Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Molecular organization in two-dimensional films of liquid I. Langmuir films of binary mixtures of liquid crystals with a crystalline mixtures terminal cyano group

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To cite this Article Martynski, Tomasz , Hertmanowski, Robert and Bauman, Danuta(2001) 'Molecular organization in two-dimensional films of liquid I. Langmuir films of binary mixtures of liquid crystals with a crystalline mixtures terminal cyano group', Liquid Crystals, 28: 3, 437 — 444

To link to this Article: DOI: 10.1080/02678290010010121

URL: http://dx.doi.org/10.1080/02678290010010121

Liquid Crystals, 2001, Vol. 28, No. 3, 437–444

Molecular organization in two-dimensional films of liquid crystalline mixtures

I. Langmuir films of binary mixtures of liquid crystals with a terminal cyano group

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(*Received 11 August 2000; accepted 14 September 2000*)

The Langmuir films of two liquid crystal materials, 4-octyl-4′-cyanobiphenyl (8CB) and 4-pentyl-4″-cyano-*p*-terphenyl (5CT), and of their mixtures have been studied by recording surface pressure–area isotherms and Brewster angle microscopy (BAM) images. The pure liquid crystals revealed very different characters of the surface pressure–area isotherms indicating different organization of the molecules and different molecular interactions in the monolayer at the water–air interface. The surface pressure–area isotherms of Langmuir films formed from 8CB/5CT mixtures give evidence for phase separation of the components over the whole range of molar fractions. Similar conclusions have been drawn on the basis of BAM image analysis.

1. Introduction

One of the most interesting and up to now incompletely resolved problems in investigations of liquid crystals is the way in which the molecules are anchored to the interface, and how these interfacial interactions affect molecular alignment in the bulk. On the other hand, it is of interest to know to what extent only the orientational order in the nematic phase, and both the orientational and positional order leading to the layered structure in the smectic phase, are preserved if we consider liquid crystal films with a thickness of the order of the molecular dimensions.

It has been found that a study of Langmuir films formed at the air–water interface plays a key role in recognition of the structure and molecular organization in ultrathin layers [1]. This technique has also been applied recently in obtaining information about the alignment of liquid crystal molecules in the monolayer [2–7]. However, to our best knowledge, up to now only single component liquid crystals have been investigated. Of course, in many applications, e.g. in liquid crystal display devices, multi-component mixtures are used, because only mixtures can completely fulfill the requirements connected with the wide temperature range and appropriate electro-optical properties of the mesophase. Therefore, in this paper we focus in particular on a study of binary liquid crystal mixtures at the air–water interface.

We present here the results of the investigation of Langmuir films obtained from the mixed system of 4-octyl-4′-cyanobiphenyl (8CB) and 4-pentyl-4″-cyano-*p*-terphenyl (5CT). These two liquid crystals have a strongly polar hydrophilic head group ($-C{\equiv}N$) and a relatively long hydrophobic terminal alkyl chain, and are known from previous studies [2–8] as compounds which are able to form monolayers at the air–water interface. In our investigations they are mixed over the whole range of mole fractions and their thermodynamical properties determined. Additionally, observations of the structure at various surface pressures by means of Brewster angle microscopy (BAM) have been made.

2. Experimental

The liquid crystals materials 8CB and 5CT were purchased from E. Merck (Germany) and were used without further purification. Their phase transition temperatures were in substantial agreement with literature data [9–11] and were as follows:

8CB Cr 21.0°C SmA 33.5°C N 40.2°C I
5CT Cr 131.6°C N 240.0°C I.

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Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2001 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290010010121

These temperatures relate to the phase transitions in the bulk and have no influence on the structure of thin films at a surface [5].

Both monolayer-forming liquid crystal materials were dissolved in chloroform (Uvasol, for spectroscopy, E. Merck) at a concentration of 0.1mM in order to obtain stock solutions. The concentrations of solutions were confirmed spectroscopically. Mixed solutions of 8CB/5CT of selected molar fractions 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 Mili-Q water purification system (Milipore Corp., Austria). A constant subphase temperature was maintained by a cooling circulator and kept constant at 25°C. The surface of the water in the Langmuir trough of area 22 950 mm^2 (306 × 75 mm^2) was carefully purified using an aspirator and then an 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. Then the floating layer was slowly compressed, symmetrically from both sides at a barrier motion speed of 5 mm min^{-1} (approximately 2×10^{-5} Å^2 molecule^{-1} s^{-1}). The data for the surface pressure versus area per molecule isotherms were acquired by an IBM-PC and processed using the software provided by KSV. The isotherms were reproducible within an error of ± 2 Å^2 molecule^{-1}. Each isotherm was obtained by averaging five runs.

The morphologies of the films at the air–water interface were studied by using a BAM2plus microscope (NFT, Germany). The green (532 nm) laser beam was directed at the Brewster angle (53.1°) onto the pure water. The light reflected from the monolayers was imaged by means of a CCD camera and recorded on video tape (Panasonic VCR). The BAM images were obtained on continuous slow film compression simultaneously with the isotherm record. Typical reproducible images for the compressed films were saved in files using a framegrabber and printed. The image features were observed with a lateral resolution of ~ 4 µm.

3. Results and discussion

3.1. *Surface pressure–area isotherms*

To obtain reference data and compare these with data given in the literature, we have measured first the dependence of the surface pressure π on the mean molecular area (Mma) for the pure liquid crystals 8CB and 5CT. The results are shown in figure 1 and indicate the difference in isotherm shape between the liquid crystals. The isotherm of pure 8CB is very similar to that presented in the literature [4–6, 12]. Following Xue *et al.* [4] we can distinguish five regions in the measured Mma range. In the region where Mma is greater than 50 Å^2, π is near to zero and constant, which indicates submonolayer coverage (coexistence of gas and liquid phases). Between 48 and 41 Å^2, the first significant increase in π up to the collapse point occurs, indicating the appearance of the completely homogenous monolayer. However, the collapse point occurs at an Mma larger by a factor of two than the theoretical molecular cross-section. Xue *et al.* [4] and de Mul and Mann [6] 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 [13] 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 Mma. When the Mma reaches about 11 Å^2, π rises sharply. This value is too small for all the molecules to remain on the water surface and therefore Xue *et al.* [4] postulated the existence of an interdigitated bilayer on top of a monolayer (trilayer) adjacent to the interface in this Mma region. After further compression a second plateau appears suggesting the creation of a multilayer.

The surface pressure–area isotherm for pure 5CT was first given by Daniel *et al.* [2]. Our results are in substantial agreement with the data presented by these authors, only the collapse pressure is slightly lower. However, similarly to [2], the Mma at the collapse point corresponds to the 5CT molecular cross-section.

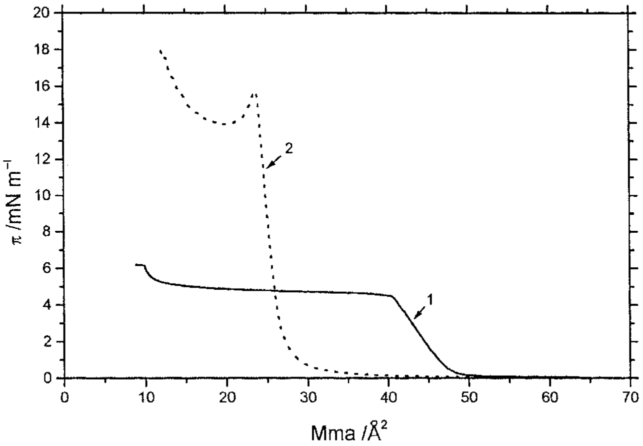


Figure 1. Surface pressure–area isotherms of the liquid crystals 8CB (1) and 5CT (2) as two-dimensional layers at the air–water interface at 25°C.

This leads to the conclusion that the repulsive forces between the electric dipoles are compensated by the attractive interactions between the three phenyl rings and suggests that the 5CT molecules can locate very close to each other. As a result the 5CT film has a higher packing factor than the 8CB film and the molecules are aligned almost perpendicular to the water surface. Such a behaviour of 5CT molecules has been confirmed by spectroscopic investigations [3, 14]. From the higher collapse pressure of 5CT ($\pi = 17\,\mathrm{mN\,m^{-1}}$) in comparison with that of 8CB, it follows that the monolayer formed by 5CT is more stable and rigid than the 8CB monolayer. No plateau after the collapse point is observed, which means that the formation of any regular bilayer or multilayer does not occur.

We expected that 5CT might improve the molecular packing of 8CB molecules and their alignment with respect to the water surface. Therefore we undertook a study of Langmuir film isotherms for 8CB/5CT mixtures. The results for various molar fractions (MF) of 5CT in 8CB are presented in figure 2. It is seen that with rise in molar fraction of 5CT the monolayer collapses at regularly smaller and smaller Mma values. The plateau region becomes narrower and at the concentrations of 0.6 and 0.8 MF two kinks in the isotherm are seen distinctly. However, the second kink occurs at a surface pressure about half that at the collapse point of pure 5CT. This would suggest that the rigidity in the mixed monolayers (even at small 8CB concentrations) significantly decreases in comparison with the rigidity of 5CT.

In order to establish the miscibility of the two components in the 8CB/5CT monolayers, the average area per molecule and the collapse pressure need to be analysed against the monolayer composition. If the components are not miscible, the monolayer will exist as patches of one monolayer in the other. In this case the average area per molecule will follow the additivity rule:

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

where A_{12} is the Mma of the mixed monolayer, A_i are Mma values of the single component monolayers at the same π, and x_i are the molar fractions of the components [14].

Figure 3 shows the excess area per molecule, $A_E = A_{12} - (x_1 A_1 + x_2 A_2)$ for the 8CB/5CT mixtures investigated. It is seen that the deviation from zero can here be neglected, which would indicate phase separation of the two components. This criterion is however not definitive, because additive values can indicate either complete mixing or phase separation of the components [1, 15]. Therefore additional information about the miscibility must be obtained from the relationship between the collapse pressure of the monolayers π_C and the mixture composition. This relationship for 8CB/5CT mixtures is shown in figure 4. According to thermodynamic surface phase rule [1, 15], variation of π_C with mixture composition indicates miscibility of the components, whereas a constant π_C reveals phase separation. Precisely speaking, the equilibrium spreading pressure (*esp*) should be measured as a function of mixture composition. However, such a measurement is difficult to carry out and in the case of 8CB/5CT mixtures, where the collapse pressure is clearly evident from the isotherm, it is sufficient to measure the collapse pressure instead of *esp*. From the results presented in figure 4 it follows that π at the first kink of the isotherms, which corresponds to the collapse of 8CB, remains constant over the whole range of molar fractions of 5CT in 8CB. This suggests phase separation of the components. It seems that the interactions between different molecules are weaker than the interactions between the same molecules. Probably the strong attractive

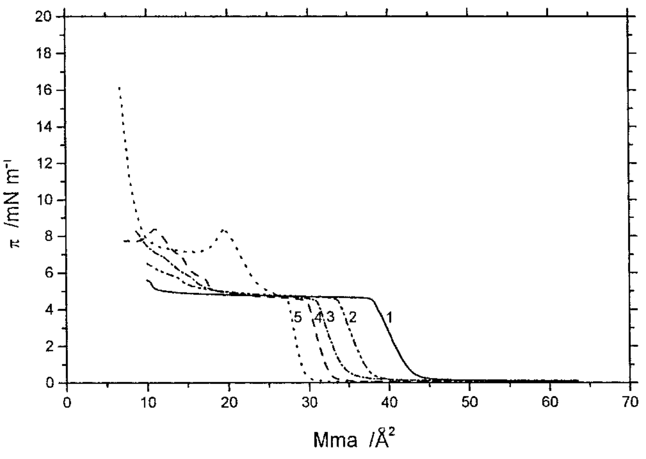


Figure 2. Surface pressure–area isotherms of Langmuir films of binary mixtures of 8CB/5CT with molar fractions MF of 5CT of 0.2 (1), 0.4 (2), 0.5 (3), 0.6 (4) and 0.8 (5) at 25°C.

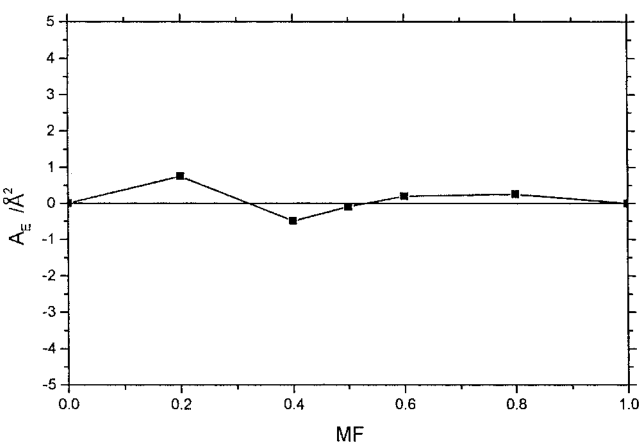


Figure 3. Plot of the deviation of the average area per molecule (A_E) for 8CB/5CT Langmuir films as a function of the molar fraction of 5CT at a surface pressure of $4\,\mathrm{mN\,m^{-1}}$.

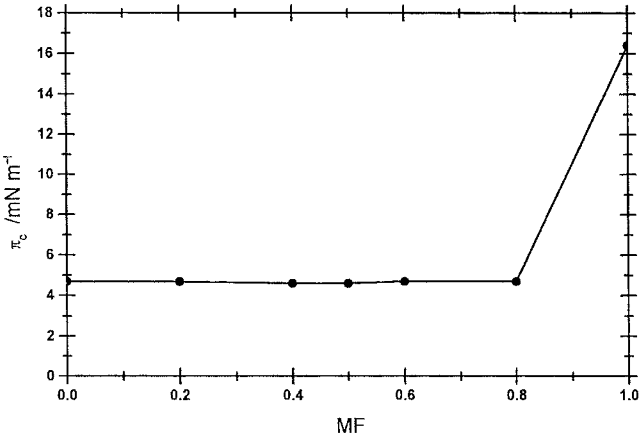


Figure 4. Collapse surface pressure of 8CB/5CT mixtures as a function of the molar fraction of 5CT.

forces between 5CT molecules possessing three phenyl rings cause the phase separation, and the 8CB molecules cannot achieve closer packing. We assume, that the mean angle between the long axes of the 8CB molecules and the normal to the water surface decreases only slightly in the mixed films.

3.2. *Brewster angle microscopy images*

Direct evidence about the molecular organization, as well as the miscibility or phase separation of 8CB/5CT mixtures in Langmuir films can be obtained by means of Brewster angle microscopy at the air–water interface. Imaging of the surface morphology was performed at different surface pressures π during slow, continuous monolayer compression. BAM images presented below correspond to various stages of Langmuir film creation.

3.2.1. *Single component monolayers*

BAM images of pure 8CB recorded by us were similar to those described previously in the literature [5, 12] and are therefore not presented here. In the region of coexistence of the gas and liquid phases (submonolayer) we observed condensed monolayer islands in equilibrium with a foam-like structure. As the surface pressure was raised, the islands packed together into a completely packed monolayer, giving a homogeneous picture. Just after the collapse point in the first plateau region, small brighter circular domains were observed, and these grew with reduction of the film area. When the domains became sufficiently large, they deformed and coalesced, because the stress at the domain boundary lines crossed a certain threshold value. Collapsed domains of 8CB in the plateau region appeared to be of homogeneous reflectivity, meaning that they have equal thickness. Thus, we have observed the transition from a uniform monolayer to a uniform multilayer. At the second rise of π, a homogeneous multilayer structure (trilayer: monolayer covered by bilayer) has been created, and by further compression (second plateau region), new circular domains have been formed.

BAM images of 5CT, to our best knowledge, have not before been presented in the literature. They appear to be quite different from the images of 8CB. In the region of submonolayer existence, no islands created by 5CT molecules are observed. The image remains dark, which means that the molecules have no tendency to

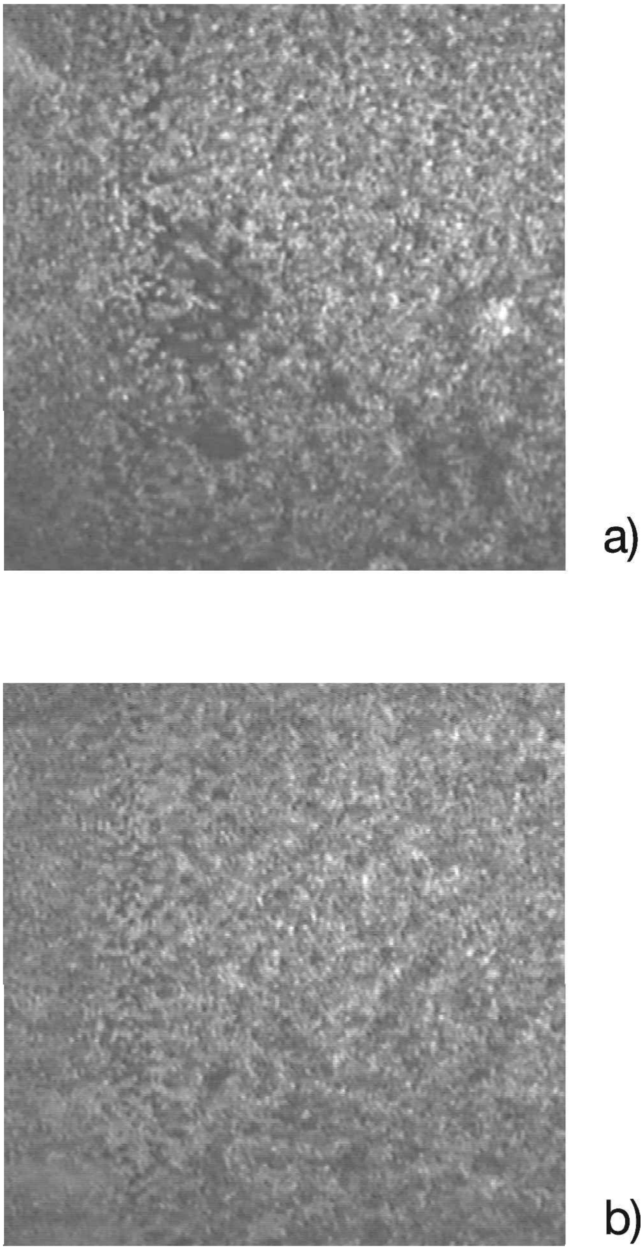


Figure 5. BAM images of a two-dimensional film of pure 5CT at surface pressure $\pi = (a)$ 12 and (*b*) 20 mN m^{-1}. The scale of the images is 0.3×0.4 mm^2.

nucleation, and single molecules are aligned perpendicular to the water surface. When the surface pressure increases (at Mma $\approx 28\,\text{Å}^2$), another picture is seen. It is represented in figure 5, which shows the Brewster angle micrographs for pure 5CT at Mma $= 25\,\text{Å}^2$ (*a*) and $15\,\text{Å}^2$ (*b*). The images resemble orange-peel and it is seen that with the increase in π they remain almost unchanged, only brightening up a little. This indicates increase in the density (greater packing of 5CT molecules). Such images confirm conclusions drawn from the surface pressure–area isotherms about the alignment and the stability of the molecules in 5CT films.

3.2.2. *Two component monolayers*

BAM images of Langmuir films formed from 8CB/5CT mixtures were recorded for various molar fractions of 5CT in 8CB, changing from 0.1 to 0.9 in steps of 0.1. If the MF of 5CT was equal to 0.1, the BAM images were very similar to those of pure 8CB. Figures 6, 7 and 8 show some examples of BAM images for MF equal to 0.2, 0.5 and 0.8, respectively. The image presented in figure 6 (*a*) corresponds to the state on the first plateau of the surface pressure–area isotherm, just after the collapse point. On the almost homogeneous monolayer, the brighter trilayer domains are observed. This

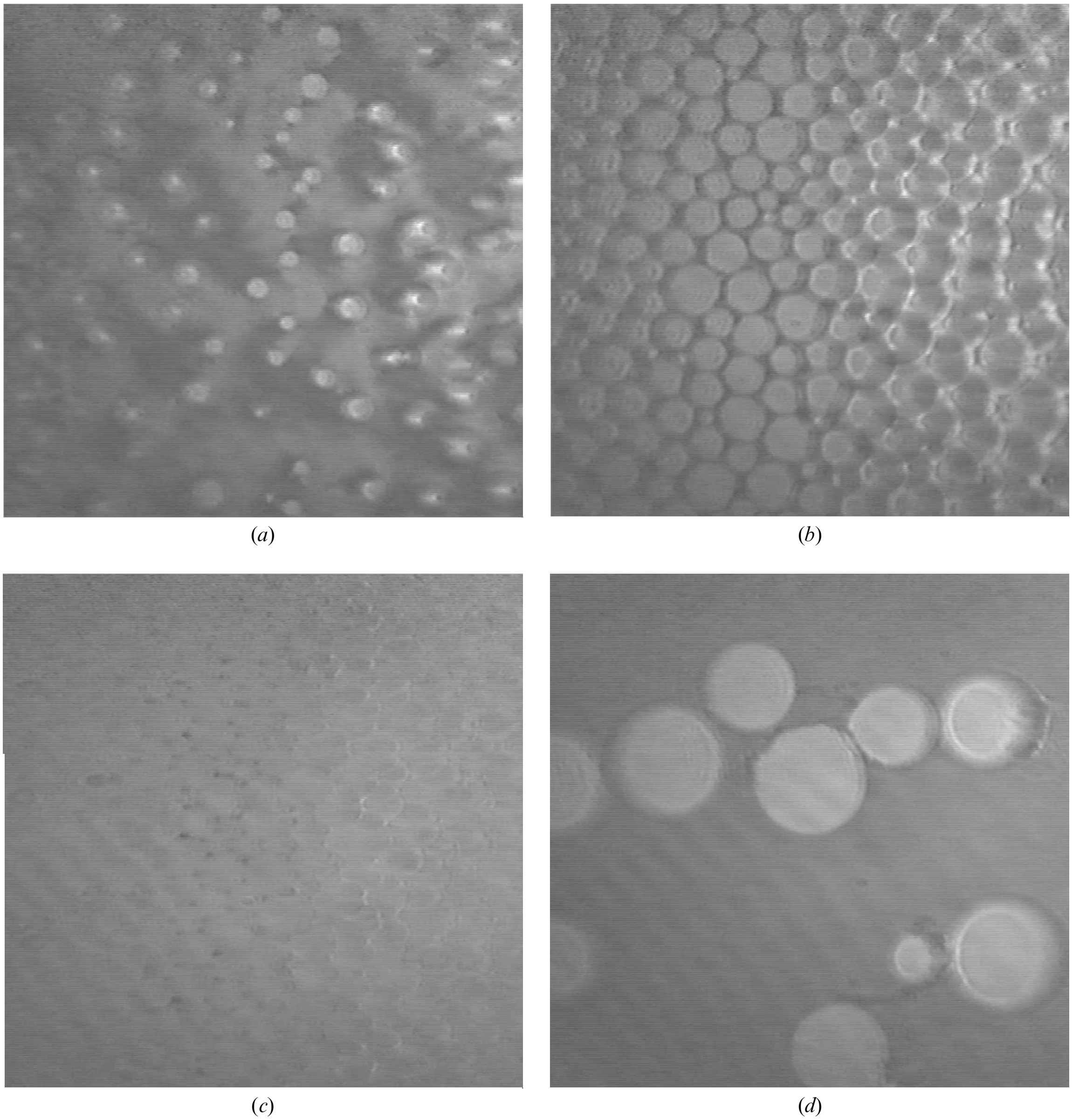
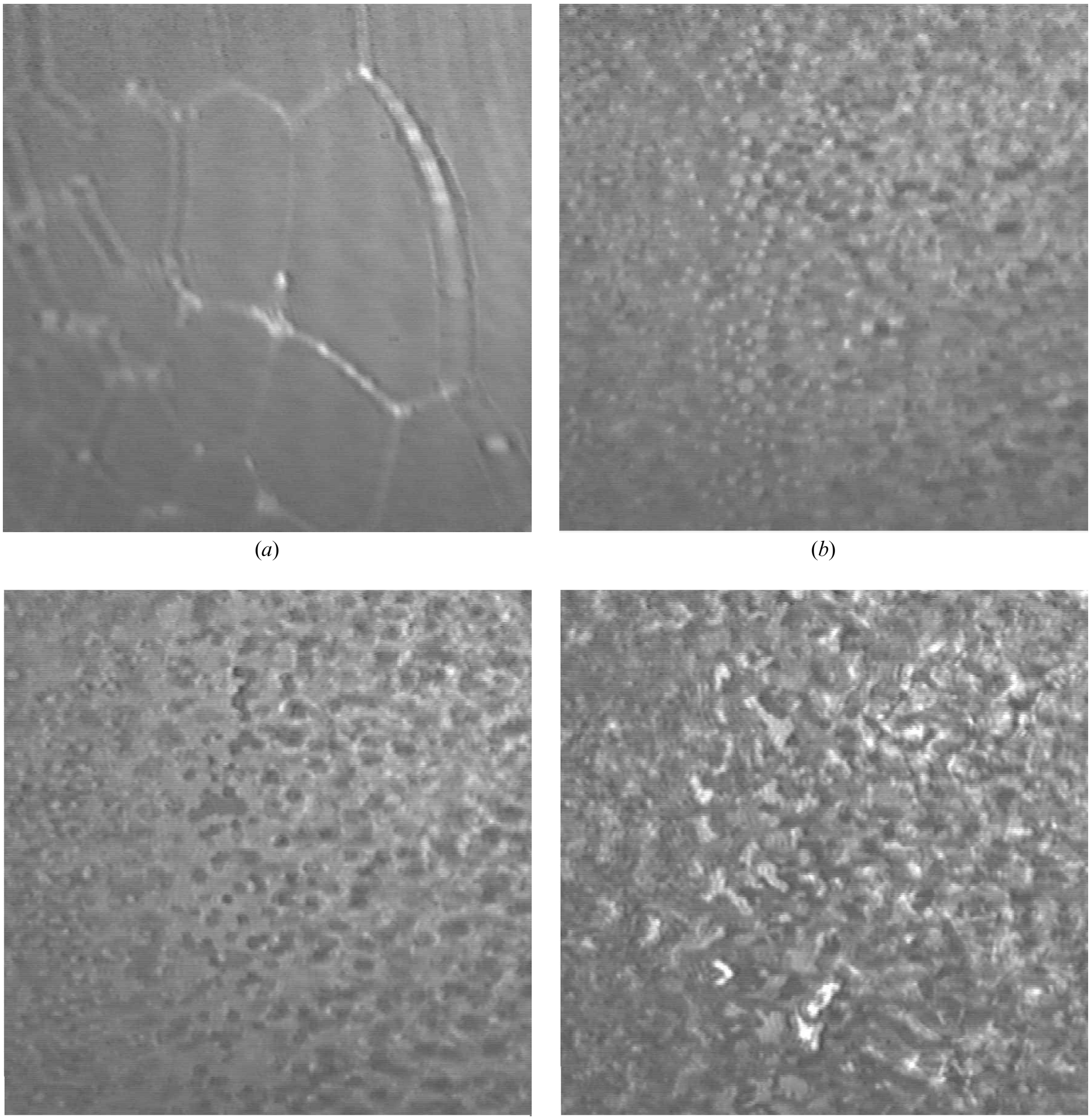

(*a*) (*b*)
(*c*) (*d*)

Figure 6. BAM images of a Langmuir film of a binary mixture of 8CB/5CT (MF = 0.2) at surface pressure $\pi =$ (*a*) 4.2, (*b*) 4.3, (*c*) 4.8 and (*d*) 5.2 mN m^{-1}. The scale of the images is $0.3 \times 0.4\,\text{mm}^2$.



(*a*) (*b*)

(*c*) (*d*)

Figure 7. BAM images of a Langmuir film of a binary mixture of 8CB/5CT (MF = 0.5) at surface pressure $\pi =$ (*a*) 0.0, (*b*) 4.7, (*c*) 5.9 and (*d*) 7.0 $\mathrm{mN\,m^{-1}}$. The scale of the images is $0.3 \times 0.4\,\mathrm{mm^2}$.

means that at such a concentration of 5CT, the molecules of 8CB are still able to keep their own alignment. However, although phase separation is not evident, a small perturbation of the molecular organization due to the presence of 5CT molecules can be noticed: brighter clouds (with smeared domain boundaries) on the darker background appear in the monolayer. This effect could be assigned to coexistence of random populations of 5CT assemblies in 8CB monolayer. However, as some morphological instabilities of the domain boundaries are observed, it would suggest that at small concentrations of 5CT partial miscibility of both components takes place. With increase in π, the domains grow continuously, figure 6 (*b*), and come into contact giving as a result a homogeneous picture, figure 6 (*c*), corresponding to the uniform bilayer formed on the monolayer (second rise of π). Figure 6 (*d*) presents the BAM image recorded in the region of the second plateau on the isotherm. The creation of circular domains is again visible, similarly to the case for pure 8CB.

The contrast between the image for pure 8CB and those for 8CB/5CT mixtures grows with increasing MF of 5CT. This is related to the tendency for phase separation to occur in the monolayers at higher 5CT concentration.

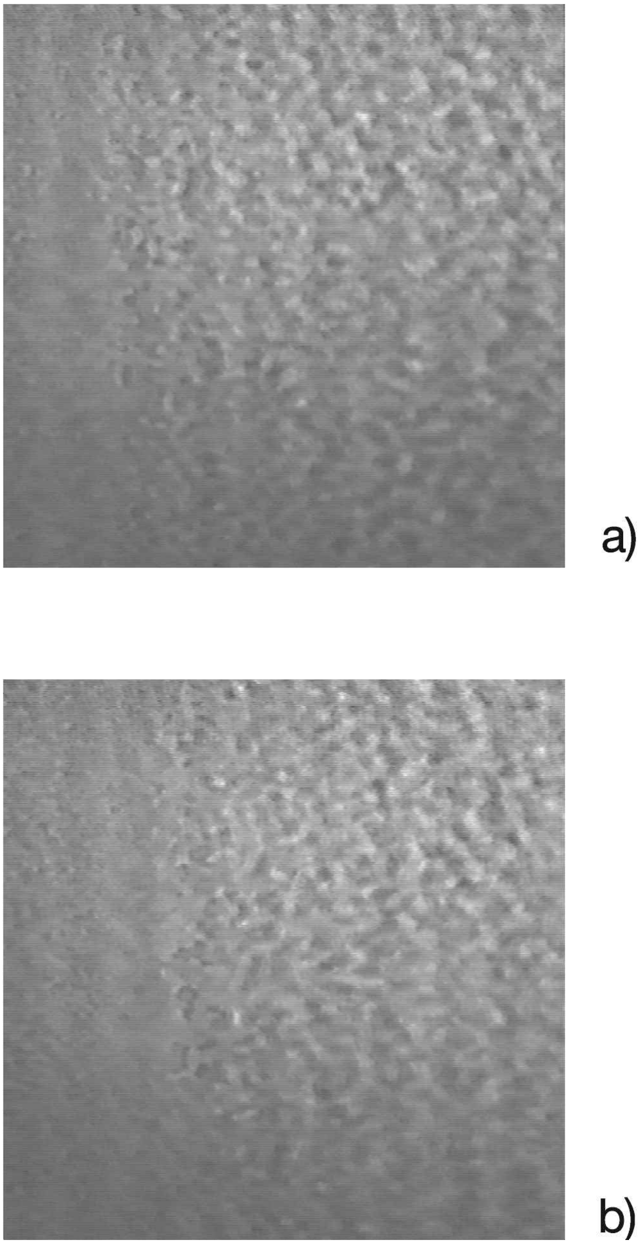


Figure 8. BAM images of a Langmuir film of a binary mixture of 8CB/5CT (MF = 0.8) at surface pressure π = (*a*) 1.0 and (*b*) 7.0 mN m^{-1}. The scale of the images if $0.3 \times 0.4\,\mathrm{mm}^2$.

BAM images recorded at MF = 0.5 (figure 7) are already quite different from those at MF = 0.1 or 0.2. At zero surface pressure, dark cellular patterns are observed and give a somewhat similar image to that in the case of pure 8CB, figure 7 (*a*). However, on increasing π, no formation of circular condensed phase domains is seen, although the phase transition regions and the plateau (characteristic for 8CB) are still present in surface pressure–area isotherm of the binary film (figure 2, curve 3). In the image presented in figure 7 (*b*) we can distinguish the dark homogeneous regions giving evidence for the presence of 8CB monolayer and small irregular brighter domains deriving from 8CB bilayer. However, the collision of these domains is strongly hindered due to the presence of 5CT molecules, confirming phase separation at such a composition of the components. With the second rise in π versus Mma, the image changes only a little: the dark regions become more distinct, figure 7 (*c*). At the state corresponding to the end of the isotherm, irregular regions with three degrees of intensity can be distinguished in the BAM image: the darkest regions correspond to the monolayer, the regions with intermediate intensity are related to the trilayer and the brightest regions can be attributed to the multilayer, figure 7 (*d*).

At the higher MF of 5CT, the BAM images become more and more similar to those of pure 5CT. Examples for MF = 0.8 are seen in figure 8. Over the whole range of the surface pressure–area isotherm recorded by us the images remained almost unchanged. Figures 8 (*a*) and 8 (*b*) present BAM images recorded at the first rise of π and almost at the end of the isotherm, respectively. However we should notice that, with respect to the image of pure 5CT, the observed orange-peel texture is smoother, reflecting the presence of the small amount of 8CB.

4. Conclusions

The surface pressure–area dependence for two liquid crystals with a terminal cyano-group, 8CB and 5CT, and their mixtures have been studied. The two-dimensional Langmuir films formed from 8CB/5CT mixtures with different compositions of the components are characterized by the absence of deviation from the additivity rule for the average molecular area, equation (1). The constant surface pressures at the collapse point π_C at different 8CB/5CT compositions have provided evidence for phase separation of both components. This has indicated that stronger interactions exist between the same molecules than between different molecules. The morphology of the Langmuir films has been monitored by Brewster angle microscopy. BAM images for pure 5CT (up to now not presented in the literature) have revealed quite a different character from those observed for pure 8CB. This has confirmed the conclusion drawn from surface pressure–area isotherms that the two components are organized quite differently at the water–air interface. 8CB, which is able to form a layered smectic phase in the bulk, has a tendency to create successive antiparallel bilayers on top of the monolayer [5]. However 5CT, which in the bulk gives only the nematic phase, forms irregular patches of bilayer or multilayer. BAM images of 8CB/5CT Langmuir films recorded at various surface pressures have confirmed the phase separation of both components in the monolayer and multilayers.

The authors wish to thank Prof. Hans Riegler for the opportunity to record BAM images at the Max-Planck Institute for Colloid and Interface Science, Berlin-Golm, Germany. This work was supported by Polish Research Project No 2 P03B 027 16 coordinated by the Committee of Scientific Research (KBN).

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