langmuir–Blodgett (LB) films [21–25]. The dyes were added to the liquid crystal host at various concentrations. The main aim of our study was to check the miscibility of the components, to determine the influence of the molecular structure of the dye molecule on the molecular alignment in the L and LB films, and also to estimate the spectral properties of the dye–liquid crystal mixtures in two-dimensional layers.

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2. Experimental

The liquid crystals 4-octyl-4′-cyanobiphenyl (8CB) and 4-pentyl-4″-cyano-*p*-terphenyl (5CT) were purchased from E. Merck (Germany) and were used without further purification; their phase transition temperatures were in substantial agreement with the data given in the literature [26–28].

The molecular structures of the dyes used are presented in table 1. This table also gives the molecular mass, M, and the wavelength of the absorption maximum, λ_{max}, of the dyes in ethanol (the absorption spectra in the visible spectra region are shown in figure 1). All the dyes were synthesized and chromatographically purified in the Institute of Dyes at Łódź University of Technology, Poland.

Spectroscopic grade chloroform was used to prepare the spreading solutions. The dye–liquid crystal mixture solutions were made at a constant concentration in chloroform of 8CB or 5CT ($0.3\,\mathrm{g\,l^{-1}}$) and appropriate amounts of the dye were used to obtain molar fractions (*MF*) of the dye covering the whole range of possible concentrations (depending on the dye solubility). The guest–host mixtures were then spread from chloroform
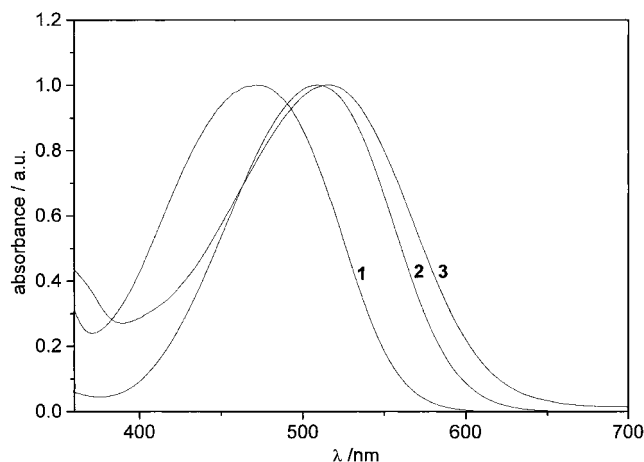
solutions onto the deionized water subphase and surface pressure–area isotherms were measured by a Whilhelmy plate balance in a Minitrough (KSV Instruments Ltd., Finland). Further experimental details about L film preparation are given elsewhere [24].

Polished quartz plates ($35 \times 10 \times 1\,\mathrm{mm^3}$) were used as solid substrates with a hydrophilic surface. The substrates were dipped and raised through the floating layer vertically at a speed of $5\,\mathrm{mm\,min^{-1}}$ at different surface pressures; the dipping stroke was 25 mm. Deposition of the film onto the quartz was successful only on raising the substrate. In the case of 8CB, repeated attempts to transfer a floating layer onto quartz slides failed. Therefore, for all substances investigated, only one dipping and one raising process were used. The transfer ratio TR, defined as the ratio of the actual decrease in the subphase area to the actual area on the substrate coated by the floating layer, was estimated to be between 1.0 and 1.3.

The absorption spectra of the LB films were recorded in the UV-Vis region by means of a spectrophotometer SPECORD M40 (Carl Zeiss Jena), equipped with Glan–Thomson polarizers and an angular sample holder. The measurements were performed in the geometry presented in figure 2.

Figure 1. Normalized absorption spectra of dyes **1** (1), **2** (2) and **3** (3) dissolved in ethanol.
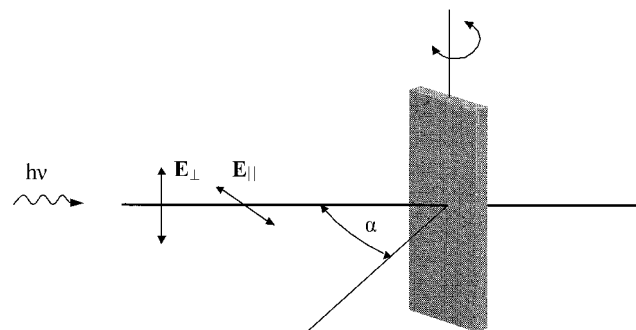
Figure 2. Geometry of the linear dichroism measurements. $\mathbf{E}_\parallel$ and $\mathbf{E}_\perp$ are the electric vectors of the light polarized parallel and perpendicular to the plane of incidence, respectively; α is the angle of incidence with respect to the substrate.

Table 1. Data for the azo dyes used.

Dye	Molecular structure	M/g	λ_{max}/nm
1		329	472
2		403	515
3		298	507

3. Results and discussion

3.1. *Langmuir films*

The dependences of the surface pressure π on the mean molecular area *Mma* (π–*Mma* isotherms) for the pure liquid crystals 8CB and 5CT in Langmuir films obtained in this study were in substantial agreement with those given in the literature [21–25].

After spreading solutions of the azo dyes at the air–water surface, we observed large patches of the dye on the water, and the surface pressure did not rise upon reduction of the trough area. Thus none of the azo dyes under investigations can produce a stable and compressible monolayer. However, when the dyes were mixed with 8CB and 5CT at appropriate concentrations, compression was possible and we obtained π–*Mma* isotherms. They were recorded for dyes **1**–**3** dissolved in 8CB or 5CT up to the concentration at which, just after spreading, microcrystallites in the chloroform solution were not visible with the naked eye. The isotherms are presented in figures 3–5 and 7–9.

3.1.1. *Langmuir films of dye/8CB mixtures*

Dye **1** was the most soluble and for **1**/8CB mixtures the π–*Mma* isotherms were recorded up to a *MF* of **1** equal to 0.8 (figure 3). It is seen, that with increase in *MF* the increase of π begins at smaller and smaller *Mma* values. The plateau region, very characteristic for pure 8CB [23–25], becomes narrower and already at $MF = 0.4$ disappears. At $MF \geqslant 0.4$ a rapid increase of π is observed. The collapse point for two concentrations, corresponding to *MF* equal to 0.4 and 0.5 occurs at very similar values of *Mma* ($\approx 23\,\text{Å}^2$), and at higher concentrations it appears at $Mma < 15\,\text{Å}^2$. This latter value
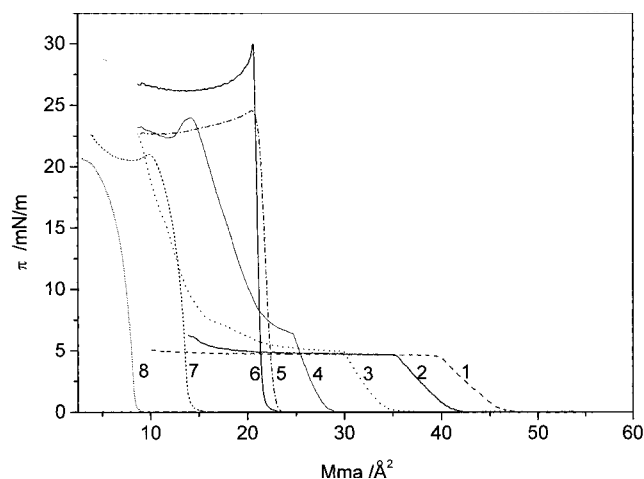

Figure 4. Surface pressure–mean molecular area isotherms of Langmuir films of pure 8CB (1) and of binary mixtures of dye **2**/8CB with *MF* of **2** of 0.1 (2), 0.2 (3), 0.3 (4), 0.4 (5), 0.5 (6) and 0.6 (7).
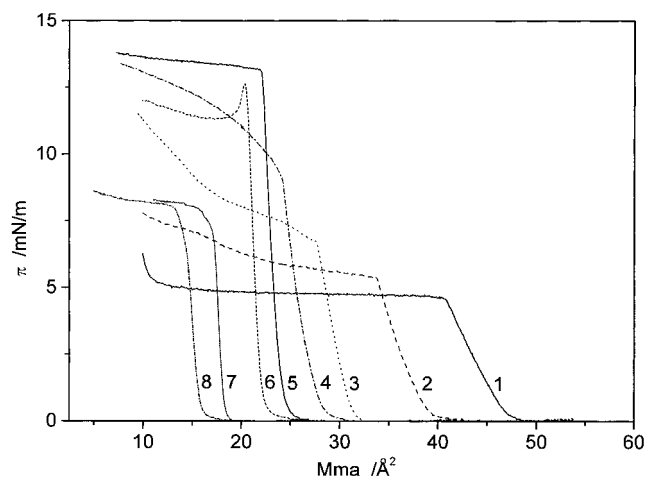
Figure 5. Surface pressure–mean molecular area isotherms of Langmuir films of pure 8CB (1) and of binary mixtures of dye **3**/8CB with *MF* of **3** of 0.1 (2), 0.2 (3), 0.3 (4), 0.4 (5), 0.5 (6), 0.6 (7) and 0.7 (8).

is too small for even the most dense packing of the molecules in a monolayer, which suggests the creation of three-dimensional (3D) groups. It seems that up to some limiting concentration of **1** in 8CB ($MF \approx 0.5$), the presence of the dye gives a greater stability to the liquid crystalline host, as is confirmed by the increase of the isotherm slope with increase in *MF*. When the content of **1** is higher than that of 8CB, the liquid crystal cannot play the role of host. While it is true that 8CB molecules can be further aligned on the water (compression is possible), the molecules of **1** create irregular 3D groups and therefore the average area per molecule grows smaller.

Figure 3. Surface pressure–mean molecular area isotherms of Langmuir films of pure 8CB (1) and of binary mixtures of dye **1**/8CB with *MF* of **1** of 0.1 (2), 0.2 (3), 0.3 (4), 0.4 (5), 0.5 (6), 0.6 (7) and 0.8 (8).
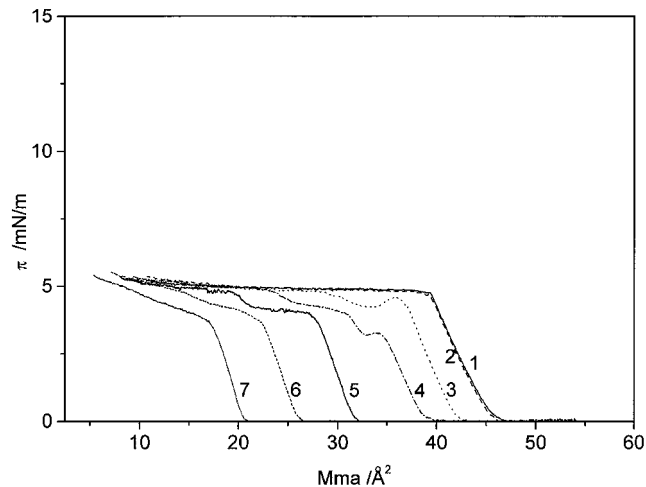
The mixtures of dye **2** with 8CB behave differently from those of **1** with 8CB. At a relatively small concentration ($MF = 0.1$), the isotherm has an identical shape to that for pure 8CB (figure 4), indicating that the dye and liquid crystal molecules are aligned in the same way (tilted with respect to the water surface). When the concentration of the dye increases, the collapse point appears at smaller and smaller Mma values, and the shape of the isotherm becomes irregular. Simultaneously, coloured shadows are observed on the water surface. This would suggest that **2** is no longer soluble in 8CB.

In the case of the isotherms for dye **3**/8CB mixtures (figure 5), a systematic decrease of Mma and increase of the surface pressure at the collapse point (π_C) up to $MF = 0.4$ is observed. Moreover, the slope of the isotherm increases, similarly to that in the case of **1**/8CB mixtures. This means that dye **3** is also able to make the 8CB at the air–water surface more stable. At MF greater than 0.5 a monolayer cannot be formed, although compression is still possible.

In order to establish whether in the two-component Langmuir film miscibility or phase separation occurs, the mean molecular area as a function of the monolayer composition should be analysed. If the components are not miscible, the area occupied by the combined film will be the sum of the area of the separate films and the mixed monolayers will obey the equation [29]:

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

where A_{12} is the average molecular area in the two-component film, x_1 and x_2 are the molar fractions of the components, and A_1 and A_2 are the single component Mma values at the same π.

The excess area per molecule $A_E = A_{12} - (x_1 A_1 + x_2 A_2)$ for dye/8CB mixtures in Langmuir films at a surface pressure smaller than π_C is plotted in figure 6 as a function of the dye concentration. It is seen that the additivity rule is not followed at any MF investigated. Indeed, we observed small but noticeable deviations (predominantly negative) from the additivity rule for **1**/8CB and **3**/8CB mixtures and a more distinct positive deviation for **2**/8CB mixtures. The negative deviation means a contraction of the two-component films due to the attractive interactions among the dye and liquid crystal molecules [29, 30]. This fact, together with the behaviour of π_C versus mixture composition, gives evidence, that the molecules of **1** and **3** are at least partially miscible with 8CB. In contrast, the mixture of **2**/8CB demonstrate rather that phase separation occurs. Although the additivity rule is not fulfilled and the positive value of A_E indicates the existence of repulsive intermolecular interactions, the constant value of π_C suggests that the molecules of **2** are not miscible with 8CB.
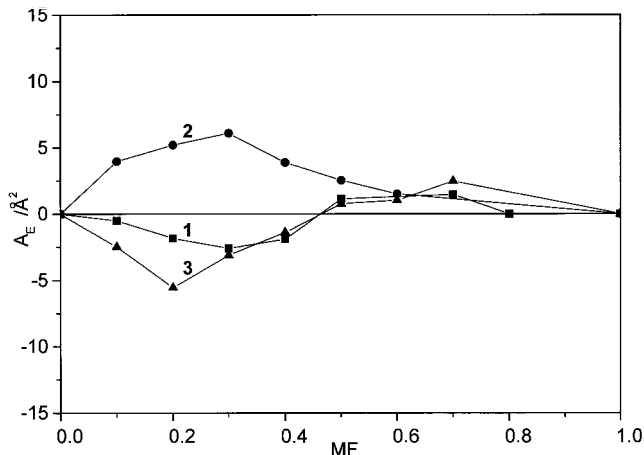

Figure 6.   Plot of the deviation of the mean molecular area per molecule (A_E) for the dye/8CB Langmuir films as a function of MF of dye at $\pi = 4$ mN m^{-1} (**1**), 2.5 mN m^{-1} (**2**) and 4 mN m^{-1} (**3**).

3.1.2. *Langmuir films of dye/5CT mixtures*

All the dyes investigated were of good solubility, at least up to $MF = 0.5$, in the liquid crystal 5CT.

For dye **1**/5CT mixtures (figure 7) up to $MF = 0.5$, the value of π_C increases with increase in the dye concentration, although Mma at the collapse point changes irregularly. It seems, however, that the addition of **1** to 5CT improves somewhat the molecular packing of the liquid crystal. At higher concentrations ($MF = 0.8$ and 0.9), similarly to the case for **1**/8CB mixtures, compression is still possible, but the occurrence of the increase in π at very small values of Mma indicates that 3D objects or groups are formed.

In the case of dye **2**/5CT mixtures (figure 8), the π_C value increases systematically, but up to $MF = 0.2$ the
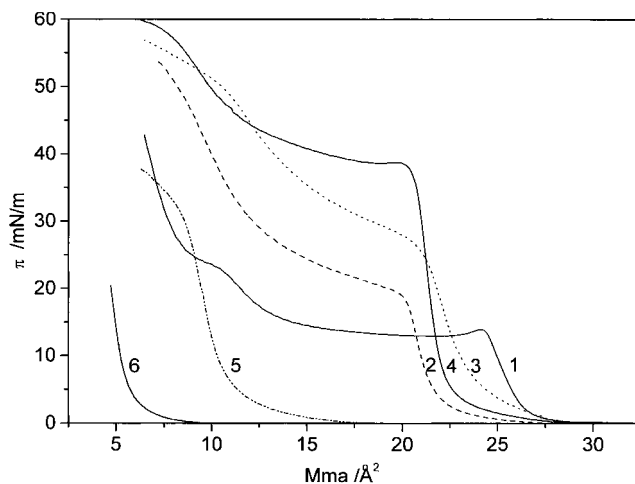

Figure 7.   Surface pressure–mean molecular area isotherms of Langmuir films of pure 5CT (1) and of binary mixtures of dye **1**/5CT with MF of **1** of 0.1 (2), 0.2 (3), 0.5 (4), 0.8 (5) and 0.9 (6).
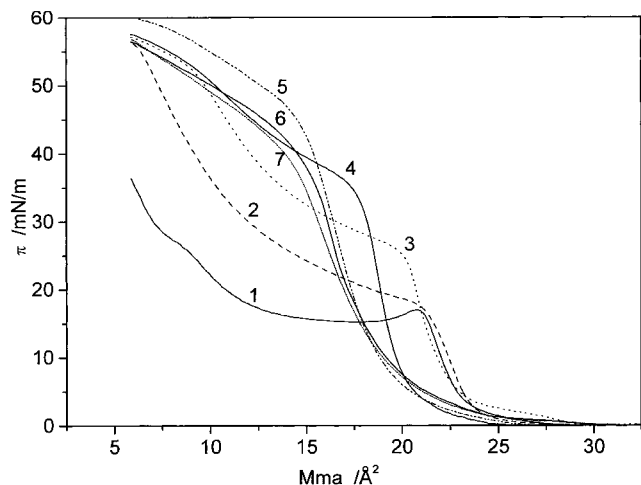
Figure 8. Surface pressure–mean molecular area isotherms of Langmuir films of pure 5CT (1) and of binary mixtures of dye **2**/5CT with *MF* of **2** of 0.1 (2), 0.2 (3), 0.3 (4), 0.5 (5), 0.7 (6) and 0.8 (7).

collapse point appears at similar *Mma* values to that for pure 5CT. The slope of the isotherms does not change, which means a lack of any influence of the dye on the stability of the Langmuir film of 5CT molecules. At higher concentrations (*MF* ⩾ 0.3), the *Mma* at collapse point grows smaller, but the slope of the isotherm would indicate that the stability of the film is not improved. From *MF* = 0.5, the monolayer seems to be no longer homogeneous (3D objects or groups can be created).

The isotherms of dye **3**/5CT mixtures have another characteristic (figure 9). π_c for all the mixtures is smaller than that for pure 5CT, but it remains constant. The decrease of π_c may be connected with an incompatibility in the molecular lengths of the components. At concen-
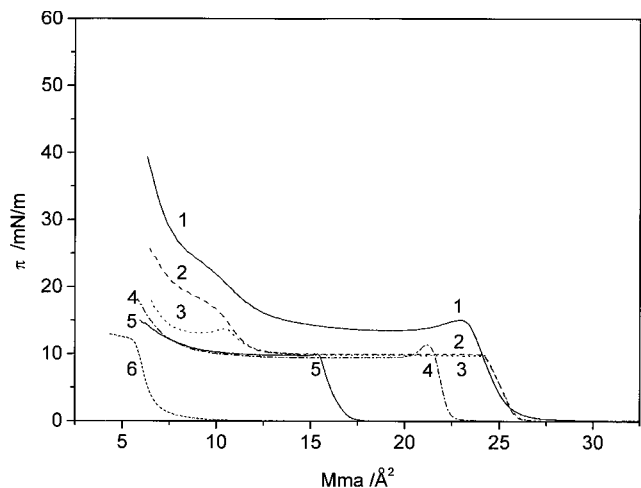
trations smaller than 0.5, except for the monolayer, 3D groups must be formed.

Figure 10 presents the concentration dependence of the excess area per molecule A_E for dye/5CT mixtures in Langmuir films at a surface pressure below the collapse point. The results reveal that in all cases repulsive interactions among the dye and 5CT molecules dominate. However, only for dye **1**/5CT and dye **2**/5CT mixtures one can assume that the two components have good miscibility because of the change of π_c. In the case of the dye **3**/5CT mixtures, π_c is constant, independent of the mixture composition and therefore one should expect phase separation of the components.

3.2. *Langmuir–Blodgett films*

The Langmuir–Blodgett films from the dye/liquid crystal mixtures were deposited onto quartz slides at a surface pressure below the collapse point, meaning here when the Langmuir film on the water surface formed a homogeneous monolayer.

The most complex investigations were performed for **1**/8CB mixtures, they were made for various *MF* of dye **1** in 8CB. Figure 11 shows two polarized components of the absorption spectra for **1**/8CB at *MF* = 0.5 deposited onto quartz at $\pi = 12$ mN m^{-1}, as an example. In the spectra two absorption bands can be distinctly distinguished: the band in the UV region with a maximum at about 280 nm, which is connected with the absorption transition moment of 8CB, and the band with a maximum at about 450 nm, related to the transition moment of **1** giving the absorption in the Vis region. The values of the positions of the absorption maxima are given for the parallel component of the spectrum. The positions

Figure 9. Surface pressure–mean molecular area isotherms of Langmuir films of pure 5CT (1) and of binary mixtures of dye **3**/5CT with *MF* of **3** of 0.1 (2), 0.2 (3), 0.3 (4), 0.6 (5) and 0.8 (6).
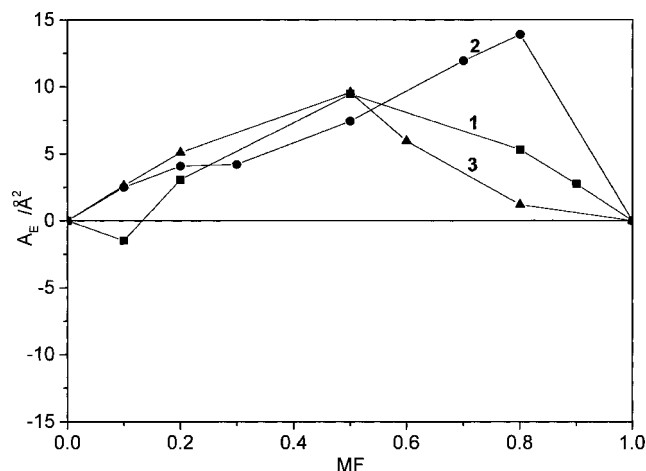

Figure 10. Plot of the deviation of the mean molecular area per molecule (A_E) for the dye/5CT Langmuir films as a function of *MF* of dye at $\pi = 10$ mN m^{-1} (**1**), 13 mN m^{-1} (**2**) and 8 mN m^{-1} (**3**).
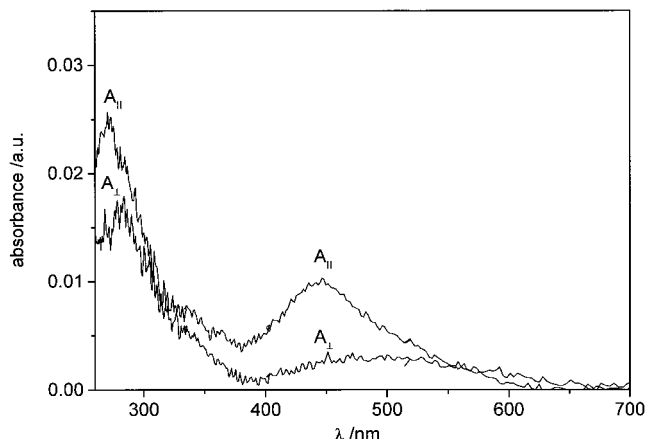
Figure 11. Absorption spectra for parallel ($A_\parallel$) and perpendicularly polarized light ($A_\perp$) for the dye **1**/8CB Langmuir–Blodgett film at $MF = 0.5$.

of the maxima for the perpendicular component, both for 8CB and the dye, are shifted towards longer wavelengths. This effect, although difficult to explain, was also observed previously for other dyes dissolved in 8CB [18]. It is too large to be connected only with varying values of the refractive index for the two polarized components; other factors have to play some role. Nevertheless, comparing the spectra of **1** with 8CB in the LB film with that in ethanol (figure 1), it is seen, that the absorption maximum of the parallel component is distinctly shifted towards shorter wavelengths. Similarly, a hyposochromic shift for another compound in the LB film was found by Sakuhara *et al.* [21].

On the basis of the polarized absorption spectra, the linear dichroisms (*LD*) for both absorption bands were determined. Following N′soukpoé-Kossi *et al.* [31] *LD* was defined as:

$$LD = \frac{A_\parallel - A_\perp}{A_\parallel + A_\perp} \qquad (2)$$

where $A_\parallel$ and $A_\perp$ are the absorbance values at the maxima for the light polarized parallel and perpendicularly to the plane of incidence, respectively (see figure 2).

LD can also be connected with the angle of incidence α in the following way [31]:

$$(LD)_\alpha = \frac{(2 - \tan^2 \beta)}{2 + \tan^2 \beta(1 + \cos^2 \alpha)/\sin^2 \alpha} \qquad (3)$$

where β is the angle between the transition dipole moment vector and the normal to the plane of the monolayer. Here, we assume that the molecules both of the liquid crystal and the dye are distributed in the cone, uniformly on the slide surface, with their transition

moment direction tilted at an angle β with respect to the normal.

The values of the angle β for the 8CB (β_H) and **1** (β_G) molecules obtained in this study are listed in table 2. These are the mean values of at least three results obtained with independent preparations.

We assume that the transition moment direction of elongated molecules, like those of the liquid crystals and the dyes investigated, is parallel (or almost parallel) to the molecular long axis; then, on the basis of the results given in table 2 we are able to draw conclusions about the alignment of the molecules with respect to the quartz slides.

For pure 8CB, it was previously found [18], that the angle β_H between the molecular long axis and the normal to the slide surface in an LB film is about 60°, similar to the angle in the L film, measured with respect to the normal to the water surface [32]. The results from table 2 show that at relatively small concentrations of **1** ($MF \leqslant 0.3$) the angle β_H does not change. Meanwhile, β_G is $\approx 13°$, which means an almost vertical alignment of the dye **1** molecules. With increase in the dye concentration up to $MF = 0.4$, both β_H and β_G grow smaller, indicating an increase in the molecular packing density. It seems, that dye **1** 'stiffens' the 8CB molecules and improves their stability. A similar effect was observed for this dye dissolved in 8CB and other liquid crystals in bulk [13, 15, 33, 34]: dye **1** was able to improve the molecular order of the liquid crystalline hosts. When the contents of **1** and 8CB in the LB films are the same, the values of β_H and β_G become close. However, at $MF = 0.6$, we observed a return of β_H to the value of $\approx 60°$ and simultaneously an increase of β_G. This is probably because at such a concentration we no longer have a homogeneous monolayer in the L film (see §3.1.1.). Therefore, in the LB film the dye molecules are unable to maintain their alignment at the small angle with respect to the quartz slide normal and they incline. The molecules of 8CB align independently of those of **1**.

Only for **1**/8CB mixtures was it possible to obtain an LB film with the transfer ratio $TR = 1.0$. For the other mixtures, in the dipping process movement of the trough barriers was always observed. As a result TR was greater than 1.0. This means that we are not sure that we really

Table 2.   Tilt angles of 8CB (β_H) and dye **1** (β_G) molecules with respect to the normal to the quartz slide in the LB film.

MF	π/mN m^{-1}	β_H/deg	β_G/deg
0.3	4	59.19	13.04
0.4	7	49.56	11.73
0.5	12	45.99	33.87
0.6	12	57.87	42.92

have a monolayer in the LB film. It is possible that the monolayer occurs, but it has another packing from than that in the L film. Therefore, the data gathered in table 3 should be considered carefully and rather as indicatory results. In this table there are no data for the mixtures of both 8CB and 5CT with dye **2**, because in these cases the attempts at deposition of the floating layer onto the quartz failed.

Figure 12 shows the polarized components of the absorption spectra for **1** in 5CT ($MF = 0.5$) deposited onto a quartz slide at $\pi = 15 \text{ mN m}^{-1}$. In the spectra, similarly to the case for 8CB, two absorption bands are seen: a band in the UV region with the maximum at about 300 nm, assigned to the transition moment of 5CT, and a band in the Vis region connected with the absorption of **1**. Here the positions of the maxima for both components are almost the same. However, similarly to the case for dye/8CB mixtures, the hyposochromic shift with respect to the absorption band positions in ethanol is observed. It seems, that this effect is characteristic for monolayers formed from the liquid crystals used.

From the π–*Mma* isotherm for pure 5CT (figures 5–7), it follows that the molecules of this liquid crystal create

only a very small angle with the normal to the water surface in the L film. Sakuhara *et al.* [21] also found that in LB films the terphenyl group of 5CT is oriented nearly perpendicular to the film plane. However, from the results presented in table 3, it follows that in LB films of **1**/5CT, both the dye molecules and those of the liquid crystal are tilted strongly with respect to the quartz slide surface. Similar observations can be made for the dye **3**/5CT mixture, although here both β_H and β_G are slightly greater than in the case of dye **1**/5CT.

The data for dye **3**/8CB indicate that the dye molecules create an angle greater than 50° with the normal to the film plane and do not affect significantly the alignment of the 8CB molecules ($\beta_H \approx 60°$). Moreover, from the results presented in table 3 it follows that the angle β is essentially independent of the surface pressure at which the deposition onto the quartz slide takes place.

4. Conclusions

Two-component Langmuir (L) films at the air–water interface as well as Langmuir–Blodgett (LB) films on a quartz slide formed from non-amphiphilic azo dye–liquid crystal mixtures were investigated. None of the azo dyes used spreads at the air–water interface to produce a stable and compressible monolayer. However, when the dyes are mixed with 8CB or 5CT it is possible to obtain compressible L films on the water surface. From the results obtained in the investigations, the following conclusions were drawn.

(1) On the basis of the dependence of the surface pressure (π) on the mean molecular area (*Mma*) it was ascertained that the azo dyes, even when without a polar terminal group, at the appropriate concentration influence strongly the alignment and the packing of the liquid crystal molecules at the air–water interface. Characteristic dye concentrations are $MF = 0.4–0.5$. At such contents of the dye, it is able to 'stiffen' the liquid crystal molecules, as seen especially for 8CB. This liquid crystal is tilted at a very large angle ($\approx 60°$) with respect to the normal to the water surface and is therefore unstable. The addition of the dye increases its packing density and simultaneously its stability.

(2) Variation of the surface pressure at the collapse point (π_C) with the mixture composition, and deviation from the addivity rule for the average molecular area, indicate that the dye–liquid crystal system investigated are at least partially miscible. In most cases a positive value of the excess area (A_E) is observed, which suggests the predominance of repulsive interactions among molecules.

Table 3. Tilt angles of the liquid crystal (β_H) and dye (β_G) molecules with respect to the normal to the quartz slide in the LB film.

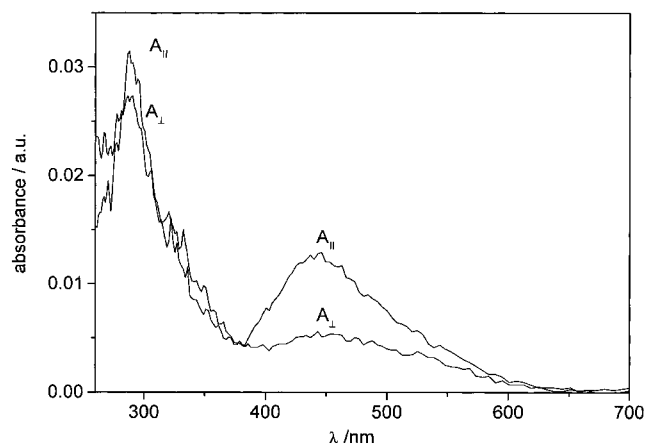| Liquid crystal	Dye	$\pi/\text{mN m}^{-1}$	*MF*	β_H/deg	β_G/deg
5CT	**1**	15	0.5	50.75	39.98
5CT	**1**	25	0.5	50.35	42.45
5CT	**3**	7	0.5	57.37	53.27
8CB	**3**	4	0.3	57.46	53.27
8CB	**3**	9	0.5	62.09	51.93

Figure 12. Absorption spectra for parallel ($A_\parallel$) and perpendicularly polarized light ($A_\perp$) for the dye **1**/5CT Langmuir–Blodgett film at $MF = 0.5$.

(3) Reliable LB films were obtained only for **1**/8CB mixtures. From the spectral investigations it follows that similarly to the case for L films, the dye **1** at $MF = 0.4$–0.5 'stiffens' the liquid crystal molecules. The unexpected shift of the perpendicular component of the absorption spectra both for dye and 8CB with respect to the parallel component remains, however, to be clarified.

(4) Other dye–liquid crystal mixtures give LB films with transfer ratios (TR) greater than 1.0. The results of the absorption measurements obtained for these mixtures in LB films suggest that the molecules of 5CT are tilted with respect to the surface normal at a significantly larger angle than in L films. It is however possible, that in this case, because $TR > 1.0$, instead of a monolayer, an irregular multilayer is formed on the quartz slide. In order to solve which possibility occurs, it is necessary to make comparative measurements of the absorption of the LB film on quartz and *in situ*, and this means directly on the water (for the L film).

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