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Molecular organization in binary mixtures of derivatives of naphthalenebicarboxylic acid and naphthoylenebenzimidazole with a liquid crystal in two-dimensional layers

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Molecular organization in binary mixtures of derivatives of naphthalenebicarboxylic acid and naphthoylenebenzimidazole with a liquid crystal in two-dimensional layers

I. Langmuir films

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Langmuir films of some dichroic dyes, namely derivatives of naphthalenebicarboxylic acid and derivatives of naphthoylenebenzimidazole, as well as of their mixtures with the liquid crystals 4-octyl-4′-cyanobiphenyl (8CB) and 4-pentyl-4″-cyano-*p*-terphenyl (5CT) were prepared. Surface pressure/mean molecular area isotherms were recorded from which some information about the alignment of molecules in a monomolecular layer at an air–water interface could be deduced. It was found that the properties of the monolayer are highly sensitive to the molecular structure of the side groups substituted on the main skeleton of the dye molecule, and to the mixture composition. Moreover, information about the miscibility or the phase separation of the two components in Langmuir films formed from dye/liquid crystal mixtures was obtained by using the excess area criterion and surface pressure rules.

1. Introduction

It is well known that water-insoluble amphiphilic molecules are able to form stable monolayers at an air–water interface (Langmuir film), and that these can be transferred onto solid substrates (Langmuir–Blodgett films) [1–4]. Therefore it is not surprising that it is possible to create Langmuir (L) and Langmuir–Blodgett (LB) films from the molecules of compounds which dissolved in an isotropic solvent give lyotropic liquid, crystalline phases. Molecules of thermotropic liquid crystals cannot be treated in the same way as amphiphilic systems; nevertheless, it was found that many of them are able to form stable two-dimensional layers both at air–water and air–solid substrate interfaces [5]. Among calamitic mesogens such compounds were intensively investigated in which the attachment of an alkyl chain to a rigid core, built of aromatic or aliphatic rings carrying a polar cyano group, gives rise to distinct amphiphilic properties [6–13]. There are, however, other molecules, which, despite being non-amphiphilic, can form stable L and LB films. These are, for example, polymers [14], various biomolecules [15], porphyrins [16], phthalocyanines [17, 18], derivatives of perylene [19–23], quinones [24], oligothiophenes [25, 26], fullerenes [27], and other macro-heterocyclic compounds [28].

In previous papers [21, 29] we have reported the investigation of L and LB films made from binary mixtures of a perylene derivative with liquid crystals 8CB (4-octyl-4′-cyanobiphenyl) or 5CT (4-pentyl-4″-cyano-*p*-terphenyl). We obtained information about the alignment of molecules and intermolecular interactions in such systems. Some of the perylene derivatives investigated, due to their good dichroic and excellent fluorescent properties, can be used in guest–host liquid crystal displays (GH LCDs), working in both passive and active modes [30, 31]. Similarly, derivatives of naphthalenebicarboxylic acid and of naphthoylenebenzimidazole have brilliant yellow to red colours, good dichroic properties and, dissolve in liquid crystalline solvents, and emit light with a high efficiency in a spectral region where for the human eye is sensitive [32, 33]. Therefore they can also be used as guest species in GH LCDs. Recently, we found that some of these dyes

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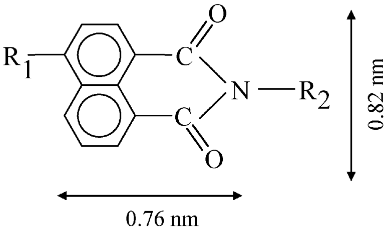
can form stable and compressible monolayers at an air–water interface [34].

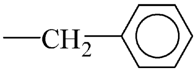
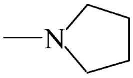
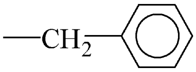
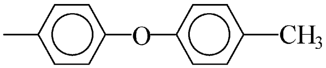
In this paper we describe the study of binary mixtures of some naphthalene derivatives of bicarboxylic acid and derivatives of naphthoylenebenzimidazole with the liquid crystals 8CB or 5CT, spreading on the air–water interface. It was our intention to investigate the molecular organization and intermolecular interactions in two-dimensional films composed of molecules with a different shape: amphiphilic calamitic molecules of the liquid crystal on the one hand and plate-like molecules of the dye on the other.

2. Experimental

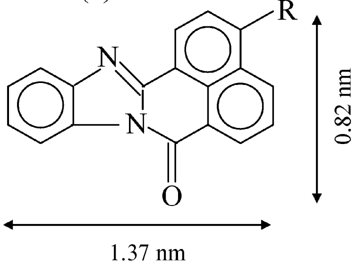
The following dyes were studied:

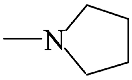
1. Derivatives of naphthalenebicarboxylic acid



Dye code	R_1	R_2
1	$—NH(CH_2)_3CH_3$	$—(CH_2)_3CH_3$
2	$—NH(CH_2)_4CH_3$	$—CH_2CH_3$
3	$—NH(CH_2)_{11}CH_3$	$—CH_2CH_3$
4	$—NH(CH_2)_3CH_3$	
5		
6	$—N(C_8H_{17})_2$	

(a)



Dye code	R
7	$—N(CH_3)_2$
8	

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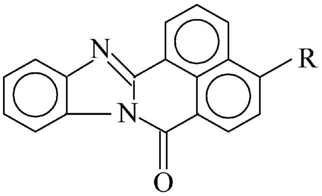
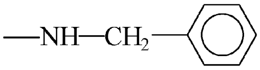


Dye code	R
9	$—NH(CH_2)_2CH_3$
10	

2. Derivatives of naphthoylenebenzimidazole

All the dyes were synthesized and chromatographically purified at the Institute of Dyes, Łódź University of Technology, Poland. The liquid crystal materials 4-octyl-4′-cyanobiphenyl (8CB) and 4-pentyl-4″-cyano-*p*-terphenyl (5CT) were purchased from E. Merck (Germany) and used without further purification.

In order to obtain Langmuir films the compounds investigated were dissolved in chloroform (Uvasol, for spectroscopy, E. Merck) at a concentration of 0.1 mM to provide stock solutions. Solution concentrations were confirmed spectroscopically. Mixed solutions of a dye/liquid crystal of selected mole fraction (MF) were prepared at room temperature shortly before spreading at the air–water interface.

Monolayer studies were performed by using a Minitrough 2 (KSV Instruments Ltd., Finland). This trough was equipped with two barriers for monolayer compression, a Wilhelmy plate balance for surface pressure determination, and a temperature control system. The subphase was deionized water obtained from a Milli-Q water purification system (Millipore Corp., Austria). A constant subphase temperature was maintained by a cooling circulator and kept constant at 22°C. The surface of the water in the trough of area $306 \times 75\,mm^2$ was carefully purified using an aspirator and then the appropriate amount (from 70 to 150 μl) of the mixed solution was spread drop by drop from a microlitre syringe (Hamilton, England). The chloroform was allowed to evaporate for about 15 min after spreading; the floating layer was then slowly compressed, symmetrically from both sides at a barrier motion speed of 5 mm min^{-1} (approximately 2×10^{-7} nm^2 molecule^{-1} s^{-1}), while the surface pressure (π) versus area per molecule (A) isotherm was recorded. Stability tests were done for L films checking the area per molecule variation to keep the pressure constant during 1 h. L films were found to be stable and data for π–A isotherms were acquired by an IBM-PC and processed using the software provided by KSV. The isotherms were reproducible within an error of 0.02 nm^2 molecule^{-1}. Each isotherm was obtained by averaging at least five runs.

3. Results

The measurement of the surface pressure/mean molecular area (π–A) isotherm is a basic and widely used technique for the characterization of Langmuir films. The surface pressure π is a measure of the change in surface tension of the water covered with a monolayer, with respect to pure water. The π–A isotherm represents the plot of the change of the π value as a function of the average area occupied by one molecule on the water surface during the compression process. In our experiment, the isotherms were recorded during the expansion process also and no significant differences in the two runs were found. We take this to indicate that equilibrium conditions has been attained.

Figures 1 and 2 show π–A isotherms for naphthalene derivatives of bicarboxylic acid and derivatives of naphthoylenebenzimidazole, respectively. It is seen that all the dyes chosen for the study are able to form a stable and compressible floating monolayer at an air–water interface. The increase in π begins at the area equal to A_0, being the first edge of the phase transition. It indicates the formation of the monolayer, which collapses at the area A_C and the surface pressure π_C. 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.

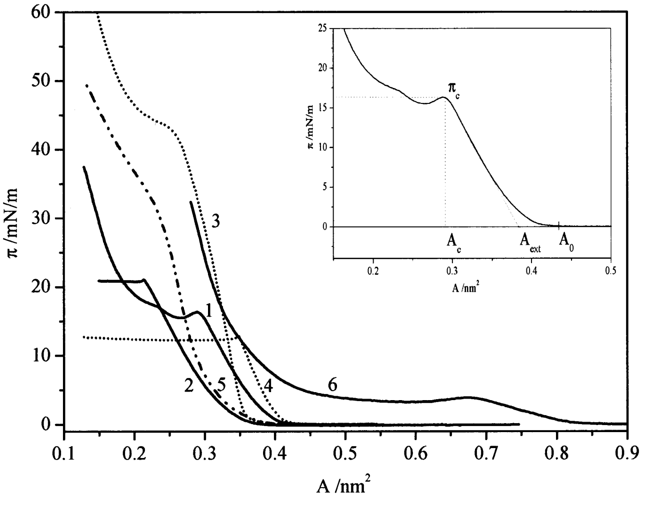


Figure 1. Surface pressure–mean molecular area isotherms of Langmuir films of derivatives of naphthalenebicarboxylic acid: **1** (1), **2** (2), **3** (3), **4** (4), **5** (5) and **6** (6).

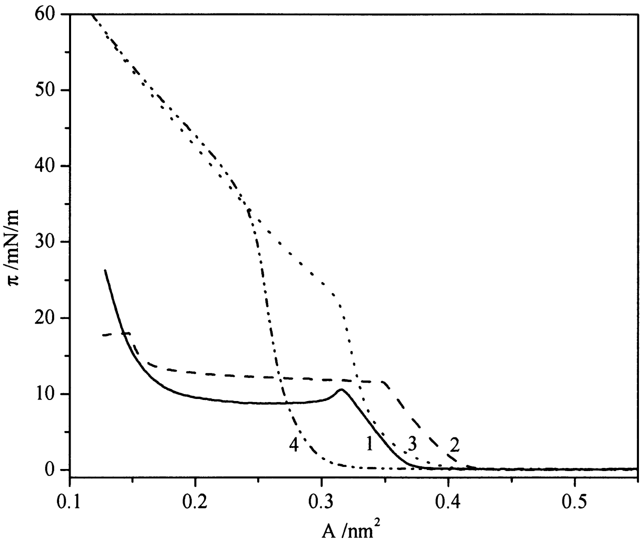


Figure 2. Surface pressure–mean molecular area isotherms of Langmuir films of derivatives of naphthoylenebenzimidazole: **7** (1), **8** (2), **9** (3) and **10** (4).

The examples of π–A diagrams for L films formed from dye/liquid crystal mixtures with different mole fraction (MF) of a dye are shown in figures 3–6, together with the isotherms of pure compounds. The π–A runs for pure liquid crystals 8CB and 5CT are in agreement with those given in the literature [6–10].

Tables 1–4 contain the characteristic values of π–A isotherms for L films of pure dyes, liquid crystals and dye/liquid crystal mixtures of three different MF of a dye. The following data are presented: A_{ext} = the value of the area obtained by extrapolating the tangent of tilt angle of the π–A plot (the part representing the compressed monolayer creation) to $\pi = 0$ (see insert in figure 1), A_C = the value of the collapse area and π_C = the value of the collapse pressure. The meaning of the angle δ will be explained in the next section.

In order to establish whether, in L films formed of binary mixtures, miscibility or phase separation occurs, the plots of mean molecular area and collapse pressure versus the film composition were analysed [1]. Let us define the excess of the average area per molecule, A_E,

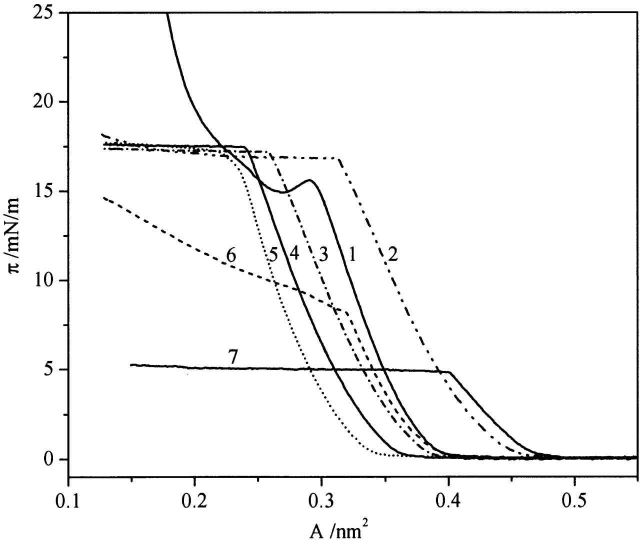


Figure 3. Surface pressure–mean molecular area isotherms of Langmuir films of **1**/8CB mixtures; the molar fractions MF of **1** = 1.0 (1), 0.8 (2), 0.6 (3), 0.5 (4), 0.4 (5), 0.2 (6) and 0.0 (7).

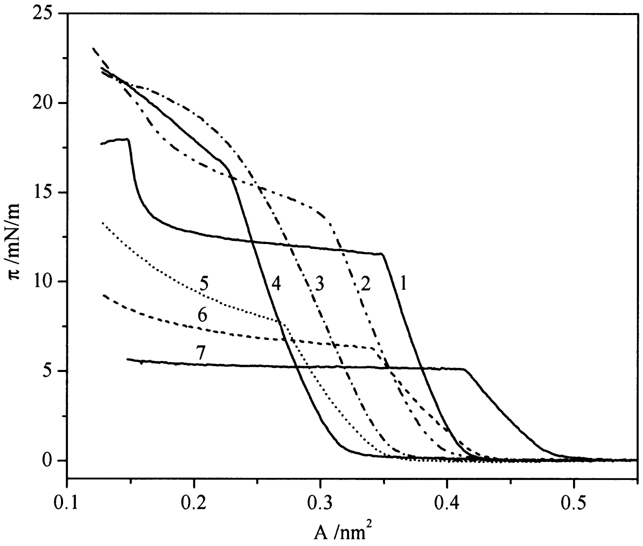


Figure 5. Surface pressure–mean molecular area isotherms of Langmuir films of **8**/8CB mixtures; the molar fractions MF of **8** = 1.0 (1), 0.8 (2), 0.6 (3), 0.5 (4), 0.4 (5), 0.2 (6) and 0.0 (7).

at given surface pressure as:

$$A_E = A_{12} - (x_1 A_1 + x_2 A_2) \qquad (1)$$

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

If A_E is equal to zero, the average area per molecule follows the additivity rule, $A_{12} = x_1 A_1 + x_2 A_2$, which means that in the mixture there is either ideal mixing on the one hand, or complete immiscibility on the other. Deviation from zero, either positive or negative, indicates some degree of miscibility coupled with non-ideal behaviour. Figures 7–10 show the values of A_E at the surface pressure corresponding to the compressed monolayer creation (before the collapse point) as a function of MF of a dye for dye/liquid crystal mixtures in L films studied. It is seen that in

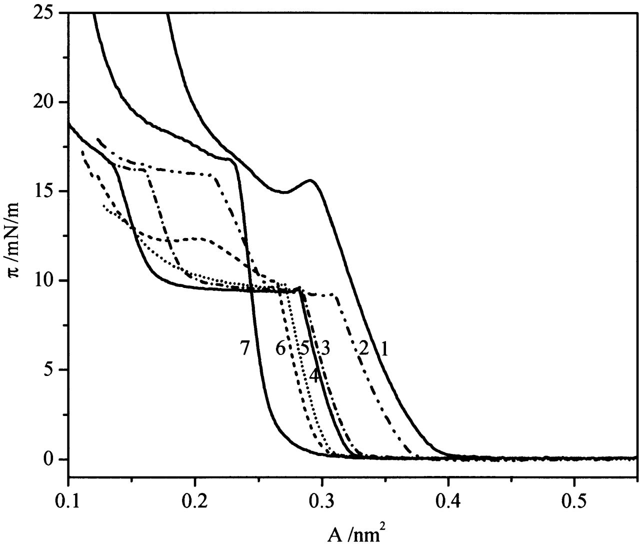


Figure 4. Surface pressure–mean molecular area isotherms of Langmuir films of **1**/5CT mixtures; the molar fractions MF of **1** = 1.0 (1), 0.8 (2), 0.6 (3), 0.5 (4), 0.4 (5), 0.2 (6) and 0.0 (7).

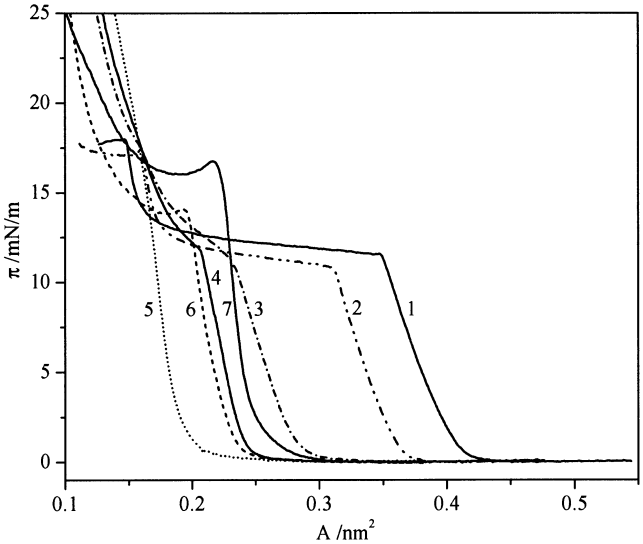


Figure 6. Surface pressure–mean molecular area isotherms of Langmuir films of **8**/5CT mixtures; the molar fractions MF of **8** = 1.0 (1), 0.8 (2), 0.6 (3), 0.5 (4), 0.4 (5), 0.2 (6) and 0.0 (7).

some cases $A_E \approx 0$, and therefore the second criterion is needed in order to decide whether in the mixed film the complete mixing or phase separation of components occurs. Additional information can be obtained from the surface phase rule [1]. This rule states that if the components are immiscible, the equilibrium spreading pressure (esp) should be constant and not vary with the mixture composition. In some cases, however, the esp value is difficult to determine and, therefore, for systems where the L film collapse point is easily detectable, it is sufficient to estimate the collapse pressure π_C instead of esp. The dependence of π_C value on the composition of L films formed from dye/liquid crystal mixtures can be inferred from the basis of data given in tables 1–4.

4. Discussion

4.1. *Derivatives of naphthalenebicarboxylic acid*

The cross-sectional area of the naphthalene skeleton with two –C–O groups, calculated on the basis of the space-filling model, including van der Waals radii of the terminal atoms [35], is 0.62 nm^2. Thus, the results presented in tables 1 and 2 for pure dyes show that in

Table 1. Values of the area per molecule, collapse pressure and average angle between the normal to the water surface and rigid molecular cores, for derivatives of naphthalenebicarboxylic acid mixed with 8CB.

Compound	MF of dye	A_{ext}/nm^2	A_C/nm^2	π_C/mN m^{-1}	δ_{av}/°
8CB	—	0.50	0.42	5.0	61
1	1.0	0.39	0.29	16.3	39
1/8CB	0.8	0.42	0.31	16.9	43
	0.5	0.36	0.24	17.2	38
	0.2	0.37	0.32	8.2	40
2	1.0	0.35	0.20	21.0	34
2/8CB	0.8	0.38	0.24	17.0	38
	0.5	0.41	0.26	10.7	43
	0.2	0.49	0.36	6.7	57
3	1.0	0.35	0.25	43.4	35
3/8CB	0.8	0.36	0.33	13.3	37
	0.5	0.43	0.37	8.1	47
	0.2	0.52	0.43	6.6	65
4	1.0	0.40	0.35	13.0	40
4/8CB	0.8	0.43	0.34	13.2	45
	0.5	0.43	0.27	15.0	46
	0.2	0.49	0.37	7.8	58
5	1.0	0.31	0.24	30.2	29
5/8CB	0.8	0.31	0.30	5.1	31
	0.5	0.32	0.25	13.8	32
	0.2	0.40	0.34	6.5	44
6	1.0	0.82	0.68	3.9	90
6/8CB	0.8	0.84	0.74	2.2	—
	0.5	0.70	0.50	7.4	—
	0.2	0.65	0.47	7.1	—

Table 2. Values of the area per molecule, collapse pressure and average angle between the normal to the water surface and rigid molecular cores, for derivatives of naphthalenebicarboxylic acid mixed with 5CT.

Compound	MF of dye	A_{ext}/nm^2	A_C/nm^2	π_C/mN m^{-1}	δ_{av}/°
5CT	—	0.26	0.23	16.7	19
1	1.0	0.39	0.29	16.3	39
1/5CT	0.8	0.36	0.31	9.3	33
	0.5	0.32	0.29	9.6	27
	0.2	0.29	0.26	10.0	23
2	1.0	0.35	0.20	21.0	34
2/5CT	0.8	0.37	0.29	9.1	34
	0.5	0.36	0.30	9.2	31
	0.2	0.31	0.28	9.2	25
3	1.0	0.35	0.25	43.4	35
3/5CT	0.8	0.34	0.29	25.1	31
	0.5	0.31	0.22	26.0	26
	0.2	0.29	0.24	24.4	22
4	1.0	0.40	0.35	13.0	40
4/5CT	0.8	0.42	0.38	7.5	40
	0.5	0.40	0.36	7.7	34
	0.2	0.36	0.29	11.1	28
5	1.0	0.31	0.24	30.2	29
5/5CT	0.8	0.31	0.29	11.5	28
	0.5	0.28	0.27	11.5	24
	0.2	0.30	0.27	11.7	24
6	1.0	0.82	0.68	3.9	90
6/5CT	0.8	0.60	0.74	8.1	—
	0.5	0.52	0.50	8.6	—
	0.2	0.42	0.47	8.9	—

Table 3. Values of the area per molecule, collapse pressure and average angle between the normal to the water surface and rigid molecular cores, for derivatives of naphthoylenebenzimidazole mixed with 8CB.

Compound	MF of dye	A_{ext}/nm^2	A_C/nm^2	π_C/mN m^{-1}	δ_{av}/°
8CB	—	0.50	0.42	5.0	61
7	1.0	0.37	0.32	10.6	19
7/8CB	0.8	0.37	0.32	8.1	22
	0.5	0.31	0.23	17.2	22
	0.2	0.39	0.33	6.7	36
8	1.0	0.40	0.35	11.5	21
8/8CB	0.8	0.38	0.31	13.5	20
	0.5	0.30	0.22	14.5	15
	0.2	0.41	0.34	6.3	15
9	1.0	0.34	0.31	22.3	18
9/8CB	0.8	0.38	0.32	13.0	22
	0.5	0.35	0.25	20.1	25
	0.2	0.37	0.31	7.6	33
10	1.0	0.28	0.24	35.0	14
10/8CB	0.8	0.25	0.20	24.8	14
	0.5	0.31	0.23	8.7	22
	0.2	0.39	0.33	6.6	35

compressed monolayers the central parts of the molecules **1**–**5** do not lie flat at the water surface. It could be considered that the molecules assume the edge-on configuration and form columns, similar to some discotic liquid crystals [36, 37] and aromatic lyotropic molecules in chromonic mesophases [38, 39]. However, the values of the areas found from the π–A isotherms do not agree with such an arrangement, when one takes into account that the aromatic cores are oriented predominantly perpendicularly to the surface. It is, therefore, reasonable to assume that the molecules of **1**–**5** create a columnar stacking tilted with respect to the water surface. Tables 1 and 2 contain the values of the tilt angle δ estimated as the angle between the rigid molecular core of dyes **1**–**6** and the normal to the water surface in the compressed monolayer before the collapse point.

The results obtained show that the shape of π–A isotherm for derivatives of naphthalenebicarboxylic acid is strongly dependent on the molecular structure of two side substituents. In some cases, behind the collapse point a broad plateau region is observed, while in the others, the pressure rises monotonically with a decrease of the available area. However, the shapes of all π–A isotherms obtained for the dyes investigated can be found in the literature for other compounds [6–23]. Although the relationship between substituent molecular structure and the isotherm run is not very simple, some comments can be made. Comparing the data for dyes **2** and **3**, which have the same R_2 substituent, it is seen that both the value of π_C and the slope of the isotherm increase with increasing chain length in R_1, indicating an increase of the monolayer stability and rigidity. When the *n*-alkylamine chain in R_1 is replaced by a pyrolidine ring an increase of π_C is observed and the shape of the isotherm changes appreciably (compare the results for **4** and **5**). The data for **1** and **4** indicate that the molecular structure of the R_2 substituent also plays some role and affects both the π_C value and the isotherm slope. Dye **6** is the only example among all the derivatives of naphthalenebicarboxylic acid investigated where A_{ext} has a value greater than the cross-sectional area of the naphthalene skeleton. This suggests that, in the monolayer, the rigid cores of the dye molecules lie flat on the water surface. Such molecular alignment can be explained in terms of presence of two benzene rings in R_2, which, in the first stage of the compressed monolayer formation, do not allow the tilted arrangement of the molecules and also occupy some area on the water surface.

Table 4. Values of the area per molecule, collapse pressure and average angle between the normal to the water surface and rigid molecular cores, for derivatives of naphthoylenebenzimidazole mixed with 5CT.

Compound	MF of dye	A_{ext}/nm^2	A_C/nm^2	π_C/mN m^{-1}	δ_{av}/°
5CT	—	0.26	0.23	16.7	19
7	1.0	0.37	0.32	10.6	19
7/5CT	0.8	0.20	0.14	25.0	11
	0.5	0.23	0.20	11.2	14
	0.2	0.27	0.22	13.8	18
8	1.0	0.40	0.35	11.5	21
8/5CT	0.8	0.36	0.31	10.8	20
	0.5	0.24	0.21	11.7	15
	0.2	0.23	0.19	14.1	15
9	1.0	0.34	0.31	22.3	18
9/5CT	0.8	0.38	0.35	3.3	21
	0.5	0.35	0.32	3.3	21
	0.2	0.31	0.29	4.5	21
10	1.0	0.28	0.24	35.0	14
10/5CT	0.8	0.30	0.26	14.7	17
	0.5	0.28	0.25	11.1	17
	0.2	0.27	0.25	11.8	18

From the analysis of the shapes of the isotherms and the data given in tables 1 and 2 for L films formed from binary mixtures of derivatives of naphthalenebicarboxylic acid with the liquid crystals 8CB or 5CT, it follows that the packing density of molecules, as well as the rigidity and the stability of the monolayer at the air–water interface, depends strongly not only on the molecular structure of the dye and the liquid crystal but also on the film composition. The value of π_C for 8CB is smaller, whereas A_{ext} and A_C values are greater, than the appropriate values for dyes **1**–**5**. But only in the case of dyes **2** and **3**, a regular decrease of π_C and simultaneously an increase of A_{ext} and A_C values are observed with the rise of the 8CB content in the mixture. For dyes **1**, **4** and **5** both the area and the surface pressure at the collapse point change irregularly (see figure 3 for **1**/8CB mixtures as an example). The π_C of **1**/8CB and **4**/8CB mixtures does not decrease distinctly before MF of the dye is equal to 0.2, whereas A_{ext} and A_C values of these mixtures are smallest for MF = 0.5. Similar behaviour of A_C can be seen for **5**/8CB mixtures, but here at this concentration the π_C value is highest. In the case of dye **6** the opposite situation in comparison with dyes **1**–**5** occurs: π_C is now smaller, and A_{ext} and A_C values are larger than those for 8CB. Therefore it is not surprising that the addition of the liquid crystal causes an increase of surface pressure and a decrease of the area at the collapse point.

The changes of the isotherm run with the L film composition for dye/8CB mixtures give some indication of the interactions between dye and liquid crystal molecules. The nature of these interactions can be followed in figure 7. However, first it is necessary to notice that all the derivatives of naphthalenebicarboxylic acid under investigation are miscible with 8CB,

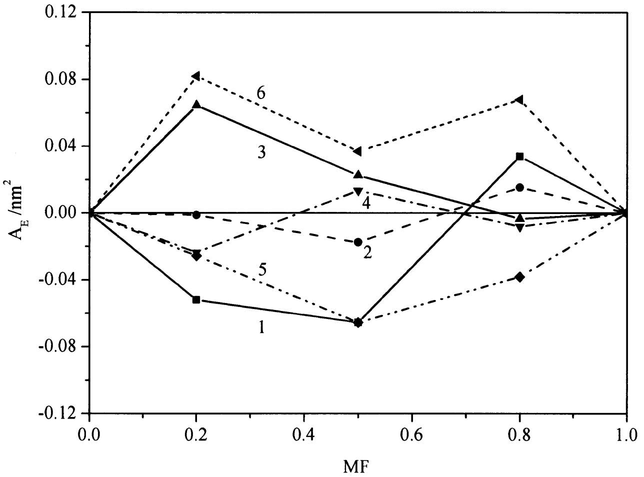


Figure 7. Plot of the excess of the average area per molecule, A_E, of derivatives of naphthalenebicarboxylic acid mixed with 8CB versus the molar fraction of a dye at $\pi = 4\,\mathrm{mN\,m^{-1}}$: **1** (1), **2** (2), **3** (3), **4** (4), **5** (5), and **6** at $\pi = 1.5\,\mathrm{mN\,m^{-1}}$ (6).

because $A_E \neq 0$. This is confirmed by the changes of π_C value with the mixture composition. The negative deviation from the additivity rule, which is clearly observed for **1** and **5** mixed with 8CB, means a contraction of the two-component films due to attractive interactions between dye and liquid crystal molecules [1, 40]. The positive deviations are characteristic of miscible components with repulsive intermolecular interactions [1, 40] and they occur here in the **3**/8CB mixture at low dye concentrations and in the **6**/8CB mixture over the whole composition range. A_E values for **2**/8CB and **4**/8CB systems indicate that the interactions between dye and liquid crystal molecules are weak and change from attractive to repulsive as the mixture composition changes. It is possible that we have to deal here with only partial miscibility.

Langmuir films of binary mixtures of derivatives of naphthalenebicarboxylic acid with 5CT behave differently from those of these dyes with 8CB. This is probably because the monolayer formed from pure 5CT is more stable and rigid than the 8CB monolayer, and the molecules are aligned at a small angle with respect to the water surface normal [6, 7, 12]. A_{ext} and A_C values for dye/5CT mixtures vary rather regularly: with few exceptions they decrease with the rise of the liquid crystal content. However, the values of π_C remain almost constant in the mixed films, although for the mixtures of dyes **1**–**5** with 5CT they are smaller than those for pure components, indicating a decrease of the films' stability. This behaviour of dye/5CT systems was previously for a perylene-like dye [21]. For **6**/5CT mixtures it is seen that the addition of 5CT causes an increase of π_C, even at very low liquid crystal content. The slope of the isotherms increases with a decrease in the MF of **6** (data not shown), giving clear evidence that 5CT improves not only the stability but also the rigidity of the L film formed of **6**.

The lack of π_C changes with mixture composition would indicate immiscibility in the dye/5CT systems. However, for dyes **2**, **4** and **6** the deviation from additivity rule (figure 8) is clearly observed. Therefore, it should be expected that in these cases the dye molecules are at least partially miscible with 5CT molecules. Note that for **6**/5CT mixtures attractive interactions predominate, in contrast to **6**/8CB mixtures.

Knowing the δ angles for pure compounds, and taking into account the mixture composition, we have tried to estimate the average angle created by the rigid cores of molecules with the normal to the water surface in mixed L films. The estimated values for mixtures of derivatives of naphthalenebicarboxylic acid with 8CB or 5CT are gathered in tables 1 and 2, respectively. From the data given in table 1, it follows that 8CB molecules do not significantly influence the alignment of **1** molecules at the air–water interface. In the cases of dyes **2**–**5** mixed with 8CB, it is seen that an increase of the content of the liquid crystal molecules causes a regular increase of δ_{av}. This indicates the greater tilt of the dye molecules to the water surface in the presence of 8CB. For dye/5CT systems a decrease of δ_{av} with the rise of liquid crystal content is observed, which means that, in mixed films, the dye molecules assume a more vertical arrangement. The data obtained for **6**/liquid crystal mixtures make the estimation of δ_{av} impossible.

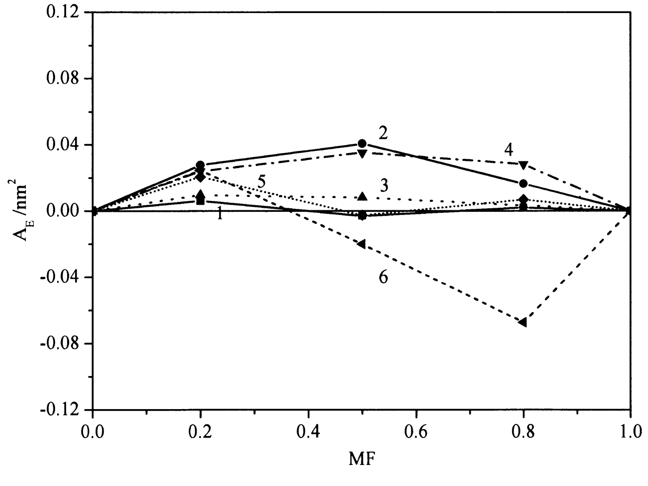


Figure 8. Plot of the excess of the average area per molecule, A_E, of derivatives of naphthalenebicarboxylic acid mixed with 5CT versus the molar fraction of a dye: **1** at $\pi = 6.5\,\mathrm{mN\,m^{-1}}$ (1), **2** at $\pi = 7.0\,\mathrm{mN\,m^{-1}}$ (2), **3** at $\pi = 12.0\,\mathrm{mN\,m^{-1}}$ (3), **4** at $\pi = 6.0\,\mathrm{mN\,m^{-1}}$ (4), **5** at $\pi = 9.0\,\mathrm{mN\,m^{-1}}$ (5), and **6** at $\pi = 2.7\,\mathrm{mN\,m^{-1}}$ (6).

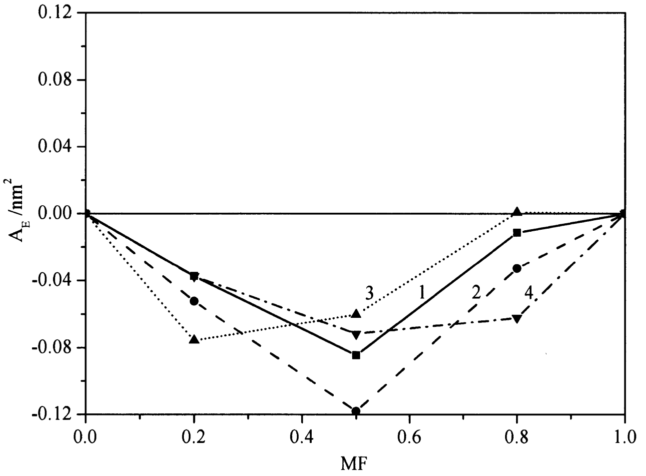


Figure 9. Plot of the excess of the average area per molecule, A_E, of derivatives of naphthoylenebenzimidazole mixed with 8CB versus the molar fraction of a dye at $\pi = 4\,\mathrm{mN\,m^{-1}}$: **7** (1), **8** (2), **9** (3) and **10** (4).

4.2. *Derivatives of naphthoylenebenzimidazole*

A cross-sectional area of the rigid cores of naphthoylenebenzimidazole derivatives, calculated in the same manner as for naphthalene derivatives of bicarboxylic acid, can be assumed to be $1.12\,\mathrm{nm^2}$. Therefore, it is clear from the data presented in tables 3 and 4 that, as in the previous case, for these dyes also, a tilted arrangement of the molecules in the L film occurs. The calculated δ angles are given in tables 3 and 4 and it is seen that they are significantly smaller than those listed in tables 1 and 2. This means that derivatives of naphthoylenebenzimidazole are aligned more vertically with respect to the water surface than naphthalene derivatives of bicarboxylic acid. However, similarly to the previous case, both the π_C values and the isotherm slopes are different for various dyes, indicating the influence of the substituent molecular structure on both monolayer stability and rigidity. It should be noted that an increase in the alkyl chain length, as well as the presence of a benzene ring in the substituent, causes a rise of π_C value and also of the isotherm slope. The properties of the monolayer can depend also to some extent on the position of the *R* substitution.

Similarly to the case of dyes **1**–**5**, π_C values of dyes **7**–**10** are higher than that of 8CB, and A_{ext} and A_C are smaller. With an increase of 8CB content in the L film the area and the surface pressure at the collapse point change irregularly (see for example the data presented in figure 5). However, it is worth pointing out that for the mixtures of dyes **7**–**9** with 8CB, the molecular packing density and the film stability are the highest at MF of the dye equal to 0.5. In the case of dye **10** the addition of 8CB even at low concentration decreases the π_C value of the L film, but up to MF = 0.5 improves the molecular packing. This influence of the liquid crystal content on the properties of the monolayer formed of derivatives of naphthoylenebenzimidazole mixed with 8CB is reflected in the results shown in figure 9. It is seen that in L films of these mixtures attractive interactions occur, which are very strong up to MF = 0.5.

When the liquid crystal 5CT is mixed with derivatives of naphthoylenebenzimidazole the very different behaviour of **7**/5CT and **8**/5CT mixtures in comparison with **9**/5CT and **10**/5CT should be noted. In the case of dyes **7** and **8** the addition of 5CT causes a decrease of the A_{ext} and A_C values up to MF = 0.5 for **7**/5CT and MF = 0.4 for **8**/5CT (see figure 6), indicating a rise in the molecular packing density. The value of π_C does not change significantly (except for **7**/5CT at MF = 0.8), similar to the case of dyes **1**–**6** mixed with this liquid crystal. This would indicate immiscibility of these dyes molecules with molecules of 5CT. However, the data presented in figure 10 show a significant deviation from the additivity rule for **7**/5CT and **8**/5CT mixtures, which gives evidence for attractive interactions. This means that at least partial miscibility occurs. From the results given in table 4 for dyes **9** and **10** it follows that the presence of 5CT does not significantly influence the molecular packing of the L film; it significantly decreases its stability, however: π_C decreases rapidly after addition of the liquid crystal and is then almost independent of the mixture composition. The values of A_E (figure 10) for **9**/5CT and **10**/5CT mixtures indicate only small deviations from the additivity rule with a predominance of repulsive interactions.

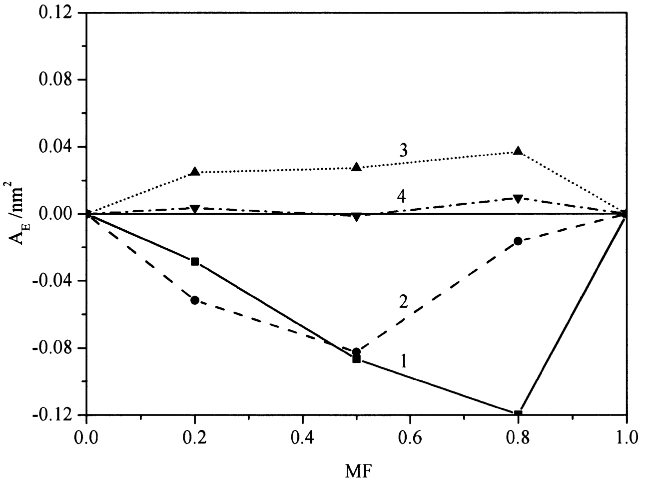


Figure 10. Plot of the excess of the average area per molecule, A_E, of derivatives of naphthoylenebenzimidazole mixed with 5CT versus the molar fraction of a dye **7** at $\pi = 8.0\,\mathrm{mN\,m^{-1}}$ (1), **8** at $\pi = 8.0\,\mathrm{mN\,m^{-1}}$ (2), **9** at $\pi = 2.8\,\mathrm{mN\,m^{-1}}$ (3), and **10** at $\pi = 8.0\,\mathrm{mN\,m^{-1}}$ (4).

Therefore one should expect here the phase separation of components or at most small partial miscibility.

The deduced δ_{av} angle values for the mixtures of derivatives of naphthoylenebenzimidazole with the liquid crystal show that, similarly to the case of dyes **1**–**5**, the presence of 8CB causes the molecules in the L film to be tilted to the water surface at an angle higher than for L films formed of pure dye. Such behaviour of molecules is observed also for the mixtures of dyes **9** and **10** with 5CT. However, in L films of **7**/5CT and **8**/5CT, the molecules assume more vertical arrangements when the liquid crystal content rises.

5. Conclusions

It has been shown that it is possible to prepare stable and compressible Langmuir films from some dichroic dyes, namely derivatives of napthalenebicarboxylic acid and naphthoylenebenzimidazole. Binary mixtures of these dyes with the liquid crystal 8CB or 5CT can also form homogeneous monolayers at an air–water interface. The monolayer properties (packing density, stability and rigidity) depend strongly on the structure of dye and liquid crystal molecules as well as on the mixture composition, where MF = 0.5 seems to be some 'limiting' concentration. At this concentration for some mixtures, especially with 8CB, the maximum stability and packing density occur. This may indicate an arrangement of the two types of molecules A and B in a regular ABAB stacking. Mixtures of the dyes with 8CB are miscible over the whole range of composition, while for dye/5CT systems, immiscibility or only very small partial miscibility of components is observed. It is, however, noteworthy that for many mixtures the best miscibility occurs at MF = 0.5, which supports the suggestion of the ABAB stacking of the molecules in mixed L films.

Since the shape of the dye molecules under investigation is quite different from conventional amphiphiles and 'amphiphilic' calamitic liquid crystals, we expected that spreading the dye/liquid crystal mixtures at the air–water interface would result in L films of new structures. The analysis of π-A isotherms gave only preliminary results. Mixed films need now to be further investigationed by means of, for example, Brewster angle microscopy and *in situ* absorption measurements. However, our finding that dyes other than perylene derivatives with good fluorescent properties can form stable and compressible monolayers at an air–water interface, and can then be transferred onto a solid substrate (LB film) [41], provides new perspectives for the application of such compounds, not only as guest species in LCDs but also as active layers in organic light emitting diodes [42–44].

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