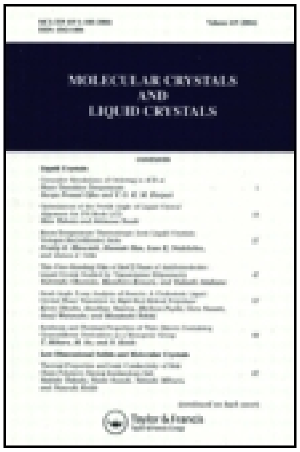

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Bowl-Shaped Liquid Crystals at the Air-Water Interface

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BOWL-SHAPED LIQUID CRYSTALS AT THE AIR-WATER INTERFACE

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We studied, at the air-water interface, monolayers of bowl-shaped liquid crystals (BLC). These compounds exhibit columnar mesophases. They consist of an either rigid or flexible central core to which are attached several hydrophobic aliphatic chains. We investigate experimentally in this work, using different technique (mainly Langmuir balance and displacement current technique), the molecular organization of these compounds at the air-water interface and we discuss some of their structural aspects. We show also the flexibility of the central core in the case of the 4BCD and discuss its effect on the structure of the monomolecular films.

1. Introduction

We were interested in previous works [1-5] in the structural and the dynamic behavior of Langmuir films of pyramidic liquid-crystals [6-8]. The molecules of these compounds are pyramidic-like. They admit in average a three fold symmetry axis. In the bulk phase, these compounds exhibit columnar mesophases which are stable at room temperature. The interests of this study derives from different points. The first one is their peculiar shape; in particular, the hydrophilic part of the molecule is located between two hydrophobic parts and not, as usual, at one edge of the molecule. The second point is the existence of a net dipole moment of the molecules along the C_3 symmetry axis of the molecules.

Since different possible orientations of the net molecular moment dipole are allowed at the air-water interface, one may speculate on the existence of monolayers and thin films of new structures. These compounds are also a good candidate for a better understanding of the correspondence between the phases of amphiphilic compounds in monolayers at the air-water interface and bulk mesophases. The organization of mesogenic compounds at the air-water interface should shed light on short range interactions between molecules Whereas the self-organization in liquid-crystalline phases results from LC molecule-LC molecule interactions, the organization also depends on the LC molecule-aqueous subphase interactions. This point is crucial in the case of columnar liquid crystals. Molecular interactions within the film promote the formation of columns, whereas, depending on the shape of the molecule and the distribution of hydrophilic and hydrophobic elements, the interactions with the water subphase fix the orientation of an individual molecule at the interface, which would not allow the formation of columns. In the case of Bowlic liquid crystals, the balance between both types of interactions can be changed by varying the hydrophilic part and the side-chain length. In this paper, we shall discuss some structural aspects of the Langmuir films of three members of the pyramidic liquid crystals class from this point of view.

The fact that these molecules carry a net dipole moment μ, oriented along their symmetry axis, make the displacement current technique very suitable to their study at the air water interface. The displacement current technique consists of an electrical current measuring technique [9,10]. In this technique, the monolayer is compressed under an electrode. During compression, an induced charge is generated on the electrode when either orientation of polar molecules on the interface or the number of molecules under the electrode is changed. A displacement current I flows in the electrical circuit and can be measured by means of a very sensitive electrometer

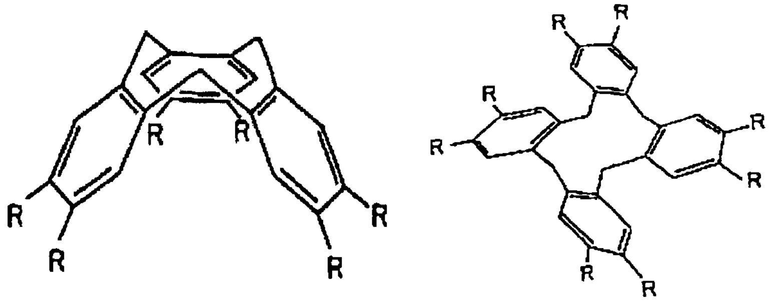
2. Experimental

The compounds used for films preparation were synthesized and purified by Zimmermann [6]. The columnar structure of these mesophases in the bulk was shown by optical microscopy [6,7] and x-ray patterns[11]. Referring to the nature of the central core of the molecules, two classes of compounds were used: a first class (3BCN, named previously PLC) for which molecules present a rigid central core to which six long side chains are bound and a second class (4BCD) for which molecules consist of an admitted high flexible central core to which eight long side chains are bound (Figure 1) [9]. For each class, the lateral chains were alkanoyloxy C_nH_{2n+1} COO-.

The different used compounds in this study are reported in the table below:

Class	**Lateral chains $C_{n-1}H_{2n-1}$COO-** **n**
3BCN-I	9, 14, 15
4BCD-I	12,14

The bowlic compounds were spread from a C = 2.5 10^{-4} M chloroform solution (Normapur, Prolabo). The deionized water was purified using a UHQ II Elga system. The isotherm diagrams of surface film pressure π versus molecular area A were obtained with a Lauda trough, at 20° C and pH = 5.7. The trough temperature was controlled by using RM6 Lauda thermostat. The surface pressure was measured with an accuracy of about 0.1mN.



(a) (b)

Figure 1: Schematic representation of the structure of the 3BCN (a) and 4BCD (b) bowlic compounds. The lateral chains R are alkanoyloxy $C_{n-1}H_{2n-1}COO-$.

The current measuring device was monitored together with the Langmuir balance. Figure 2 shows the experimental set-up. In this technique, two stainless steel electrodes, of rectangular shape, are placed to be parallel to the air-water interface. Electrode 1 was suspended in air and electrode 2 was immersed in water. The area of electrode 1 was $S_e = 80$ cm^2. It was electrically shielded by a surrounding metallic box. For all our experiments, we adjusted the distance between electrode 1 and air-water interface to $d_e = 1 \pm 0.2$ mm by using a micrometer screw. The displacement current I was measured by an electrometer (Keithley 617) connected to a computer. Simultaneously the surface pressure-molecular area isotherm were recorded. The accuracy of the current measurements was about 5.10^{-3} pA. To compensate water evaporation, the water level was maintained constant using a LevelOmatic device frc

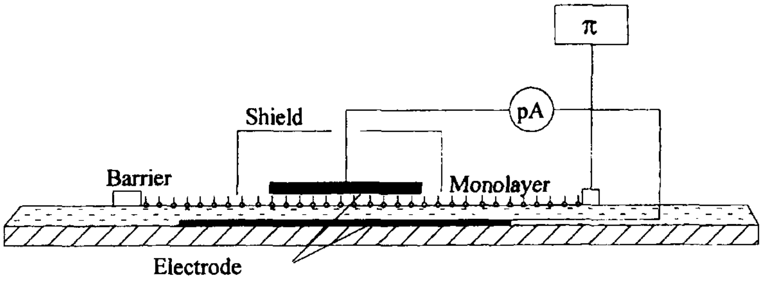


FIGURE 2 Schematic representation of the displacement current measurement device.

III-Results and Discussion

Surface pressure vs molecular areas isotherms: Figures 3 and 4.

3BCN compounds: We report in Figures (3a , 4a) the surface pressure-area isotherm obtained for 3BCN-I/(n=9, 14) respectively. For 3BCNI/9, the molecular organization of this compound has been discussed in details previously[1,2]. The molecular area range 3 nm^2 - 2.30 nm^2 corresponds to a liquid-expanded phase (LE). In this phase, the base of the pyramids are "flat" lying at the air-water interface: side-on (SO) arrangement. The molecular areas lower than 0.66 nm^2 correspond to a condensed phase are found to be about A = 66 $Å^2$. One can explain the low molecular areas of this phase by considering an Edge On (EO) arrangement [2-5,13,14] for which the base of the pyramidic core is perpendicular to the air-water interface, three of the aliphatic chains of the molecules are into the water subphase and the three others are in the air.

The main shape of the π-A isotherm of 3BCNI/14 can be also explained by an LE -EO phase transition. We have shown in a previous work [7] that the π-A isotherm of 3BCN-I/15 shows that the molecular area in the condensed phase is 1.25 nm^2 which is compatible with a SO arrangement if we consider that the lateral hydrocarbon chains are in a condensed or solid phase.

4BCD compounds: Figure (5a, 6a) shows the surface pressure isotherm of the 4BCD-I/12 and 14. The first compound exhibits a SO phase where the molecular area is about 1.5 nm^2 (which corresponds to an area about 0.19 nm^2 per hydrocarbon chain) and an EO phase where the molecular area is about 0.75 nm^2 (which corresponds also to an area about 0.19 nm^2 per hydrocarbon chain due to the EO arrangement). At 20 °C, the compound 4BCD-I/14 exhibits only a SO phase where the molecular area is about 1.25 nm^2 (which corresponds to an area about 0.16 nm^2 per hydrocarbon chain which is too small).

Influence of the hydrophobic chains length: the effect of the aliphatic chains length is shown comparing the results obtained on the 3BCNI/14 and 3BCNI/15 [3,4]. We note that the molecular area for the LE phase are getting smaller as the length of the chains is getting greater. This result is in agreement with the general behavior of classical amphiphiles at the air-water interface [15]. We would like to point out that at about 22 °C, the π-A isotherm of the 3BCNI/15 shows the occurrence of an EO-SO phase transition. For the two studied 4BCD compounds we notice also the same effect induced by increasing the length of the lateral chains : the SO / EO phase transition is inhibited when the number of carbon atoms is increased. This effect may be understood since the EO arrangement forces the lateral hydrophobic chains to be in contact with water.

Influence of the core mobility: Comparing now the π–A isotherm diagrams of 3BCN and 4BCD films, we notice that although each 4BCD molecule has eight aliphatic chains, the molecular area in the side-on phase are half smaller than for the 3BCN molecules which possess six chains. This behavior should be attributed, in the case of the 4BCD, to the already suggested [15] high flexibility of the bowlic core which allows for a close packing of the hydrocarbon chains. This close packing of the lateral chains is allowed by a "saddle" conformation of the bowlic core where four hydrophilic groups are anchored at the air-water interface.

Displacement current vs. molecular area isotherms:

The increase in displacement current is related to changes in i) the number N of spread molecules under the electrode 1, and ii) the perpendicular component μ_Z of the mean molecular dipole moment [13].

$$I = \frac{\mu_z}{d_e}\frac{dN}{dt} + \frac{N}{d_e}\frac{d\mu_z}{dt} \qquad (1)$$

If we assume that the surface potential ϕ_S of the water does not change during the compression of a homogeneous phase, where the molecular dipole moment orientation remains constant, then a displacement current I flows between the two electrodes which intensity is given by :

$$I = \frac{\mu_z}{d_e}\frac{dN}{dt} = \frac{\mu_z}{d_e}\frac{S_e L v}{N_0 A^2} \quad , \qquad (2)$$

where L, v and N_0 represent respectively the width of the trough, the barrier speed and the total number of the spread molecules.

3BCN compounds:

3BCN-I/9: Figure 3b shows a I-A diagram obtained for a film of 3BCNI/9 which was compressed from a molecular area of about 4.2 nm^2 until 1.2 nm^2. The spread volume was equal to 70 μl, the barrier speed was v = 0.4 mm/s and the electrode height was d_e = 1 mm. We would like to point out that we obtained an important variation of the displacement current I starting at large molecular areas and ending when the surface pressure starts to increase. This feature was found for all the studied compounds and for all core orientations. We attribute this variation of the current I to a rising of the lateral hydrocarbon chains under compression. We will discuss this effect in more details at the end of this paragraph.

The measured value of the displacement current in these experimental conditions for a molecular area of 2.5 nm^2 was I = + 0.04 pA. The polarity of the induced current is positive, i. e. the current flows from the upper electrode towards the electrode 2. The net dipole moments are oriented from water towards electrode 1.

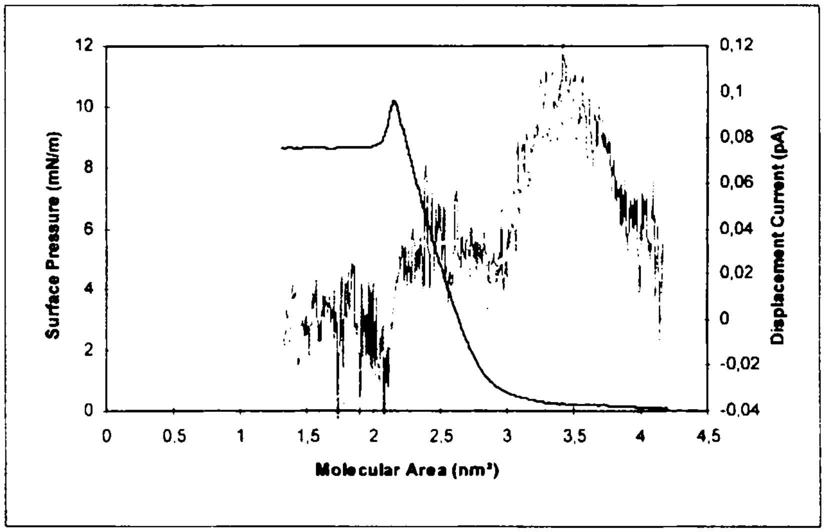


FIGURE 3: (3a) π-A (Thick line) and (3b) I-A (thin line) diagrams of 3BCN-I/9 film spread at the air-water interface and compressed from the liquid expanded phase. Barrier speed : 0.4 mm/s; pH = 5.7; T = 20°C; electrode height d_e = 1 mm.

From the above measured value of the current, at A = 2.5 nm^2 , we can deduce a value of μ_z equal to 3.3 D. This total dipole moment μ_z results from two contributions: i) the hydrophilic part (-COO-) to which is associated a dipole moment noted μ_1, and ii) the terminal C-H bond of the aliphatic chains to which is associated a dipole moment noted μ_2. The value of the vertical component μ_{z1} of μ_1 is about 0.5 D, in the expanded phase [19] and the vertical component μ_{z2} of μ_2 is about μ_{z2} = 0.2 D [12,13]. Since both μ_{z1} and μ_{z2} are directed in the same way, from water to air, a resulting value of μ_z for our pyramidic molecule is $\mu_z = 6(\mu_{z1} + \mu_{z2}) \approx 4.2$ D. This value is in good agreement with the value of μ_z deduced from the above measured displacement current.

It is interesting to note the existence of a break in the current increase during compression of the side-on phase, at a molecular area about 2.5 nm^2. This break has also been reported by M. Iwamoto *et al.*. It has been explained by a decrease of μ_z, due to a change in the configuration and in the moment bonds of the hydrophilic carboxylic head group.

Therefore, in our study a similar re-arrangement may occur within the hydrophilic part of the pyramidic molecule, which is the ester function that links the aliphatic chains to the pyramidal core.

At the start of the side on-edge (SO-EO) transition, we observed an abrupt jump of the current I from +0.02 pA to -0.01 pA. This jump to a negative value is a direct proof for the already stated SO-EO transition. Indeed, since a horizontally oriented dipole induces no charges on the upper electrode, the transition of the molecular dipole moment from a vertical to a horizontal direction leads to a decrease of the electrode charge. However, during the SO-EO transition two phases coexist. This means that all the dipoles do not rotate to the horizontal direction at the same time. Consequently, the induced displacement current I at a given molecular area A, results from two currents. The first one, which have a positive polarity, is due to the increase of the number N of the still vertically oriented dipoles (SO phase) at the given molecular area A. The second one, which have a negative polarity, is due to the decrease of N following the molecular reorientation. Thus it is necessary in this case to calculate the net variation dN/dt.

According to the lever rule, the number N of the vertical dipoles under the upper electrode, at the molecular area A, is given by :

$$N = \frac{S_e}{A}\frac{(A - A_{EO})}{(A_{SO} - A_{EO})}$$

where A_{SO} is the molecular area in the side on phase and A_{EO} the molecular area in the edge on phase. From the π-A isotherm, we can deduce $A_{SO} = 3\ \mathrm{nm}^2$ and $A_{EO} = 0.66\ \mathrm{nm}^2$ by extrapolating to zero π pressure. The net variation of N is :

$$\frac{dN}{dt} = -\frac{A_{EO}S_e vL}{(A_{SO} - A_{EO})N_0A^2}$$

Hence we can deduce the expression of the displacement current I' during the SO-EO transition:

$$I' = -\frac{\mu_z}{d_e}\frac{A_{EO}S_e vL}{(A_{SO} - A_{EO})N_0A^2} \qquad (3)$$

If we apply equation (2) to calculate I' at a molecular area equal to 2 nm^2 and in the experimental conditions used in figure 4, we find $I'_{calc} = -0.014$ pA which is of the same order as the measured displacement current I' = - 0.01 pA for a molecular area A = 2 nm^2. Thus, we showed clearly by means of the displacement current technique that the main transition corresponds to a side on -edge on phase transition .

3BCN-I/14: Figure (4. B) shows an I-A diagram obtained for a film of 3BCNI/14 for a cycle of compression-decompression. We observe a quasi-perfect symmetry of the I-A isotherm obtained during compression and decompression. Note that we obtained a similar results for the 3BCN-I/9. This result indicate a total reversibility of the processes involved. The monolayer was compressed from a molecular area about 7.5 nm^2 to 2.2 nm^2. The spread volume was equal to 40 μl, the barrier speed was v = 0.4 mm/s and the electrode height d_e = 1.5 mm. The measured value of the displacement current in these experimental conditions for a molecular area of 3.0 nm^2 was I = + 0.03 pA. We can deduce a value for the dipole moment of the 3BCN molecule about 3.0 D. For this compound, the side-on/edge-on phase transition has been also observed but the corresponding data are not represented for sake of simplicity.

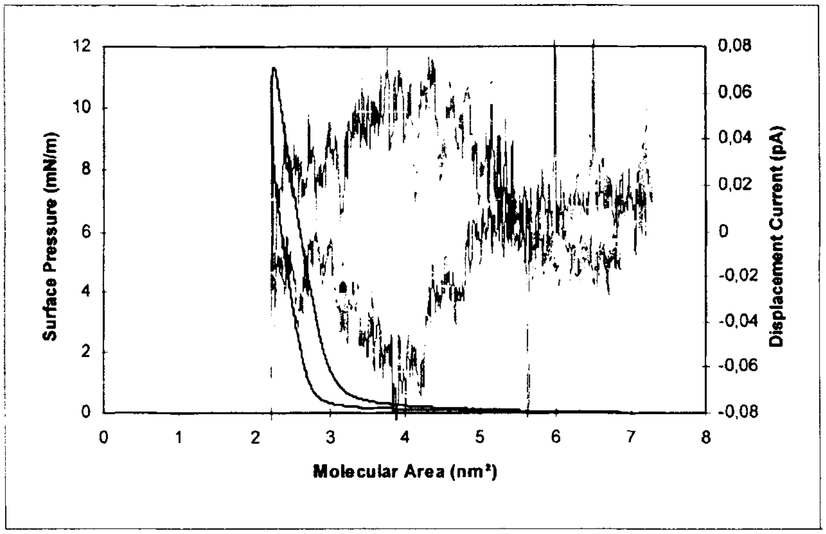


FIGURE 4 π-A (thick line) and I-A (thin line) diagrams of 3BCN-I/14 film spread at the air-water interface and compressed from the liquid expanded phase. Barrier speed : 0.4 mm/s; pH = 5.7; T = 20°C; electrode height d_e = 1.5 mm.

4BCD compounds:

4BCD-I/12: Figure (5. b) shows the I-A diagrams obtained for the film 4BCN-I/12 which was compressed from a molecular area of about 2.2 nm^2 to 0.8 nm^2. The spread volume was equal to 130 μl, the barrier speed was v = 0.4 mm/s and the electrode height was equal to d_e = 1 mm. The measured value of the displacement current in these experimental conditions for a molecular area about 1.5 nm^2 was I = + 0.017 pA. We can deduce an experimental value of μ_z equal to 1.0 D. If one consider a crown conformation of the flexible core of the 4BCD-I/12 molecule, a calculated value of μ_z in the side-on phase would be [13] about $\mu_z = 8 \times \mu'_z \approx 5.6$ D. Comparing then the measured and the calculated values of the dipole moments, we can conclude that the 4BCD core should adopt a conformation different from the crown one. A possible adopted conformation would be the "saddle" one, where only four of the eight polar groups are anchored at the air-water interface. However, we think that the resulting moment dipole value would be about $4 \times \mu'_z \approx 2.8$ D. A better arrangement an intermediate conformation: between the crown and the saddle conformation. In this intermediate conformation, the core would have a net moment dipole about zero, due to the a quasi-horizontal orientation of μ_1, dipoles (which are associated to the hydrophilic part (-COO-) of the core). Consequently, the net dipole of the 4BCD molecules is only due to the terminal C-H bond of the aliphatic chains which vertical component μ_{z2} of μ_2 would be about $\mu_{z2} = 0.2$ D. This statement leads to a net dipole moment value of the 4BCD molecule about 1.6 D which is in better agreement with the measured value above (1.0 D).

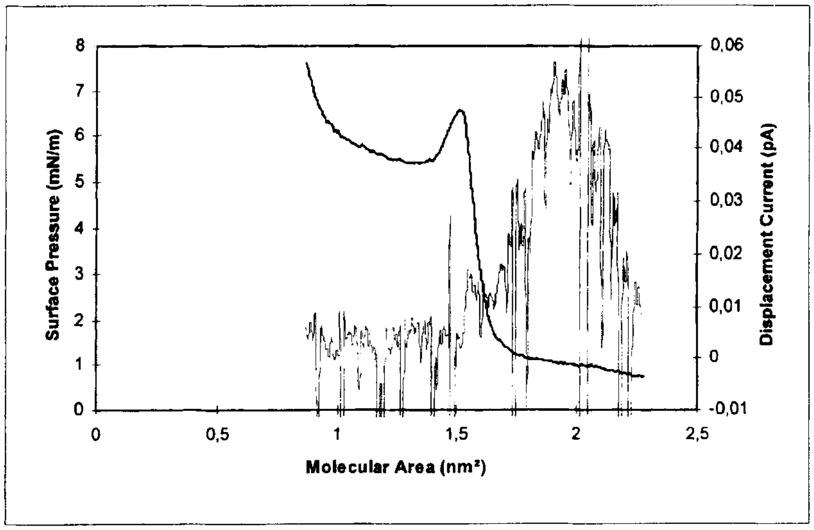


FIGURE 5: (a) π-A (Thick line) and (b) I-A (thin line) diagrams of 4BCN-I/12 film spread at the air-water interface and compressed from the liquid expanded phase. Barrier speed : 0.4 mm/s; pH = 5.7; T = 20°C; electrode height d_e = 1 mm.

Now we consider the molecule on its edge at the air-water interface. If we assume, as we did for the 3BCN-I/9 compound, that the net dipole moment is oriented parallel to the interface in the EO phase and if one applies relation (3), replace A_{EO} and A_{SO} by their experimental values, respectively 1.5 nm² and 0.8 nm², then Γ' would be approximately equal to (-I). The current I' should take symmetrical values compared to those taken by I before the transition. As we can see clearly, this is not the case: during the SO/EO transition, the measured current I is practically equal to zero. This leads us to assume a non horizontal orientation of the dipole moment of the 4BCD molecules in the EO phase. We will call this EO phase a tilted EO phase (EO_{tilt}). The number N' of the total molecules under the upper electrode, at the molecular area A, is given by the lever rule:

$$N' = \frac{S_e}{A}\frac{(A - A_{EO})}{(A_{SO} - A_{EO})} + \frac{S_e}{A}\frac{(A_{SO} - A)}{(A_{SO} - A_{EO})}$$

Where the first term is the number of molecules in the SO phase (vertical dipoles) and the second term is the number of molecules in the tilted EO phase (tilted dipoles) under the electrode. Hence we can deduce the expression of the displacement current I' during the SO-EO transition:

$$I' = \frac{S_e vL}{d_e}\frac{(\mu_{ztilt}A_{SO} - \mu_z A_{EO})}{(A_{SO} - A_{EO})N_0 A^2} \qquad (4)$$

I'_{tilt} would be approximately equal to zero if $\mu_{z\ EO\ tilt} = 2\text{x}\ \mu_{z\ SO} = 0.5$ D (we considered the experimental value of $\mu_{z\ SO}$ obtained above).

<u>4BCD-I/14:</u> Figure (6. b) gives I-A diagrams obtained for the film 4BCD-I/14 which was compressed from a molecular area of about 2.5 nm^2 to 0.8 nm^2. The spread volume was equal to 130 μl, the barrier speed was v = 0.4 mm/s and the electrode height was equal to d_e = 1 mm. The measured value of the displacement current in these experimental conditions for a molecular area about 1.8 nm^2 was I = + 8.10^{-3} pA. We can deduce an experimental value of μ_z equal to 0.6 D. This result confirms the value of the dipole moment (i.e. , 0.5 D) found in the EO phase of 4BCD-I/12. Compressing the film untill 1.3 nm^2 leads to a zero value of I. In turn this indicates that the vertical component of the net dipole moment of the 4BCD-I/14 molecule is decreasing probably due to a further deformation of the core.

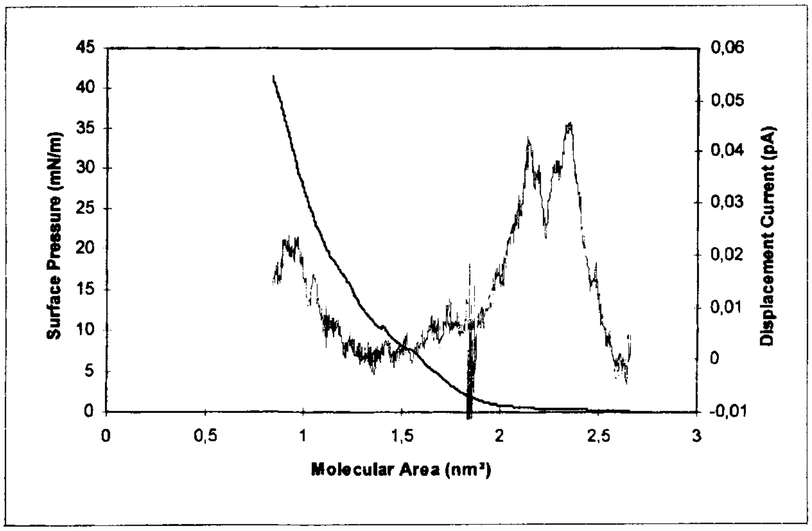


FIGURE 6: (a) π-A (thick line) and (b) I-A (thin line) diagrams of 4BCN-I/114 film spread at the air-water interface and compressed from the liquid expanded phase. Barrier speed : 0.4 mm/s; pH = 5.7; T = 20°C; electrode height d_e = 1 mm.

As we noticed earlier, the π–A isotherm diagrams of the 4BCD-I/14 film exhibits too small molecular areas that cannot be explained by the close packing EO arrangement. Moreover, by means of optical microscopy, we observed at high compression rates the formation of 3D domains within the film. These domains indicate the occurrence of a collapse process at high compression rate. This shows that for long aliphatic chains, molecules tend to collapse instead of undergoing an edge-on organization. Consequently, to understand the increase of the displacement current for these small molecular areas one should take into account this collapse process.

Rising of the lateral hydrocarbon chains effect:

As we can see all the I-A isotherms present an important variation of the displacement current I starting at large molecular areas and ending when the surface pressure starts to increase. The rising of the lateral hydrophobic chains will increase noticeably the vertical component of the total dipole moment: i) for the limiting case where the aliphatic chains are lying horizontally at the air-water interface, the only contribution to the vertical component μ_z of the total dipole moment is due to the net dipole moment of the bowlic core. This value can be deduced, for the 3BCN molecules, from the experimental value obtained for the SO phase (3.3 D) and from the experimental value of μ_{zCH3} found in the literature (0.2 D): $\mu_z = 6\mu_{z1} = 3.3 - 6\mu_{z2} \approx 2.1$ D; ii) The other case corresponds to the SO phase. We have already deduced, from figure 6, a total value of 6 μ_z equals to 3.3 D. Hence the increase of the total vertical dipole moment is about 50 % when the molecules transit from the gas phase to the SO phase. Consequently, this will bring a second contribution to the displacement current (see relation 1). Moreover, one should remark that the variation for the 3BCN compounds is greater than that for the 4BCD compounds. For the first class, six chains are lift whereas for the second class eight chains are lift. This should induces a greater variation for the displacement current obtained for 4BCD compounds, unless we take into account the deformation of the 4BCD core (which lowers, as we showed, the vertical component μ_z of the central core).

Conclusion:

In this work, we show that the organization of bowlic liquid crystals spread at the air-water interface depends on the nature (the mobility) of the central core and on the length of the hydrophobic chains. We show that the rising of the hydrophobic chains occurs during the film gas-Side On phase transition from horizontal (or random) orientation to an upwards orientation. For the 4BCD compounds, this rising occurs simultaneously with the deformation of the flexible core. At further compression rates, a transition to an Edge On phase occurs. We show that in the Edge On phase, the base of the molecules is oriented perpendicular to water interface for the 3BCN compounds whereas it is tilted with respected to the air-water interface for the 4BCD compounds. The dipole moment of the molecules was also deduced from experimental data and was compared with the calculated values.

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