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

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To cite this Article Martynski, Tomasz , Hertmanowski, Robert and Bauman, Danuta(2002) 'Molecular organization in two-dimensional films of liquid crystalline mixtures III. Langmuir films of binary mixtures of liquid crystal materials with terminal CN o r NCS group', Liquid Crystals, 29: 1, 99 — 105

To link to this Article: DOI: 10.1080/02678290110093840

URL: http://dx.doi.org/10.1080/02678290110093840

LIQUID CRYSTALS, 2002, VOL. 29, NO. 1, 99–105

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Molecular organization in two-dimensional films of liquid crystalline mixtures

III. Langmuir films of binary mixtures of liquid crystal materials with terminal −CN or −NCS group†

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(*Received 6 June 2001; accepted 12 July 2001*)

Langmuir films of binary mixtures of the following liquid crystal materials: 4-octyl-4′-cyanobiphenyl (8CB) or 4-pentyl-4″-cyano-*p*-terphenyl (5CT) with 4-(*trans*-4′-octylcyclohexyl)-isothiocyanatobenzene (8CHBT), *trans*-4-octyl(4′-cyanophenyl)cyclohexane (8PCH) or 4-octyl-4′-isothiocyanatobiphenyl (8BT) were investigated. Surface pressure–mean molecular area isotherms were recorded at various mixture compositions. It was found that only liquid crystal materials for which the molecules have a terminal −CN group are able to form a stable monolayer at the air–water interface. Moreover, information about the miscibility or the phase separation of the two components in the mixures was obtained by using the excess area criterion and surface phase rules.

1. Introduction

As is known, some thermotropic liquid crystal materials whose molecules possess a strongly polar hydrophilic head group and a hydrophobic alkyl chain can form stable two-dimensional monolayers at the air–water interface (Langmuir films) [1–9]. Such monolayers are very simple systems in which the intermolecular interactions can be easily investigated [10]. Moreover, by studying Langmuir films formed from liquid crystal materials it is possible to obtain information about the way in which the molecules are anchored to the interface, and how these interfacial interactions affect the macroscopic molecular alignment in the bulk. On the other hand, it has to be kept in mind that the kind of mesophase for a thermotropic mesogen is normally related to the bulk. The liquid crystals investigated [1–9] were studied in monolayers mostly well below the transition temperature from bulk crystalline to bulk liquid crystalline phases. Thus, the question arises as to how far the ability to form the appropriate phase in the bulk influences the molecular organization in the ultrathin film at the air–water interface.

It is, of course, possible to study monomolecular Langmuir films containing more than one chemical compound, and such liquid crystalline monolayers are of considerable importance because of their relevance to applications, e.g. in liquid crystal displays, where mostly multi-component mixtures are used in order to obtain the required properties for the mesophase. Therefore, we have undertaken the study of Langmuir films formed from binary mixtures of liquid crystal materials. In our preceding papers [8, 9] we investigated mixtures of two mesogens with the −CN terminal group: 4-octyl-4′-cyanobiphenyl (8CB) and 4-pentyl-4″-cyano-*p*-terphenyl (5CT), as well as mixtures of 8CB and 5CT with a perylene-like dye which is able to form a columnar hexagonal liquid crystalline phase in the bulk [11].

In this paper we present the results of the thermodynamic study of Langmuir films formed from binary mixtures of 8CB or 5CT with three liquid crystal materials having the strongly polar −CN or −NCS terminal group, namely: 4-(*trans*-4′-octylcyclohexyl)isothiocyanatobenzene (8CHBT), *trans*-4-octyl(4′-cyanophenyl)cyclohexane (8PCH) or 4-octyl-4′-isothiocyanato-biphenyl (8BT). These liquid crystal materials create various mesophases in the bulk (nematic, smectic A, CrE). In our investigations we investigate the miscibility of the components and the intermolecular interactions in the

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†For parts I and II see [8] and [9], respectively.

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2002 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290110093840

ultrathin films. Moreover, we try to obtain information about the influence of the kind of mesophase in the bulk and the molecular structure of the liquid crystal on the ability to form a stable monolayer at the air–water interface, as well as on the molecular packing in a Langmuir film.

2. Experimental

The liquid crystal materials 8CB and 5CT were purchased from E. Merck (Germany), while 8CHBT, 8PCH and 8BT were synthesized in the Prof. R. Dąbrowski Laboratory of the Military Academy of Technology, Warsaw (Poland). All substances were used without further purification; their phase transition temperatures in the bulk, determined on the basis of textures observed by means of polarizing optical microscopy in conjunction with a hot stage, were in substantial agreement with literature data [12–16] and were as follows (all in °C):

8CB	Cr 21.0 SmA 33.5 N 40.2 I
5CT	Cr 131.6 N 240.0 I
8CHBT	Cr 28.0 N 48.0 I
8PCH	Cr 37.3 N 56.5 I
8BT	Cr 30.4 CrE 69.4 I.

The liquid crystal materials were dissolved in chloroform (Uvasol, for spectroscopy, E. Merck) to give stock concentrations of 0.1 mM and kept refrigerated. The concentrations of the solutions were confirmed spectroscopically. Mixed solutions of 8CB or 5CT with 8CHBT, 8PCH or 8BT of selected molar fractions were prepared at room temperature shortly before spreading at the air–water interface.

The monolayers of the pure liquid crystal materials and the binary mixtures were spread from chloroform solutions onto the deionized water subphase and surface pressure–area isotherms were measured by a Wilhelmi plate balance in a Minitrough (KSV Instruments Ltd., Finland). Further experimental details about Langmuir film preparation are given elsewhere [8].

3. Results and discussion

Previously [1, 2] it was found that the amphiphilic character of liquid crystals and their insolubility in water are not sufficient conditions for the formation of stable and compressible monolayers at the air–water interface. From our study, the mesogens 8CHBT and 8BT are examples of compounds which are unable to form a homogeneous monomolecular layer when they are spread onto a pure water subphase. 8CHBT gave a monolayer which did not resist barrier compression; the molecules were expelled and the formation of an irregular bulk phase was observed. It was suggested [1], that such a behaviour may be connected with the replacement of the benzene ring by the cyclohexane ring, which causes a reduction in packing efficiency. However, our results for 8PCH do not confirm this suggestion: in spite of the presence of the cyclohexane ring, 8PCH is able to form a stable and compressible Langmuir film. In the case of 8BT, three-dimensional (3D) microcrystallites were created, presumably as a result of the interactions leading to the crystal E phase in the bulk. This highly ordered mesophase is often called a 'soft smectic crystal' and apart from the smectic layer structure is characterized by a strong herringbone array [17, 18]. Such a well-packed structure may prefer a 'crystal-like' (3D) arrangement and prevent the formation of the monomolecular (2D) layer. However, when 8CHBT or 8BT are mixed with 8CB or 5CT, which are known as liquid crystals that form stable floating monolayers at the air–water interface [1, 3, 4, 8], compression is possible and we obtained surface pressure (π)–mean molecular area (*Mma*) isotherms. π–*Mma* isotherms for the binary mixtures of 8CHBT, 8PCH and 8BT with 8CB or 5CT at various mixture compositions are presented in figures 1–3.

From figure 1 (*a*), which shows the isotherms for 8CHBT/8CB mixtures, it is seen that already at the molar fraction (*MF*) of 8CHBT of 0.2, the surface pressure at the collapse point has diminished rapidly and no distinct plateau is observed. When the content of 8CHBT increases, the defined collapse point is missing and the surface pressure rises at very small *Mma* only. This means that the formation of homogeneous monomolecular layer is impossible.

The Langmuir film from 5CT is more stable and rigid than that from 8CB [1, 8]. Therefore, the behaviour of the monolayers of 8CHBT/5CT and 8CHBT/8CB mixtures is different. In the case of Langmuir films from 8CHBT/5CT in π–*Mma* isotherms, figure 1 (*b*), the collapse point is remarkable, occurring as late as a *MF* of 8CHBT equal to 0.6. However, at a higher content of 8CHBT the formation of a defined monolayer is no longer possible.

Figure 2 (*a*) presents π–*Mma* diagrams for 8PCH/8CB mixtures for the whole region of *MF*. It is seen that all the isotherms are very similar: between 55 and 45 Å^2, increase in the surface pressure up to the collapse point occurs, indicating the appearance of the completely homogeneous monolayer. However, the collapse point always occurs at *Mma* larger by a factor of 2–3 than the theoretical molecular cross-section (≈ 20 Å^2), which in the case of 8CB was explained in terms of strong repulsive interactions between the electric dipoles of the cyano groups [4]. As a result of such interactions, the 8CB molecules create an angle of about 60° with the normal to the air–water interface [4]. Our investigations indicate that 8PCH molecules in the Langmuir film behave almost identically to 8CB molecules.

(*a*)

(*b*)

Figure 1. Surface pressure–area isotherms of Langmuir films for: (*a*) pure 8CB (1) and binary mixtures of 8CHBT/8CB with molar fractions *MF* of 8CHBT of 0.2 (2), 0.4 (3), 0.5 (4) and 0.6 (5); (*b*) pure 5CT (1) and binary mixtures of 8CHBT/5CT with molar fractions *MF* of 8CHBT of 0.2 (2), 0.4 (3), 0.5 (4), 0.6 (5) and 0.8 (6).

The results for various *MF* values of 8PCH in 5CT are presented in figure 2 (*b*). It is seen that with rise in the *MF* of 8PCH, the monolayer collapses at regularly larger and larger *Mma* values and the plateau region becomes clearer. At concentrations of 0.2 and 0.4 *MF*, two distinct kinks in the isotherm are seen. However, the second kink occurs at a surface pressure significantly lower than in the case of pure 5CT. This would suggest that the rigidity in the mixed monolayers (even at small 8PCH content) decreases in comparison with the rigidity of 5CT. Thus, the behaviour of 8PCH/5CT mixtures in Langmuir films is very similar to that of 8CB/5CT mixtures [8].

The isotherm data for mixed 8BT/8CB monolayers are shown in figure 3 (*a*). With the increase in *MF* of 8BT, the Langmuir film collapses at regularly smaller and smaller *Mma* values. The plateau region becomes narrower and at an 8BT *MF* less than 0.5, no defined plateau is observed and the collapse point occurs at *Mma* equal to $\approx 15\,\text{Å}^2$. This value is too small for even

(*a*)

(*b*)

Figure 2. Surface pressure–area isotherms of Langmuir films for: (*a*) pure 8CB (1) and binary mixtures of 8PCH/8CB with molar fractions *MF* of 8PCH of 0.2 (2), 0.4 (3), 0.5 (4) and 0.6 (5), 0.8 (6) and 1.0 (7); (*b*) pure 5CT (1) and binary mixtures of 8PCH/5CT with molar fractions *MF* of 8PCH of 0.2 (2), 0.4 (3), 0.5 (4), 0.6 (5) and 0.8 (6) and 1.0 (7).

the most dense packing of the molecules in a monolayer. Therefore, such behaviour must suggest the creation of the next layer on top of the monolayer floating on the water.

In the case of Langmuir films from 8BT/5CT mixtures, the surface pressure π_C and *Mma* at collapse point decrease systematically with the increase in *MF* of 8BT up to 0.6. At higher content of 8BT, monolayer formation at the air–water interface is no longer observed.

In order to establish whether in the two-component Langmuir film, miscibility or phase separation occurs, the mean molecular area and the collapse pressure were analysed in relation to monolayer composition. 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 [10]:

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

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

(*a*)

(*b*)

Figure 3. Surface pressure–area isotherms of Langmuir films for: (*a*) pure 8CB (1) and binary mixtures of 8BT/8CB with molar fractions *MF* of 8BT of 0.2 (2), 0.4 (3), 0.5 (4) and 0.6 (5), 0.8 (6); (*b*) pure 5CT (1) and binary mixtures of 8BT/5CT with molar fractions *MF* of 8BT of 0.2 (2), 0.4 (3), 0.5 (4), 0.6 (5) and 0.8 (6).

Figures 4 and 5 show the excess area per molecule $A_E = A_{12} - (x_1 A_1 + x_2 A_2)$ for the mixtures of 8CHBT, 8PCH or 8BT with 8CB and 5CT, respectively. It is seen from these figures that for 8PCH/8CB, as well as for 8PCH/5CT and 8CHBT/5CT mixtures, the deviation of A_E from zero can be neglected; this would indicate phase separation of the components. This criterion is however not definitive, because agreement with equation (1) can indicate either phase separation or complete mixing of the components [10, 19]. Additional information about the miscibility of two components can be obtained from the surface phase rule [10]. This rule states that if the components are immiscible, the equilibrium spreading pressure (*esp*) should be constant independently of the mixture composition. In some cases, however, the *esp* value is difficult to determine and therefore, for systems where the film collapse point is easily detectable it is sufficient to estimate the collapse pressure π_C instead of *esp*. From figures 1 (*b*), 2 (*a*) and 2 (*b*) it follows that π_C remains almost constant over the whole molar fraction, which confirms the phase separation of two components.

In the case of 8CHBT/8CB mixtures (figure 4), we observed mostly a negative deviation from the additivity rule. This means that the area occupied by the mixed

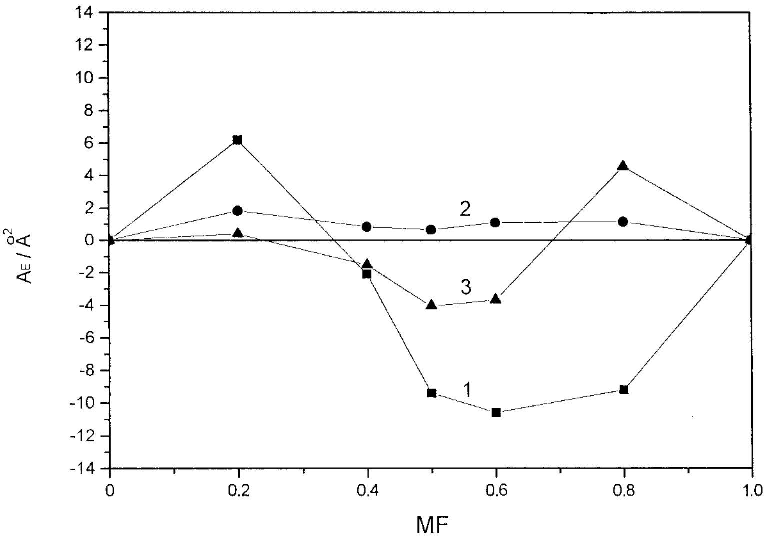

Figure 4. Plot of the deviation of the mean molecular area per molecule (A_E) for Langmuir films of binary mixtures of different liquid crystal materials with 8CB as a function of the molar fraction of 8CHBT at $\pi = 1.0\,\mathrm{mN\,m^{-1}}$ (1), 8PCH at $\pi = 4.0\,\mathrm{mN\,m^{-1}}$ (2) and 8BT at $\pi = 1.5\,\mathrm{mN\,m^{-1}}$ (3).

film at $\pi = 1.0\,\mathrm{mN\,m^{-1}}$ is smaller than the area of the same amount of the separate pure components, which suggests the existence of an attractive interaction among the 8CHBT and 8CB molecules. This observation, in conjunction with the decrease of π_C even after a small addition of 8CHBT indicates the miscibility of both components in 8CHBT/8CB mixtures in the Langmuir film.

The A_E values for 8BT/8CB mixtures (figure 4) vary only slightly with film composition. However, the π_C value, after a rapid decrease at a *MF* of 8BT of 0.2, remains constant. This gives evidence that the two components, 8BT and 8CB, are at most partially miscible in the film at the air–water interface.

For 8BT/5CT mixtures (figure 5), a positive deviation from the additivity rule, equation (1), is observed; this indicates the dominance of repulsive interactions between the 8BT and 5CT molecules. The π_C value changes distinctly with mixture composition, and therefore the conclusion can be drawn that 8BT and 5CT are perfectly miscible in the Langmuir film.

4. Conclusions

Binary mixtures of liquid crystal materials with terminal −CN or −NCS groups have been studied as Langmuir films. From the results obtained it follows that all the mesogens for which the molecules have a terminal −CN group (8CB, 5CT, 8PCH) can form a homogeneous monolayer at the air–water interface, whereas the mesogens with a terminal −NCS group (8BT, 8CHBT) are not able to create compressible Langmuir films. However, when 8BT and 8CHBT are mixed with 8CB or 5CT it is possible to obtain a floating monolayer on the water surface.

Taking into account the thermodynamic surface phase rule, as well as the excess area criterion, from the analysis

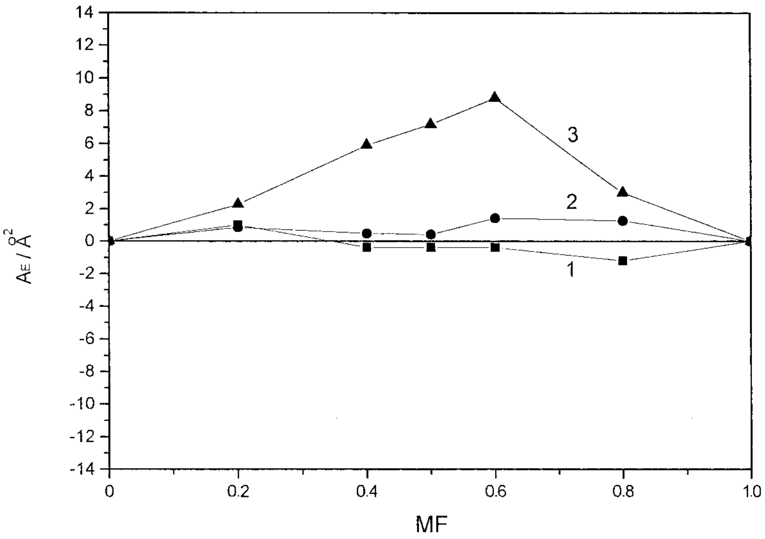

Figure 5. Plot of the deviation of the mean molecular area per molecule (A_E) for Langmuir films of binary mixtures of different liquid crystal materials with 5CT as a function of the molar fraction of 8CHBT at $\pi = 7.0\,\mathrm{mN\,m^{-1}}$ (1), 8PCH at $\pi = 4.0\,\mathrm{mN\,m^{-1}}$ (2) and 8BT at $\pi = 4.0\,\mathrm{mN\,m^{-1}}$ (3).

of *π–Mma* isotherms it follows that: (i) 8CHBT is fully miscible only with 8CB (attractive interactions dominate), whereas in 8CHBT/5CT mixtures phase separation occurs; (ii) in 8PCH/8CB and 8PCH/5CT mixtures, the two components are not miscible, similarly to the case for 8CB/5CT mixtures [8]; (iii) 8BT is partially miscible with 8CB and fully miscible with 5CT (repulsive interactions are observed).

It seems, that the ability to form stable monolayers at the air–water interface is determined mainly by the molecular structure of the terminal polar group. The kind of mesophase created in the bulk, as well as the structure of the remaining part of the molecule (benzene or cyclohexane ring) have a secondary effect. However, the miscibility and the interaction type are individual properties of the given system.

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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