Thermodynamics and mesoscopic organisation in Langmuir monolayers of an azobenzene derivative

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Abstract

We have carried out the analysis of liquid crystalline Langmuir monolayers at the air-water interface composed of the amphiphilic azobenzene derivative 8Az5COOH. By varying the temperature and the isomeric (*trans-cis*) composition, the monolayer behaviour has been studied in comparison with a shorter homologue, 8Az3COOH, by measuring the surface pressure-area isotherms along with Brewster angle microscopy (BAM). Our data with the pure *trans* isomer enable a posterior thermodynamic analysis, which was not feasible with the shorter homologue. For the mixed *trans-cis* monolayers, BAM observations reveal a phase segregation with *trans* enriched domains surrounded by a *cis* enriched matrix. Line tension between the two phases is lower than in the shorter homologue. The organisation of the rodlike molecules inside the *trans* domains results in highly symmetric textures that make the quantitative analysis of the BAM images possible, and a better understanding of the microscopic structure of the monolayer can be achieved.

Keywords: Azobenzene derivative, birefringent materials, self-assembly, Langmuir monolayers.

1. Introduction

Langmuir monolayers of insoluble amphiphiles at the air-water interface are broadly studied systems, known since the beginning of the last century[1]. Due to their experimental simplicity and control possibilities[2], Langmuir monolayers offer a great potential for the study of the organisation of soft materials under non equilibrium conditions [3], and to understand the lateral packing of molecules based on their chemical structure, intermolecular interactions, and interactions with the supporting subphase [4]. Taking into account that any biological system is composed of soft (self-assembled) materials, Langmuir monolayers can be used as a model for such self-assembly, and present a wide range of biological applications as biomimetic systems [5] that can be related to biological membranes and the processes occurring within them, and may lead to the development of biosensors [6].

Among the different types of molecules that have been used to prepare Langmuir monolayers at the air-water interface, surfactants containing an azobenzene group are of special interest for their potential applications in photomechanical devices [7, 8], optical switching, and image storing because of their high resolution and sensitivity [9, 10]. These molecules are photosensitive and exposing them to UV light can induce the reversible transition from the *trans* to the *cis* isomer. In the same way, when the *cis* form is irradiated with visible light, or through thermal relaxation, the molecule isomerizes to the *trans* form (Figure 2). This photoisomerization gives rise to changes in properties such as the cross-sectional area of the molecule, molecular conformation, and dipole moment [11]. As a result, there will be a difference in the way the two isomers organize at the air/water interface. In previous studies working with *trans* isomer monolayers of an azobenzene derivative, 8Az3COOH, a rich variety of morphologies was found, although a precise analysis of the thermodynamics of the phase change presented by such monolayers was not feasible [12]. On the other hand, it was found that monolayers prepared with a mixture of *trans* and *cis* isomers organise like a bidimensional emulsion. The structure of the disperse mesophase in such emulsions could be controlled by means of the thermodynamical variables or by light[13].

In this work we have studied the monolayer properties of an homologue compound, 4-octyl-4'-(5-carboxypentamethyleneoxy)azobenzene, (8Az5COOH in our shorthand notation, see Fig. 1), known to form mesophases in the *trans* form [14, 15, 16]. Ear-
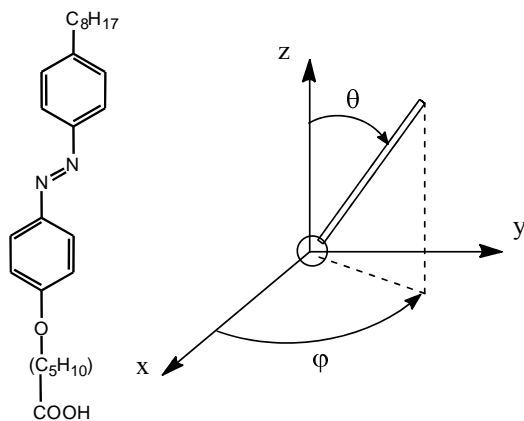
Figure 1: 4-octyl-4'- (5-carboxy-pentamethyleneoxy) azobenzene, 8Az5COOH. Chemical structure. At the right, definition of the tilt (θ) and azimuth (φ) angles that configure the orientation of the molecules on the surface.
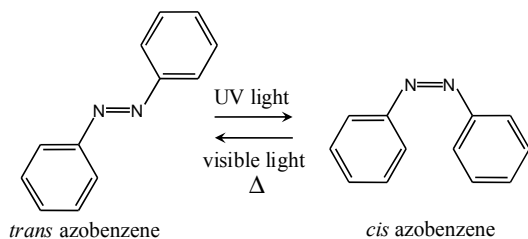

Figure 2: Illustration of the photoisomerisation of an azobenzene moiety (schematically drawn) [11].

lier studies with this compound have focused on the spectroscopic response of monolayers of the different homologues[14], the nature and extension of the supramolecular aggregates [15], and on the characterisation of stripped phases arising at high temperatures [16]. Although some compression isotherms have been reported, an accurate study of the thermodynamics of the observed first order phase transition, and the temperature-dependent mesophase configuration for a wide temperature range are lacking in this system. This information may allow a better understanding of the role of the azobenzene group in the self-assembly of these monolayers, and could reveal new photosensitive structures with potential applications, both in pure monolayers or in mixtures of the two homologues.

The first part of this work involves the study of monolayers of the pure *trans* isomer of 8Az5COOH, both by means of surface pressure - molecular area ($\pi - A$) isotherms and with simultaneous observation by Brewster angle Microscopy (BAM). The latter is sensitive to the lateral order existing in the monolayer and offers a first description of the different phases, while the former can be used to characterise the thermodynamics of the first order phase transition present in the system. The role of the azobenzene moiety in the self-assembly of these molecules is discussed by comparing the thermodynamic potentials in this system with those in monolayers of molecules with saturated aliphatic chains. The second part of this work focuses on the study of monolayers prepared with a photostationary mixture of the *trans* and *cis* isomers. We observe lateral phase separation between the two isomeric forms, our experiments suggesting that line tension between the two phases is significantly smaller for the homologue with the longer chain. Quantitative analysis of BAM images enables to characterized the molecular configuration inside circular isolated mesophase domains, whose morphology is less rich than the one reported for 8Az3COOH[17].

2. Experiments

2.1. Materials

The compound 8Az5COOH was commercially obtained from Dojindo Labs (Japan) and was used as received. The subphase was ultrapure water from a Millipore system. Spreading solutions (2mM) were prepared using chlorofom (Baker, p. a.) as solvent.

2.2. Methods

Monolayers of 8Az5COOH were spread over the air-water interface contained in a custom-built Teflon

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trough (377x90x5mm3). The trough is attached to a block of aluminum with an embedded coil for temperature control. After evaporation of the organic solvent, the monolayer was compressed by means of two spring-loaded, motorised Delrin barriers, with a velocity of 11 mm/min. The barriers provide a leak-free enclosure for the monolayer in such a way that there is no contact between the surface inside and outside the barriers. The temperature in the subphase was controlled by circulating water from a thermostatic bath with a variation of 0.2 K. The surface pressure of the monolayers was measured using a filter paper Wilhelmy plate attached to an electrobalance (Riegler and Kirstein, GmbH). The system was computer-controlled with a National Instruments DAQ board and customised software designed with LabView, and the setup was placed inside an enclosure in order to avoid air currents and to enable working in the dark for pure *trans* monolayers. Additionally, Brewster Angle Microscopy (BAM) was employed using a custom-built instrument in order to get information on the supra-molecular organisation of 8Az5COOH in monolayers at different temperatures. In the BAM, light from a 30-mW 650-nm diode laser (Monocrom, Spain) is spatially filtered and collimated to the desired beam size prior to being p-polarised by a prism and is directed toward the air-water interface. A mirror placed perpendicularly to the water surface, and held on the same mechanical arm that the laser is, deflects the incident beam prior to reflection on the interface. The laser beam is directed towards the interface at an angle close to the Brewster angle (53,1°), and the reflected light passes through a second polarizing prism prior to being focused on a CCD camera. The obtained images show a grey level distribution that can be correlated with the monolayer's local thickness and density. If the monolayer contains a mesophase, the grey scale distribution can be related to the local orientation of the molecules as well [18]. The equipment of the instrument with an XY translation stage makes following a specific region possible. BAM images were recorded using a hard disk video recorder, and digital image analysis was performed with the software ImageJ [18]. The BAM analyser, which enables to resolve the azimutal order in the monolayer, is set at 60 degrees from the incidence plane, which spans North to South in the images. Geometrical distortion due to the oblique BAM observation is digitally corrected in all images reported here. Data analysis is performed with the software IgorPro (Wavemetrics, Inc.).

3. Results and Discussion

3.1. Monolayers of trans 8Az5COOH. Compression isotherms and BAM imaging

In order to be able to consider the amount of *cis* isomer negligible in the spreading solutions, monolayers were prepared and stored in the dark. Moreover, the deposition on the air-water interface, as well as all manipulations, was performed inside the closed enclosure with the presence of only dim red light. Compression isotherms were recorded at temperatures ranging from 15 to 35 °C (Fig 3). The average of at least 5 realisations at each temperature is reported, with a maximum dispersion in the area per molecule of 5%. In all cases, the surface pressure starts rising at an area per molecule between 35 and 40 $Å^2$ and gradually increases upon compression until a pressure (depending on the temperature) in which the monolayer starts undergoing a first order phase transition signaled by a plateau region in the isotherm [1, 19]. Compression past the transition eventually results in a cusp in the isotherm, marking the collapse of the monolayer. This occurs at a surface pressure, which decreases with temperature. This dependence, which is often described in the literature[20], indicates that the collapse process is kinetically and not thermodynamically controlled, as is the case in the first order phase transition[21].

Isotherms recorded at the two lowest temperatures ($T = 15°C$ and $T = 20°C$) reveal non-equilibrium features in the plateau (phase-coexistance region), in the form of noisy jumps in the lateral pressure. BAM images prove that this is the result of the mechanical response of the monolayer, which should be regarded as a complex two-dimensional material (see below). Upon further compression, the surface pressure rises until the collapse of the monolayer occurs.

At all temperatures and positive surface pressures BAM reveals monolayers with long-range orientational order. This is in contrast to monolayers of simple amphiphiles or phospholipids, where at low pressures isotropic liquid expanded phases are found, and only at high pressures the molecules arrange into an ordered (hexatic) phase[22].

The orientation of the molecules organised on the surface is defined by two angles: a tilt angle respect to the outward normal to the interface and an azimuth angle with a reference in-plane axis (see fig. 1). 8Az5COOH molecules in the monolayer self-assemble forming domains with long range orientational order, large enough to be detected by BAM. The images that we obtained at low pressures reveal gradients in the monolayer reflectivity, which may be correlated with spatial changes
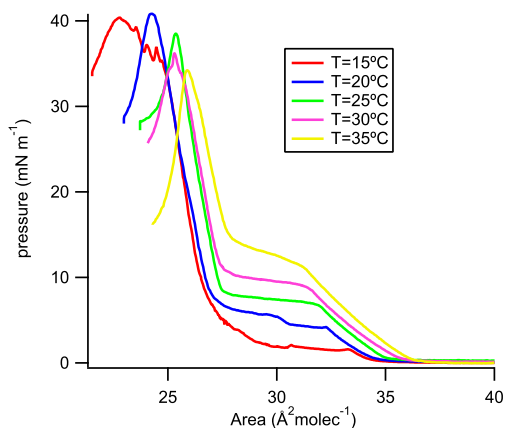
Figure 3: Compression isotherms of 8Az5COOH. The *trans*ition pressure π_c is marked in the isotherm performed at 35°C.

maximum orientational order at around 25°C.

If the monolayer is further compressed there is a first order (discontinuous) phase transition at a temperature dependent lateral pressure, π_c, and a totally new texture is achieved. BAM images obtained at high pressure show that the mesophase formed after this transition is composed of domains arranged as a mosaic (Fig. 4b, 4d, 4f, 4h, 4j). In such domains the reflectivity is constant, suggesting a parallel orientation of the molecules forming each domain, but different from the orientation of the molecules in the neighbouring domains. Further studies have been done with the homologue compound, 8Az3COOH, which presents a very similar mesophase at high pressures. The mentioned studies consisting on Grazing X-ray Diffraction analysis concluded that after the phase change an hexatic phase is obtained [24]. Similarities between BAM images of the two homologues in the low and high pressure phases [12, 17] suggest that the behaviour of the surfactant reported in this work is the same, and that the high pressure phase features hexatic order. A more detailed study should involve the use of X-Ray diffraction, which is beyond the scope of this work. At low temperatures the domains forming such mosaic are large (typical lateral size in excess of 100 micrometers) and well defined, whereas at higher temperatures the mosaic is formed by smaller domains (typical lateral size less than 50 micrometers) thus creating a fragmented texture. So in contrast with the results obtained at low pressures, in this case the orientational order decreases as the temperature increases. It is remarkable that the range of the orientational order above and below π_c is preserved if phase *trans*ition cycles are applied. For instance, the fragmented texture below π_c at 15°C leads to the large domains in the mosaic texture upon compression above π_c (see Fig. 4a, 4b), but the same fragmentation is regained if π is decreased below π_c again. This indicates that the range of the orientational order at a given π and T is inherent to the self-assembly of azobenzene molecules, and not a kinetic effect. What's more, it might be related to the formation of H-aggregates, previously reported by different groups [15, 17], the formation of which would be a stable configuration for the *trans*-8Az5COOH molecules. Such aggregates consist on the grouping of azobenzene molecules with their molecular axis parallel to each other and perpendicular to the stacking direction. In addition, at temperatures above room temperature, just before the phase transition, the stripe texture suffers a curious phenomena by which the stripes crease (see Fig. 5). Again, this is not a kinetic effect; it is seen in all experiments above room temperature, and it is reversible: the original tex-

in molecular orientation. In other words, the reflectivity (brightness) of the monolayer changes gradually as the orientation of the molecules changes, due to the optical anisotropy of the material. Monolayers spread at 15°C organize forming a stripe texture with highly branched curved lines (fig. 4a). When the monolayer is spread at 20°C or 25°C the texture becomes more labyrinthine but formed by curved lines too (fig. 4c). At this range of temperatures reflectivity gradients decrease with increasing temperature, which means that the range of the orientational order in the monolayer increases. In addition, working at 20°C and 25°C, one can detect topological defects[1] which determine the organisation of the mesogens with rotational symmetry surrounding a central point defect (Fig.4e). Configurations with this high symmetry are potentially very interesting for quantitative image analysis, from which important material parameters can be extracted [23, 12, 18]. A detailed analysis (not shown) has revealed that illumination inhomogeneities and monolayer deformations have distorted the orientational field, rendering these structures useless for a quantitative analysis. Below, we will present other configurations more amenable for this type of studies. From the BAM images one can see that the more the temperature is increased the more evident the stripe pattern is, the more straight and thin the lines become, and more fluid the mesophase is (Fig. 4g, 4i). Reflectivity gradients increase when the temperature is increased past 25°C, thus indicating the presence of a state of

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[1]Structures where the symmetry typical of the ordered phase is locally broken. They arise spontaneously during the formation of such phase. Here, these defects are points where molecules presumably orient perpendicularly to the interface.
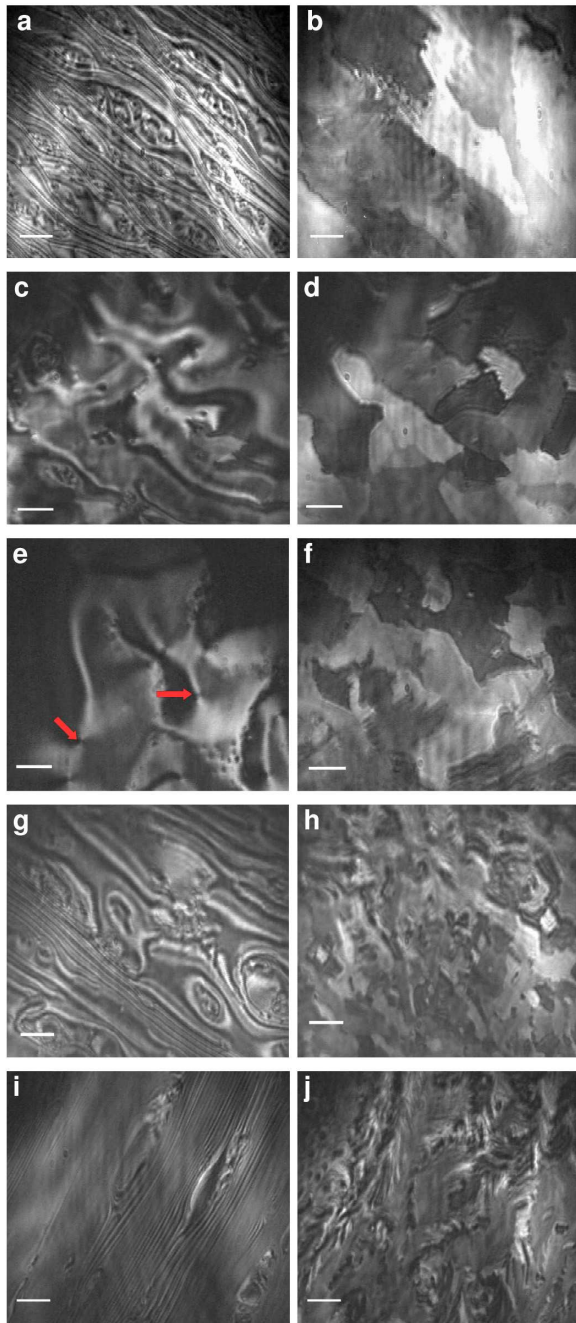
Figure 4: BAM images of *trans* 8Az5COOH monolayers at different temperatures. (a, b) are measured at 15°C, (c, d) at 20°C, (e, f) at 25°C, (g, h) at 30°C and (i, j) at 35°C. Images in the left column correspond to low-pressure textures, and those on the right column correspond to high-pressure textures above π_c , after the phase change. Arrows on (e) mark point defects. The ruler is 100 micrometers long.
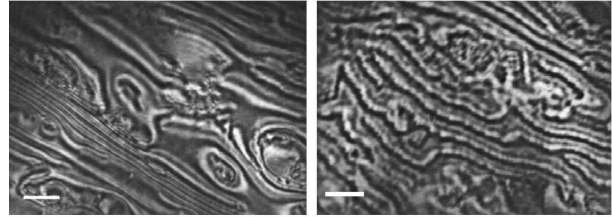

Figure 5: Creasing of the stripes prior to the phase transition. BAM images of the same region just before (left) and just after (right) the change. T= 30°C. The ruler is 100 micrometers long.

ture is regained when the pressure is decreased. Similar observations have been performed in 8Az3COOH monolayers[25], which suggests that this creasing may be the result of changes in the azobenzene-mediated self-assembly upon approaching the transition to the more ordered hexatic phase. These observations may hint towards a second-order transition. Such transitions represent a continuous change in the tilting of the molecules between two ordered phases and are difficult to detect by BAM imaging. In order to assess whether there is evidence for a second-order phase transitions, we have calculated the isothermal compressibility modulus from the isotherms [19, 1]. Nevertheless, we have been unable to detect any feature in the compressibility that might correlate with the changes observed in BAM images (Fig. 5). Further studies will be required to find an explanation for the creasing of stripes.

On the other hand, BAM imaging provides useful information to interpret the noisy isotherms in the coexistence region at the two lowest temperatures (see above). Nucleation and growth of the high pressure phase proceeds through avanlanches: sudden phase conversion occurs in finite, but macroscopic, regions in the monolayer. Such sudden changes in local density are detected by the pressure sensor, and result in jitter in the lateral pressure data within the plateau region (see Fig. 3). To the best of our knowledge this is the first time such a dynamics is observed during phase transitions in monolayers, although complex viscoplastic behavior has been reported during the collapse of monolayers[26, 20]

Finally, compression past the collapse point results in the formation of multilayers that manifest as bright spots in the BAM images (BAM reflectivity increases with the square of the monolayer's thickness [18]). Applying compression cycles it was found that the collapse of the monolayer was sometimes reversible.

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T (°C)	π_c (mN/m)	ΔA (Å^2/molec)	ΔS (J/mol)	ΔH (kJ/mol)
15	1.46	-5.79	-16.7	-4.82
20	4.19	-4.98	-14.4	-4.22
25	6.75	-4.11	-11.9	-3.54
30	8.83	-3.62	-10.5	-3.17
35	11.25	-3.16	-9.1	-2.81

Table 1: Thermodynamic phase transition data of *trans*-8Az5COOH.

3.2. Monolayers of trans 8Az5COOH. Thermodynamic study

The data just reported for 8Az5COOH can be analysed to characterise the thermodynamics of the first order phase transition, which will provide information about molecular interactions within the monolayer. The heat and the entropy of the transition can be estimated applying the Clausius-Capeyron equation,

$$\frac{d\pi_c}{dT} = \frac{\Delta S}{\Delta A} = \frac{\Delta H}{T\, \Delta A},\qquad(1)$$

where π_c is the value of the surface pressure during the phase change, ΔS, ΔH are the entropy and heat of transition respectively, ΔA is the variation of the area per molecule during the phase change, and T is the temperature.

For each of the isotherms one can graphically obtain the value of the surface pressure when the phase change starts, at every temperature. Plotting the values of π_c vs. T the equilibrium coexistence curve is obtained, the slope of which is $\Delta S/\Delta A$. The variation of the area during the phase change (in the plateau region) is graphically estimated from the isotherms by approximating a linear change in the lateral pressure in the hexatic phase, $\pi = f_T(A)$, and finding the area per molecule of this phase during phase transition by solving $f_T(A) = \pi_c(T)$. With this, the value for the transition entropy and enthalpy can be determined by simple calculations (Table 1).

Several studies determining the thermodynamic potentials of a monolayer undergoing a phase transition have been reported in the literature, but none using an azobenzene derivative. In the earlier work done in our group with 8Az3COOH, such analysis could not be performed because both the slope for π_c vs. T and ΔA could not be determined with enough precision. The situation is different for 8Az5COOH, for which all the required parameters can be measured with confidence. In order to put the values for ΔS and ΔH obtained here in the proper context, we took the values reported by Albrecht et al. [27] as a reference. Their work was based

on phospholipid monolayers, and they found for the heat of transition values around -15 kJ/mol for Dimyristoyl phosphatidic acid, and -25 kJ/mol for Dipalmitoyl lecithin (in a range of temperatures between 15 and 35°C). Notice that these are double chain molecules, so we one should consider half the reported values when comparing with a single chain molecule. Our values for 8Az5COOH are around -4 kJ/mol (in the same temperature range), which means that a lower amount of energy is required for the transition between the low and high pressure phases. A possible justification lies in the tendency of azobenzene chromophores to form H aggregates due to $\pi - \pi$ stacking, a phenomenon that has been widely studied [14, 15, 24, 28]. The ability of this kind of molecules to self assemble induces an orientational order in the expanded phase, which is a mesophase at unusually low surface densities, and this is the main difference with the totally disordered liquid expanded phase formed by phospholipids. The high-pressure phase in 8Az5COOH is, presumably, hexatic, just as liquid condensed phases in phospholipids, so a similar degree of order is expected. Therefore, ΔS should be smaller, in absolute value, for the azobenzene derivative as we do find indeed when comparing with the values reported by Albrecht et al. [27] for phospholipids, in the range -126 until -90 J/mol (temperature between 15 and 35°C). With respect to the differences between the isotherms of 8Az3COOH and 8Az5COOH, the two extra carbon atoms that the latter compound has between the azobenzene moiety and the acidic terminal group should be responsible for the thermodynamic differences. The longer chain of 8Az5COOH provides the molecule with enhanced mobility and, as a consequence, the H-aggregate system that is the responsible of the formation of the mesophase might be more perturbed when compared to the one formed by 8Az3COOH. For this reason, we expect that the mesophase formed by 8Az3COOH should be more ordered, so there would be a smaller difference between its expanded and condensed phases, and the phase change should be even less energy demanding. In fact, we found that for 8Az3COOH the values for ΔA and $d\pi_c/dT$ are significantly smaller[12], and so would be expected to be the values for the thermodynamic potentials ΔS, ΔH, although they could not be determined with confidence.

3.3. Monolayers of a cis-trans mixture

Mesogens in the *trans* configuration can be forced into the *cis* form by exposure to UV light. Although we have not measured the isotherms of the pure *cis* monolayer for 8Az5COOH, they have been previously
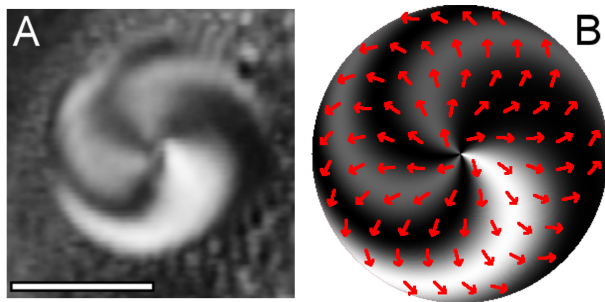
Figure 6: A: Domain of *trans*-rich phase in a matrix of *cis*-rich phase for 8Az5COOH. T=35°C. The BAM analyzer is set at 60°. The ruler is 100 μm. B: Proposed azimuth field and corresponding BAM texture for the circular domain in A, after finding all relevant material parameters.

Figure 7: Grey level as a function of the polar angle along a circumference of radius 52.5 μm, centered on the central point defect, for the droplet shown in figure 6. The solid line is a fit to the reflectivity data.

studied for the analogue compound, 8Az3COOH, showing a uniform isotropic phase, which does not undergo any phase transformation[12]. As mentioned above, spreading a roomlight photostationary mixture of the two isomeric forms of this compound resulted in a two-dimensional emulsion where *trans*-rich circular domains featured axially symmetric inner textures that depended on domain size, temperature and lateral pressure[17].

We follow a similar procedure with 8Az5COOH, in order to test how the line tension between the two phases depends on chain length, and to explore the possible textures inside isolated domains in the homologue compound. Just after spreading the photostationary *cis/trans* mixture BAM images reveal a phase-separated monolayer, with small circular domains with an inner texture that cannot be resolved due to their small size (less than 10μm in diameter). After about 20 minutes, coalescence and isomerisation into the *trans* form make these domains big enough to allow the study of their inner texture (diameter larger than 100 μm), displaying highly symmetric configurations similar to those of the shorter homologue. Although longer resting times may result in larger domains, the ripening process is much slower than in the case of 8Az3COOH, suggesting that line tension between the isotropic phase and the mesophase is much smaller in the longer homologue. Moreover, compression of the monolayer leads to a transition to the high pressure phase inside the domains, resulting in a mosaic texture analogous to the case of the pure *trans* monolayer. These indirect evidences suggest, consistently with what had been demonstrated for 8Az3COOH, that the circular mesophase domains are composed mostly of the *trans* isomer while the surrounding isotropic matrix is mostly *cis* isomer of 8Az5COOH.
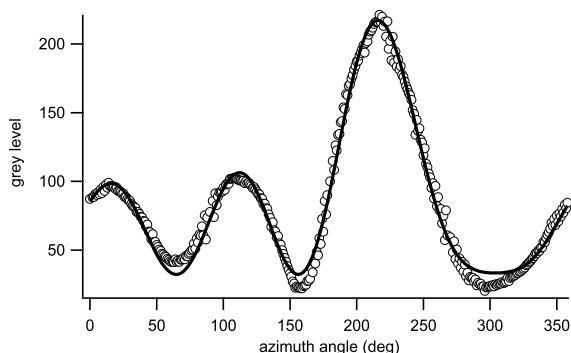
Characterisation of the inner texture of the *trans*-rich domains is possible by fitting their BAM reflectivity to a suitable spatial distribution of the azimuth field, using an optical model that assumes that the monolayer behaves as a uniaxial birefringent optical medium[29]. This fit requires knowledge of the different instrumental parameters and of material parameters such as the polar tilt angle (usually assumed uniform across regions with small reflectivity gradients) and the two dielectric coefficients that characterise the interaction of light with this medium [23, 18, 30]. Finding these parameters is possible by analysing BAM images in a region with a very symmetric or known azimuth profile, provided images are free from optical artifacts. This is a critical step since, once these parameters are known with confidence, finding the azimuth distribution inside the isolated *trans*-rich domains can be done by trial and error, even with images of modest quality [17]. We proceed to determine these required material parameters by analysing a trans-rich domain at 35°C featuring an axisymmetric spiral texture organised around a central point singularity (Fig.6). We proceed by obtaining the graylevel profile along a circumference of approximately half the domain radius (actually, we average a circular corona ten pixels thick in order to filter noise out). This profile is fitted to a reflectivity function by assuming an axisymmetric azimuth profile as described elsewhere [18]. The relevant material parameters are obtained from this fit, as summarized in Table 2.

When compared to the material parameters obtained for 8Az3COOH [12], we observe that the dielectric coefficients for light polarized parallel ($\varepsilon_{\parallel}$) and perpendicular ($\varepsilon_{\perp}$) to the alkane chains have identical values (within error), while the polar tilt angle is slightly larger for 8Az5COOH. Knowing these parameters we

Parameter	Obtained Value
$\varepsilon_\perp$ (fixed value)	2.2 ± 0.1
$\varepsilon_\parallel$	3.0 ± 0.1
Polar tilt angle	$55 \pm 3°$
Analyzer orientation (known value)	$60°$

Table 2: Material parameters extracted from the fit to the reflectivity data.

can propose an azimuth field that reproduces the observed BAM texture to a high degree of accuracy. We approximate this azimuth field with a fourth order polynomial of the distance to the central defect, and the coefficients are selected to achieve an optimal match with the experimental BAM image. We conclude that 6 the azimuth field is type bend (tangent to the circular boundary) near the central core and evolves towards a splay (radial) configuration near the boundary [17] (Fig. 6). At this point we are also able to analyze with confidence the inner texture of domains of 8Az5COOH under different experimental conditions. At 15°C, mixed monolayers feature small circular domains (diameter < 100 μm) with a bend type texture and bigger domains with a double boojum texture (two point singularities on the domain boundary[17]). As temperature increases, the size of the domains tends to increase as well, and at 25°C we find bend domains that reach sizes of around 100 μm. At this temperature we find some splay domains and double boojums too. If the temperature is increased until 35°C the monolayer presents splay and double boojum domains of variable sizes, but no bend domains are found.

To complete the comparison between photo-stationary monolayers of the two homologue compounds we check the photosensitive behaviour of 8Az5COOH monolayers. It is known that upon irradiation with polarised visible light of photo-stationary monolayers of 8Az3COOH, *trans* molecules forming splay domains tend to align with the polarisation of light. We irradiated 8Az5COOH monolayers with visible light of λ=480nm, and confirmed that splay domains do photo-align with the polarisation of light as well. On the other hand, bend and double boojum domains do not photo-align, similarly to what was observed with 8Az3COOH.

4. Conclusions

In the present work we have studied Langmuir monolayers of 8Az5COOH in comparison with a shorter homologue, 8Az3COOH, in order to demonstrate the influence of small structural changes in the capacity of amphiphilic molecules to self-assemble at the air/water interface. Yokoyama and co-workers had already reported dramatic dynamical changes following small variations in the molecular structure of monolayers of a series of homologues that included 8Az3COOH and 8Az5COOH[31], but an in-depth comparison of the equilibrium properties of the two systems was lacking. We have started with a thermodynamic analysis identifying the phases formed by *trans* 8Az5COOH at several temperatures, concluding that the surface pressure of the phase change has an increased dependence on temperature. Such dependence has permitted the analysis of the phase transition, which was not possible with 8Az3COOH. By means of the two-dimensional Clausius-Clapeyron equation, we have determined variations in the thermodynamic potentials enthalpy and entropy upon phase change. Their magnitudes are significantly smaller than those obtained for monolayers formed by phospholipids of similar chain length[27]. To explain the decrease in those values we suggest that the ability of the azobenzene molecules to self-assemble by forming H-aggregates induces an orientational order in the more expanded phase that makes the transition to the more ordered phase less energy demanding that in the case of phospholipids. Simultaneously to the thermodynamic magnitudes, Brewster angle microscopy images have been obtained for the monolayers spread at different temperatures. Images feature textures whose local brightness can be related to molecular orientation. These observations indicate the presence of a state of maximum orientational order near 25°C for the low pressure mesophase, and a steady decrease in the range of the order with temperature in the high pressure (presumably hexatic) phase[24]. We have also analysed monolayers formed by a mixture of *cis* and *trans* molecules. In such monolayer a segregation in *trans* rich domains and a *cis* rich region is observed, although the slow coarsening suggests that the two isomers have a much lower line tension than in the case of 8Az3COOH[17]. The quantitative analysis of the BAM images of an isolated domain has allowed the determination of some of the material parameters like the dielectric coefficients and the angles describing the orientational order, and has confirmed a molecular organisation with rotational symmetry. Finally, we have verified that *trans* rich domains with the splay-out configuration photo-align when shined with linearly polarized light, in analogy to the behavior of 8Az3COOH[13].

In summary, we have shown that in spite of the two homologues sharing rare features, such as the existence of a low density mesophase, the addition of two methylene groups in the alkane chain results in remarkably

different thermodynamic behavior and in a significant increase in the miscibility of the *cis* and *trans* isomers in monolayer form (a reduction in the line tension in the phase-separated monolayers). An interesting extension of this work could involve the exploration of mixed monolayers of the two homologues, 8Az3COOH and 8Az5COOH, seeking for compositions where the richer morphological and dynamical features of 8Az3COOH can be extended to wider ranges of the thermodynamic control parameters.

5. Acknowledgements

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