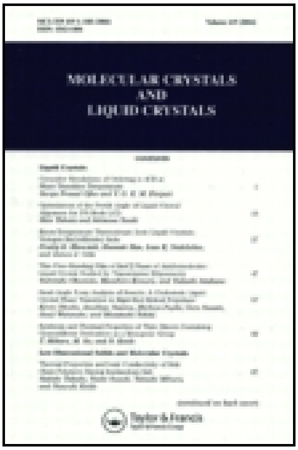

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Intermolecular Interactions in Langmuir and Langmuir-Blodgett Films of Azo Dye/Liquid Crystal Mixtures

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Intermolecular Interactions in Langmuir and Langmuir-Blodgett Films of Azo Dye/Liquid Crystal Mixtures

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Binary mixtures of the dichroic azo dye with the liquid crystal as Langmuir and Langmuir-Blodgett films have been studied. Four azo dyes with various molecular structure and liquid crystal materials: 4-octyl-4′-cyanobiphenyl (8CB) and trans-4-octyl(4′-cyanophenyl)-cyclohexane (PCH8) were used. The surface pressure as a function of the mean molecular area for Langmuir films were measured and the organization of molecules at the air-water interface was determined. Absorption spectra in situ for Langmuir films and absorption spectra by using both natural and linearly polarized light for Langmuir-Blodgett films were recorded and information about intermolecular interactions in the mixtures of the nonamphiphilic dye and the liquid crystal with polar terminal group was obtained. Conclusions about the formation of self-aggregates between dye molecules have been drawn.

Keywords: azo dye; electronic absorption; Langmuir-Blodgett film; Langmuir film; liquid crystal

1. INTRODUCTION

In guest-host liquid crystal displays (GH LCDs) a liquid crystalline matrix is doped with a dye having good dichroic properties. The parameters of GH LCD depend on these properties as well as on interactions between guest and host molecules [1]. Very simple systems in which intermolecular interactions can be easily determined are

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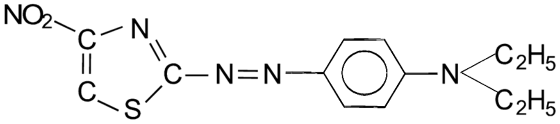
liquid-gas or solid-gas interfaces that give possibility to study matter in the form of layers one molecule thick [2–4]. Such systems are especially suited for studies of molecular aggregates formation [5] because they enable to control easily the molecular orientation and distances between molecules. Moreover, one can obtain information about the molecular orientation in the first few layers at the surface, and how the interfacial interactions affect the macroscopic molecular alignment in the bulk.

We have undertaken the study of binary mixtures consisted of a liquid crystal and a dichroic dye at air-water (Langmuir films) and air-solid substrate (Langmuir-Blodgett films) interfaces. In this paper we present results of investigations of Langmuir (L) and Langmuir-Blodgett (LB) films formed of 4-octyl-4′-cyanobiphenyl (8CB) or *trans*-4-octyl(4′-cyanophenyl)cyclohexane (PCH8) doped with azo dyes having high order parameter in liquid crystalline matrices. Both liquid crystals are known as substances which are able to form stable L and LB films due to the presence of the strongly polar −CN terminal group acting as the hydrophilic part of the molecule [6–9].

2. MATERIALS AND METHODS

The following dyes were used:

1



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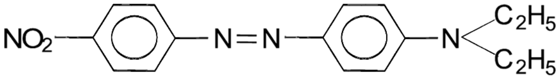

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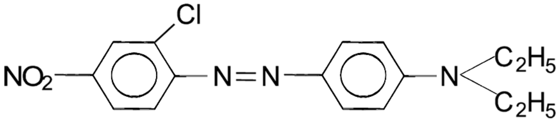

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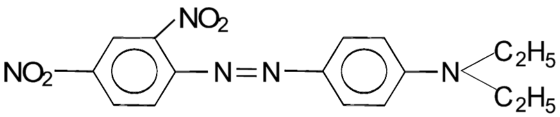

All the dyes were synthesized and chromatographically purified in Institute of Dyes at Łódź University of Technology, Poland. The liquid crystals 4-octyl-4′-cyanobiphenyl (8CB) and *trans*-4-octyl(4′-cyanophenyl)-cyclohexane (PCH8) were purchased from Prof. R. Dąbrowski

Laboratory at the Military Academy of Technology, Warsaw (Poland) and were used without further purification.

The solutions of dye/liquid crystal mixtures in spectroscopic grade chloroform were made at a constant concentration of 8CB or PCH8 (0.3 g/l) and appropriate amounts of the dye, in order to obtain the molar fraction (MF) of the dye in the whole range of possible concentrations. Each of the prepared solutions was then spread onto the deionized water subphase to form a monolayer and was equilibrated for about 15 minutes to allow the chloroform to evaporate. The surface pressure (π) as a function of the average molecular area (A) was measured by a Wilhelmy plate balance in a commercial Minitrough 2 Langmuir-Blodgett system (KSV Instruments Ltd., Finland). The experiments were performed at a subphase temperature of $(20.5 \pm 0.5)^{\circ}$C. Further experimental details about Langmuir film preparation are given elsewhere [10]. Absorption spectra of spread monolayers on the water surface were recorded *in situ* by means of a spectrophotometer CARY 400 equipped with fiber optic accessory supplied by Varian.

Polished quartz plates ($35 \times 10 \times 1\text{mm}^3$) were used as the solid substrates with a hydrophilic surface for LB film fabrication. The substrates were dipped and raised through the floating layer vertically at a speed of 5 mm/min at a constant surface pressure. The dipping stroke was 25 mm. The depositions of the film onto the quartz was successful only at raising the substrate. Repeated attempts to transfer a floating layer onto quartz slides failed. Therefore, only one dipping and one raising were made. 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 about 1.0. The absorption spectra of LB films were recorded in UV-VIS region using both, natural and linearly polarized light by means of a spectrophotometer CARY 400, equipped with an angular sample holder. Glan-Thomson polarizers were used to obtain polarized incidence light.

3. RESULTS AND DISCUSSION

3.1. Surface Pressure-Area Isotherms

After spreading solutions of the azo dyes at the water surface in the trough, we found that during compression process the dyes produce monolayers which were unable to offer any significant resistance to barriers approach: the molecules were expelled and the bulk phase was observed to form. This means that none of the azo dyes under investigations cannot produce stable and compressible monolayer.

However, when the dyes were mixed with 8CB or PCH8 at appropriate concentrations the compression was possible and we obtained π–A isotherms. They were recorded for the dyes dissolved in 8CB or PCH8 up to the concentration at which, just after spreading, microcrystallites in the chloroform solution were not visible with the naked eye. The isotherms of L films of pure liquid crystals and **1**/liquid crystal mixtures at three MF of the dye are presented in Figure 1. The increase in π begins at the area equal to A_0, which is the first edge of the phase transition – at this moment the monolayer begins to form. Table 1 contains the values of A_0 for all the mixtures investigated. In this table the values of the collapse area (A_C) and the collapse pressure (π) are

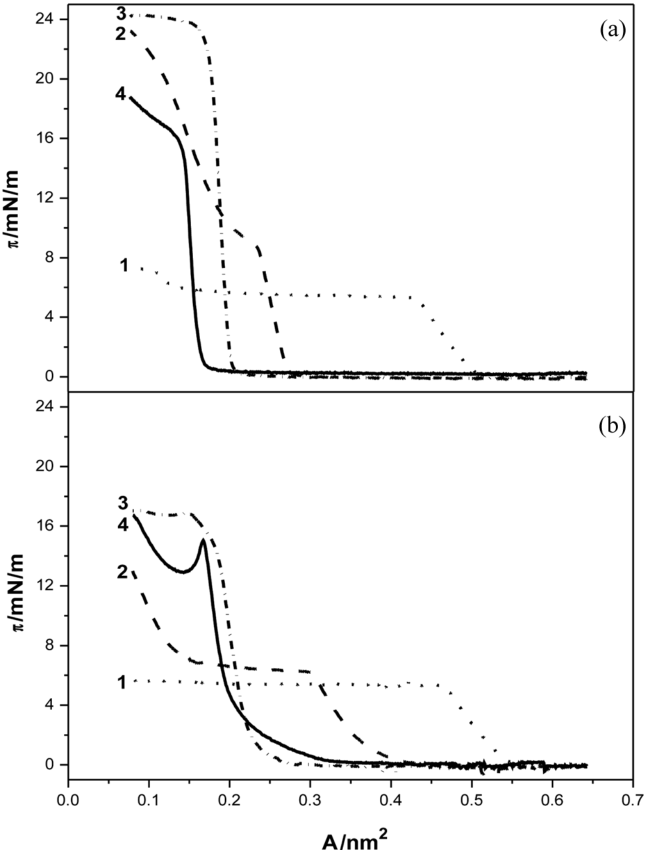

FIGURE 1 Surface pressure-mean molecular area isotherms of Langmuir films of pure liquid crystal (1) and **1**/liquid crystal mixtures with MF of a dye of 0.2 (2), 0.4 (3) and 0.5 (4) for: a) **1**/8CB and b) **1**/PCH8 mixtures.

TABLE 1 Characteristic Data of π–A Isotherm for Langmuir Films of Azo Dye/Liquid Crystal Mixtures

Mixture	MF of dye	A_0/nm^2	A_C/nm^2	$\pi_C/mN \cdot m^{-1}$
8CB	–	0.51	0.41	5.0
1/8CB	0.2	0.29	0.23	8.7
	0.4	0.22	0.16	23.0
	0.5	0.21	0.14	15.5
2/8CB	0.2	0.35	0.30	7.2
	0.4	0.28	0.24	16.4
	0.5	0.30	0.28	12.3
3/8CB	0.2	0.27	0.23	6.9
	0.4	0.26	0.17	25.5
	0.5	0.28	0.18	19.4
4/8CB	0.2	0.31	0.26	6.7
	0.4	0.25	0.20	6.4
	0.5	0.23	0.18	6.0
PCH8	–	0.55	0.47	5.4
1/PCH8	0.2	0.43	0.30	6.2
	0.4	0.28	0.18	15.3
	0.5	0.34	0.17	15.0

also given. The collapse point is recognized as the point in the isotherm where the ratio $\partial\pi/\partial A$ begins to decrease due to the next phase transition. It is seen that azo dyes at the appropriate concentration influences strongly the alignment and the packing of the liquid crystal molecules at the air-water interface. For the most dyes characteristic dye concentration is MF = 0.4. At such content of the dye, it is able to 'stiffen' the liquid crystal molecules. The molecules of both 8CB and PCH8 are tilted at a very large angle (≈60° [9]) with respect to the normal to the water surface and L films formed of them are therefore unstable. The addition of the dye increases the packing density of liquid crystal molecules and simultaneously the stability of the film. This effect depends in some extent on the kind of the liquid crystal (compare results in Figs. 1a and 1b).

The miscibility of the two components of the L film can be determined from the shape of π–A isotherms for various MFs on the basis of the surface phase rule and the excess criterion [11]. From Table 1 follows that π_C values for the most binary mixtures investigated vary with MF, which means the good miscibility of both components. The same conclusion can be drawn from the average area per molecule at a constant surface pressure: the values of A show small negative deviations from the additivity rule indicating the attractive interactions. Small positive deviation due to repulsive interactions is observed only for dyes **1** and **2** at MF = 0.5. The exception is **3**/8CB mixture. Although the additivity rule is not fulfilled and negative deviation for all MFs indicates the attractive interactions, π_C remains constant. Thus, for this case immiscibility or at least partial miscibility of dye and liquid crystal molecules can be postulated.

3.2. Electronic Absorption Spectra

Absorption spectra of a monolayer at the air-water interface of all dye/liquid crystal mixtures were recorded *in situ* at different stages of the films formation in the whole MF range investigated. Figure 2 shows representative spectra of **1**/8CB mixture for MF = 0.1 before and after the collapse point. All the mixtures were next transferred from the floating monolayer onto quartz slides at the surface pressure corresponding to the value of π before the collapse point at the π-A isotherm. Figure 3 presents longwavelengths absorption spectra of the dye/liquid crystal mixtures in LB films and for comparison, dissolved in ethanol, at the concentration of 10^{-5} mol/dm^3. MF of dyes **1**, **2** and **4** in LB films presented in Figure 3 is 0.5, and for dye **3** is 0.3. At higher MFs of the latter dye it was not possible to obtain LB films with reliable transfer ratio. Figure 4 shows absorption spectra of **1** mixed with 8CB (Fig. 4a) and PCH8 (Fig. 4b) at various MFs. A significant

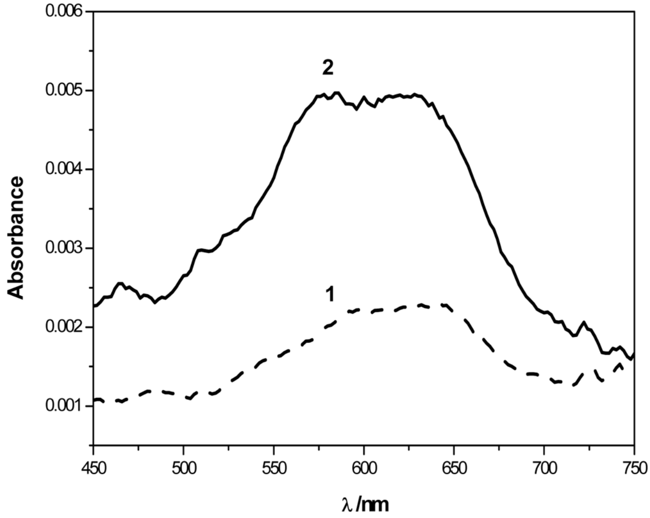

FIGURE 2 Absorption spectra *in situ* of Langmuir film of **1**/8CB mixture (MF = 0.1): before collapse point at $\pi = 5.0\,\mathrm{mN/m}$ (1) and after collapse point at $\pi = 6.0\,\mathrm{mN/m}$ (2).

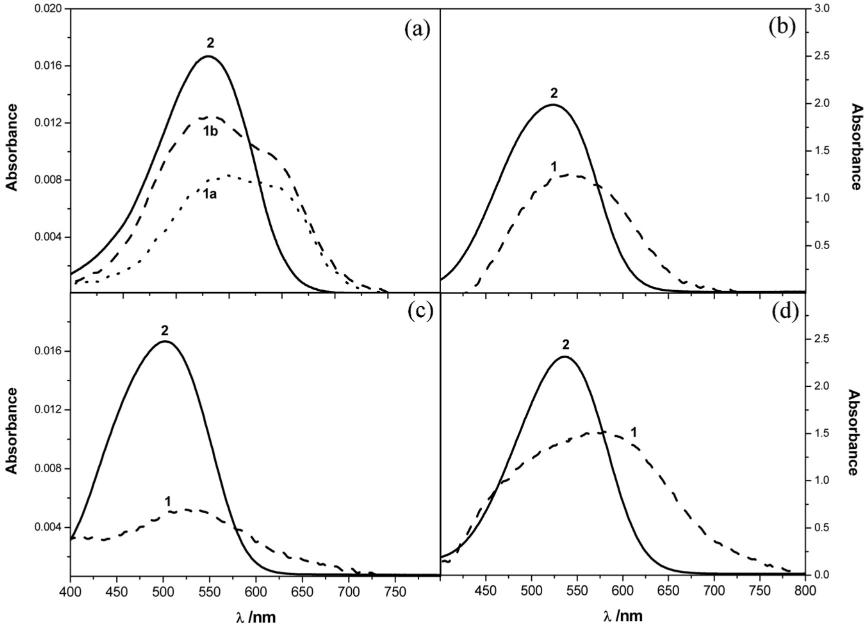

FIGURE 3 Absorption spectra in the visible region of dyes **1**–**4** mixed with liquid crystal in LB film and in ethanol (c = 10^{-5} mol/dm^3): a) LB films of **1**/8CB (1a) and **1**/PCH8 (1b) at MF = 0.5 and **1** in ethanol (2); b) LB film of **2**/8CB (1) at MF = 0.5 and **2** in ethanol (2); c) LB film of **3**/8CB (1) at MF = 0.3 and **3** in ethanol (2); d) LB film of **4**/8CB (1) at MF = 0.5 and **4** in ethanol (2). Ordinate axis: left – absorbance values of LB film, right – absorbance values of dye in ethanol.

difference in the shape of the absorption band of all the dyes in L and LB films with respect to those in ethanol is observed. The spectra are strongly broadened. For dye **1** even without Gaussian decomposition it is easy to designate that now two bands at $\lambda_{\max} = \mathbf{580}$ nm and **645** nm can be distinguished, instead of one (at $\lambda_{\max} = 580$ nm) seen in ethanol.

The strong broadening of the absorption band would suggest that in the monolayers the self-aggregates of the dye are formed. On the basis of the molecular exciton model [12] it is known that the dipole–dipole interactions result in the splitting of the energy level of the excited state into two levels with higher and lower energy relative to the undisturbed excited state. The change in energy of these two levels is called Davydov splitting and can be calculated from the equation:

$$\Delta E = \frac{2|\mathbf{M}|^2}{R^3}(1 - 3\cos^2\theta),$$

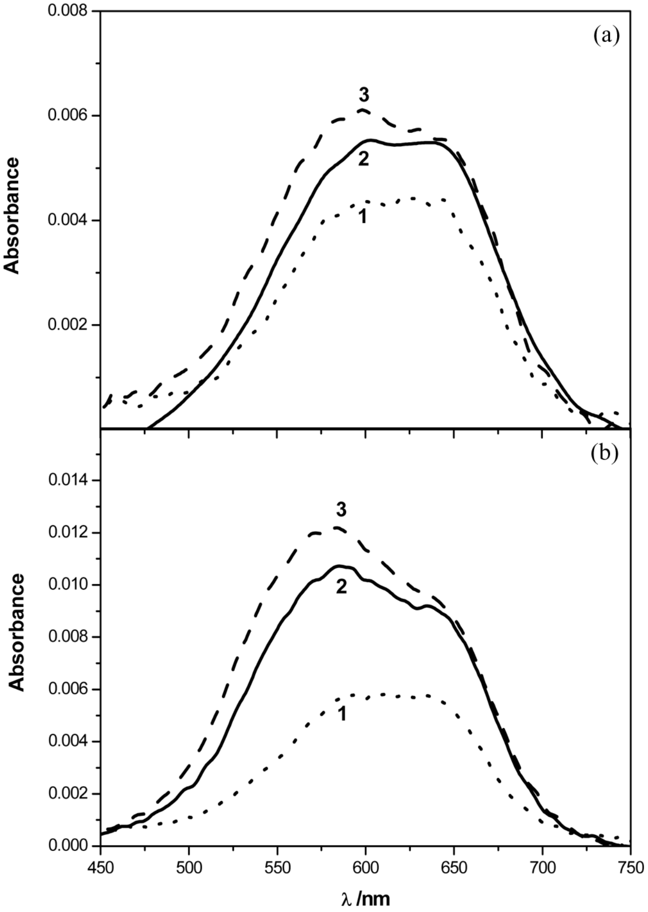

FIGURE 4 Absorption spectra of LB films formed of **1**/liquid crystal mixtures with MF of a dye of 0.2 (1), 0.4 (2) and 0.5 (3) for: a) **1**/8CB and b) **1**/PCH8 mixtures.

where **M** is the dipole moment vector of the molecule, θ is the angle between the dipole moment vector and **R** vector, and R is the length of the vector joining the centers of two dipoles. When the alignment of the dipole moments in the aggregates is such that $0^\circ < \theta < 54.7^\circ$, the exciton band is located energetically below the monomer band causing a red shift in the absorption spectrum, and created aggregates are called J-aggregates [13]. For $54.7^\circ < \theta < 90^\circ$, the exciton band is located energetically above the monomer band causing a blue shift,

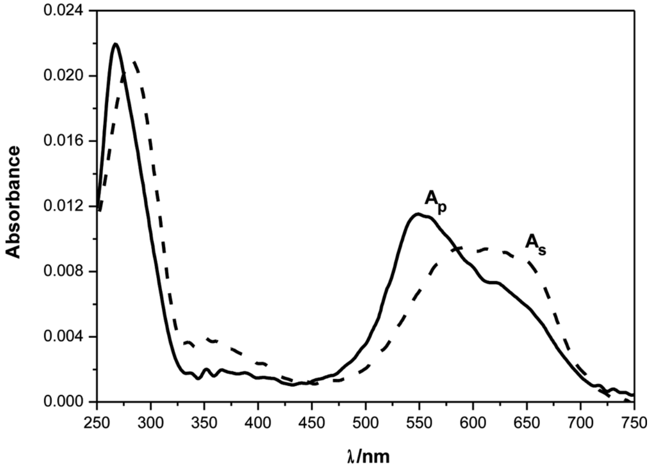

FIGURE 5 Absorption spectra for light polarized parallel (A_P) and perpendicularly (A_S) to the incidence plane for **1**/8CB mixture as LB film at MF = 0.4. The incidence angle was 60°.

and corresponding aggregates are referred to as H-aggregates [14]. When $\theta = 54.7^\circ$, no shift in the absorption spectrum is observed, and the aggregates are then called I-aggregates [15].

The presence of the additional band at the red side of the monomer band observed for azo dye/liquid crystal mixtures under investigation are indicative for J-aggregates creation between dye molecules.

Figure 5 presents examples of polarized components of absorption spectra for the **1**/8CB mixture at MF = 0.4 in the LB film. These spectra were recorded at the incidence angle $\alpha = 60^\circ$. The band occurring at $\approx$280 nm is related to 8CB absorption and its shape is the same for both components. However, the A_P and A_S for the band connected with the dye have different shapes. The same observations for mixtures of other dyes with 8CB or PCH8 were made. As the polarization of the electronic transitions of monomer and dimer is generally different, the results obtained can confirm the supposition that in LB films of azo dye/liquid liquid crystal mixtures some fraction of aggregates is created.

4. CONCLUSIONS

The binary mixtures of nonamphiphilic azo dyes with the liquid crystals 8CB and PCH8 form compressible and stable monolayer at the air-water interface up to MF = 0.5. The presence of dye molecules in 8CB or PCH8 influences the molecular packing, stability and rigidity of the Langmuir film. The effect depends on the molecular structure of both components and the dye content. A characteristic dye concentration is MF = 0.4. At such MF, the dye molecules are able to ‘stiffen’ the liquid crystal molecules, which are tilted with respect to the normal to the water surface.

Variation of the surface pressure at the collapse point with the mixture composition, and deviation from the additivity rule for the average molecular area, indicate that the dye/liquid crystal systems investigated are at least partially miscible. In most cases a negative deviation from the additivity rule is observed, which suggests the predominance of attractive interactions among molecules in Langmuir films.

Reliable LB films for **1**/8CB, **2**/8CB, **4**/8CB and **1**/PCH8 mixtures up to MF = 0.5, and for **3**/8CB mixtures only up to MF = 0.3 were obtained. This indicates the influence of the molecular structure of the azo dye on the ability to LB film formation.

Absorption spectra of both L and LB films suggest the formation of aggregates between dye molecules. According to the exciton theory, the shape and position of the absorption bands in the visible region indicate the creation of J-type aggregates.

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