

Experimental evidence for a surface concentration-dependent mechanism of formation of hemimicelles in Langmuir monolayers of semi-fluorinated alkanes

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We show that formation of surface hemimicelles by a series of molecular semi-fluorinated alkanes $C_8F_{17}C_mH_{2m+1}$ (F8Hm diblocks; $m = 14, 16, 18, 20$) in Langmuir–Blodgett monolayers is not promoted by surface pressure, but depends on the surface area available before transfer, hence on a critical surface concentration. Evidence is provided for the presence of isolated micelles at zero surface pressure (very large molecular area) for certain FnHm diblocks. It is the molecular structure of the diblock that essentially determines the morphology of the hemimicelles, independently of compression conditions.

It has been reported that Langmuir monolayers of semifluorinated alkanes $C_nF_{2n+1}C_mH_{2m+1}$ (FnHm diblocks, $n = 4–10$, $m = 14–20$), observed after transfer onto silicon wafers, consist of large (\sim a few tens of nm) surface hemimicelles of various morphologies.^{1–4} When transferred at relatively low surface pressures (π), typically $\sim 1 \text{ mN m}^{-1}$, and above, the disk-like hemimicelles form well-ordered two-dimensional hexagonal arrays.¹ Within a disk-like micelle, the hydrocarbon blocks (Hm) are directed towards the substrate, while the fluorocarbon blocks (Fn) are pointing outwards.¹ The existence of similarly sized, disk-like surface micelles, perfectly organized in hexagonal arrays, was established directly on the water surface by grazing incidence small-angle X-ray diffraction (GISAXS) at surface pressures ranging from 0.5 to 7 mN m^{-1} , which shows that the two-dimensional micelles pre-exist at the air/water interface and are not induced by the transfer.⁵ Despite the many studies that have been conducted on Langmuir monolayers of FnHm diblocks,^{6–8} the existence of surface hemimicelles had not been anticipated in spite of the known tendency of fluorinated chains to promote self-aggregation.⁹

One open question concerns the mechanism of formation of these surface micelles. There is, therefore, a need for information on the occurrence and morphology of the surface micelles at very low or zero surface pressure. Such data are, however, difficult to obtain directly at the air/water interface. On one hand, the GISAXS experiments cannot be conclusive as to whether or not hemimicelles exist at very large molecular area (zero surface pressure), since they would not be sufficiently organized to diffract the X-ray beam. On the other hand, surface micelles of a few tens of nanometer cannot be probed by mesoscopic methods such as Brewster angle microscopy. Needless to say, macroscopic information extracted from compression isotherms is of little help.

Transferring the FnHm monolayers onto a solid substrate of low roughness and using AFM to investigate the morphology of the surfaces thus represents a reasonable alternative.¹⁰

A survey of the literature shows that the surface aggregates that are the most closely related to FnHm hemimicelles are molecular clusters formed in Langmuir monolayers of partially fluorinated carboxylic acids.¹¹ A major difference, however, is that the latter clusters are formed only when the fatty acids are spread on an aqueous sub-phase containing divalent ions (Cd^{2+} or La^{2+}). Numerous studies aiming at determining the mechanisms of nucleation of an inorganic phase under an organic layer have established that the metallic ions form an organized layer, probably in the form of coordination complexes, that condense the organic monolayer and sometimes even form a superlattice that is commensurate with the lattice formed by the long chains of the surfactants.^{12,13} It is then clear that, in this case, it is the inorganic species dissolved in the sub-phase that controls the ordering of the molecules at the interface. Therefore, it is very likely that the mechanism of formation of surface micelles of partially fluorinated fatty acids is predominantly driven by the interactions between the polar heads and the divalent ions present in the sub-phase. The proposed mechanism: a spontaneous nucleation following the evaporation of the spreading solvent, and the fact that the surface micelles have been observed at zero surface pressure, confirm the existence of a strong interaction between the monolayer and the cations.

Other reported surface aggregates that are reminiscent to FnHm hemimicelles are those formed by diblock copolymers. Since the first evidence of surface micelles of polystyrene-containing A–B diblock copolymers at the air/water interface,¹⁴ surface aggregation has been found to be a general phenomenon for a number of hydrophilic B blocks.^{15,16} Three hypotheses have been proposed to explain the formation of surface micelles of diblock copolymers in Langmuir–Blodgett (LB) films. First, three-dimensional micelles would already be present in the spreading solvent and would simply be transferred to the air/water interface.¹⁷ Second, the copolymers would undergo surface pressure-induced aggregation during compression.^{18,19} Third, the copolymers would undergo spontaneous aggregation, independent of compression, with formation of hemimicelles at zero surface pressure, even for the largest surface area available on the trough.¹⁶

In the present work, we have transferred Langmuir monolayers of a series of small molecular FnHm diblocks (F8Hm, $m = 14, 16, 18$ and 20) onto silicon wafers at various large molecular areas (zero π) or at low surface pressure (0.5 mN m^{-1}), and have investigated them by AFM.

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F8Hm diblocks were synthesized according to ref. 20 and were thoroughly purified by repeated crystallizations from methanol. Purity (>99%) was determined by TLC, NMR and elemental analysis. Spreading solutions of F8Hm (1 mmol L⁻¹) were prepared in analytical grade chloroform. Water was purified using a Millipore system (surface tension: 72.1 mN m⁻¹ at 20 °C; resistivity: 18.2 MΩ cm). Surface pressure *versus* molecular area (π - A) isotherms were recorded on a Langmuir trough (NIMA 312LL, Coventry, UK) equipped with two movable barriers (total film area = 235 cm², compression rate: 20 cm² min⁻¹, *i.e.* 0.07 nm² min⁻¹ per molecule). π was measured using the Wilhelmy plate method. The errors on π and A were estimated to be ± 0.5 mN m⁻¹ and ± 0.5 Å², respectively. Temperature was regulated at 20.0 \pm 0.1 °C. 25 μ L of F8Hm solutions were spread on the water surface and 5 min were allowed for solvent evaporation.

Fig. 1 shows the π - A isotherms of F8Hm diblocks spread on water at 20 °C. The limiting molecular area values, A_∞ , (33.2, 31.9, 29.8 and 28.0 (± 0.5) Å² for F8H14, F8H16, F8H18 and F8H20, respectively) decrease when the Hm segment's length increases. The differences between A_∞ values, although small, are significant. This means that, within a hemimicelle, the diblocks with long Hm segments are more ordered than those with short ones, likely due to increased molecular freedom that allows molecules to pack in a more compact way. The collapse pressure, π_c , depends on the Hm segment's length, according to the polynomial equation $\pi_c = 30 - 3n + 0.13n^2$, where n is the number of carbon atoms in the Hm block.

The isothermal compressibility coefficients C_s of the F8Hm monolayers were calculated from π - A isotherms according to $C_s = (-1/A)(dA/d\pi)$, where A is the area per molecule and π the surface pressure. The minimum compressibility values, $C_{s,\min}$, do not vary significantly with the molecular structure, which suggests that compressibility is controlled by the length of the Fn block. The compressional moduli (the reciprocal quantity of C_s) C_s^{-1} , range from 79 to 122 mN m⁻¹, indicating that the FnHm monolayers are in a liquid-condensed state.²¹

The monolayers of F8Hm diblocks were transferred onto silicon wafers using the LB technique (one monolayer is transferred; lift speed: 1 mm min⁻¹). The transfers were achieved at molecular area values ranging from ~ 120 to 30 Å². The wafers were previously treated with a piranha solution (conc. H₂SO₄ + 30% H₂O₂ 3 : 1). No significant variations of π were detected during monolayer transfer.

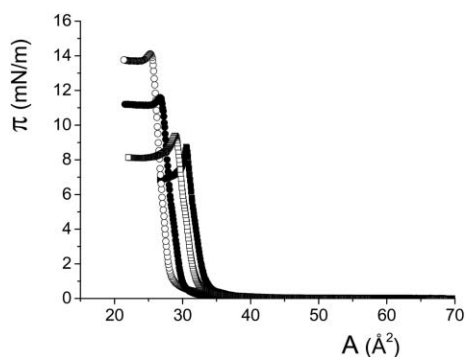


Fig. 1 Surface pressure *vs.* molecular area isotherms of Langmuir monolayers of F8H14 (■) F8H16 (□) F8H18 (●) F8H20 (○) at 20 °C.

The LB films were analyzed with an atomic force microscope (NanoScope IIIb, Digital Instruments, Santa Barbara, CA) in tapping mode, at room temperature, immediately after transfer. The cantilever (Olympus) was fitted with a 10 nm tip. The resonance frequency was 300 kHz and the spring constant 40 mN m⁻¹. At least three different samples were analyzed and several positions were scanned on the wafer for each sample. The surface roughness of the silicon wafers was lower than 1 ± 0.5 nm. The diameters of the hemimicelles were measured using the NanoScope software. The average values of these diameters (D), standard deviations (SD) and the area fraction covered by the surface micelles (ϕ) were calculated from the analysis of at least three images.

The AFM images show that, at very large molecular area values, *i.e.* from 120 to 60 Å², no surface aggregates were present for any of the diblocks investigated. For $A < 49$ Å², hemimicelles were found for F8H14, but no surface aggregates were detected for the other diblocks (Fig. 2a). The F8H14 hemimicelles are well-formed, disk-like ($D \sim 26$ nm) and have a hole at their center, as described previously for much higher π .³ For $A < 41$ Å², disk-like surface micelles were also detected for F8H16 ($D \sim 30$ nm) (Fig. 2b). At such surface concentrations, the surface pressure experienced by both F8H14 and F8H16 molecules is null. At such large A values, the hemimicelles were not organized in a regular array and some of them appear isolated.

On the other hand, no surface aggregates of any sort were seen at $\pi = 0$ for the diblocks bearing the longest Hm blocks, F8H18 and F8H20.

Transfers were then achieved at 0.5 mN m⁻¹, which corresponded to ~ 28 , 30, 33 and 35 Å² for F8H20, F8H18, F8H16 and F8H14, respectively. At this π , well-defined surface micelles were visualized in all the samples, including F8H18 and F8H20 (Fig. 3).

It can be seen that, for F8H14 and F8H16 (the two diblocks for which comparison is possible), D did not change significantly when π was increased from 0 to 0.5 mN m⁻¹ (Table 1). On the other hand, ϕ increased, as expected. It is also observed that, for a given π , D increased with the length of the Hm segment, hence with the overall length of the molecule. In addition, the hemimicelles tended to be more elongated and less regular when the Hm block's length increased, probably due to the fact that long Hm segments have more conformational freedom than short ones, and are able to adapt their conformation at the air/water surface in reaction to

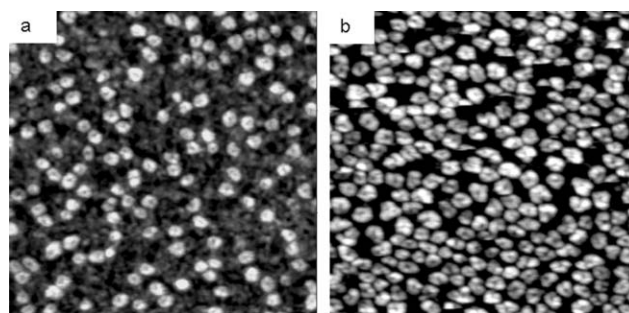


Fig. 2 AFM images (600 \times 600 nm, tapping mode, z range 5 nm) of LB films for (a) F8H14 and (b) F8H16 transferred at 49 and 41 Å², respectively, at 20 °C. At these molecular areas, $\pi = 0$ mN m⁻¹.

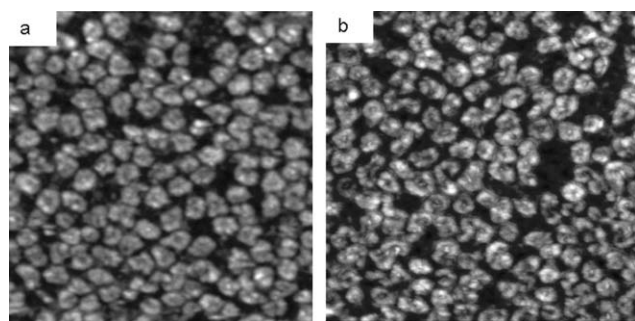


Fig. 3 AFM images (600×600 nm, tapping mode, z range 5 nm) of LB films of (a) F8H18 and (b) F8H20 after transfer onto silicon wafers at 0.5 mN m^{-1} at 20°C .

Table 1 Mean diameter (D) and area fraction (ϕ) of the surface micelles of F8Hm diblocks in Langmuir monolayers transferred at low surface pressures onto silicon wafers and investigated by AFM

F8Hm	$\pi = 0/\text{mN m}^{-1}$		$\pi = 0.5/\text{mN m}^{-1}$	
	D/nm	ϕ (%)	D/nm	ϕ (%)
F8H14	26 ± 3	24 ± 6	24 ± 3	48 ± 12
F8H16	30 ± 3	53 ± 10	33 ± 3	50 ± 9
F8H18	^a	^a	41 ± 5	55 ± 12
F8H20	^a	^a	43 ± 5	65 ± 15

^a No surface micelles observed.

compression, which may, in turn, induce a change in the micelle's morphology from a disk-like to an elongated shape.

It is noteworthy that the same trend has been observed at higher π values.³ This further indicates that the hemimicelles' morphology is predominantly determined by the molecular structure of the diblock and that the compression, *i.e.* the packing of the micelles in a lattice, does not play a decisive role.

Altogether, these results demonstrate that the formation of surface micelles of F8Hm diblocks is surface-concentration dependent, a fact that has never been established previously. The fact that the hemimicelles are not present at very large molecular area values, *i.e.* from 120 to 60 \AA^2 , demonstrates that they do not form spontaneously, as a result of a nucleation process induced by evaporation of the spreading solvent. Surface pressure is not a key parameter, at least for F8H14 and F8H16, since hemimicelles of these diblocks were evidenced at zero surface pressure. Our experimental results are in line with a recent theory for the formation of surface micelles of F8Hm diblocks.²² It is proposed that the micelles result from a liquid/liquid—rather than liquid/gas—phase separation in the Langmuir monolayer. According to

this view, the disk-like micelles consist of high density islands formed by diblocks with a roughly vertical orientation located within a matrix constituted by a lower density phase where the diblocks are oriented nearly parallel to the water surface.

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