ESRF	Experiment title: **Surface Micelles of a semi-fluorinated alkane at the air/water interface.**	**Experiment number**: SC1189
Beamline: ID10B	**Date of experiment**: from: 25-06-2003 to: 01-07-2003	**Date of report**: 18-02-2004
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Report:

The aim of the proposed experiment was to give an answer to question of the structure of monolayers of semi-fluorinated alkanes ($C_nF_{2n+1}C_mH_{2m+1}$ - FnHm diblocks) at the air-water about which a strong controversy remains since the pioneering work of Gaines. He demonstrated that these non polar amphiphiles presented π-A isotherms similar to those of Langmuir monolayers made from conventional amphiphiles[1]. Grazing incidence x-ray diffraction (GIXD) and x-ray reflectivity (GIXR) studies[2] on $F_{12}H_{18}$ concluded that the most probable model was a monolayer with the H_m segments being in contact with water and the F_n segments extending up from the surface. However, a bilayer model in which the diblocks are anti-parallel, with tilted F_8 segments outwards and interleaved H_{18} segments inwards has recently been proposed on the basis of similar x-ray reflectivity measurements[3]. After Langmuir Blodgett transfer onto silicon substrates, we have shown that surface micelles were formed using a semi-fluorinated alkane, $C_8F_{17}C_{16}H_{33}$ (F_8H_{16}). In these "hemimicelles" the fluorinated segments F8 point towards air and the hydrogenated segments H_{16} are in contact with the silicon surface[4] (see figure 1- bottom). However, the presence of surface micelles vas still contreversy. Our experiment was an attempt to determine whether or not micelles was present on the water surface.

In order to unravel the structure of semifluorinated alkane at the air/water interface, we performed Grazing Incidence x-ray Scattering on Langmuir monolayers of F8H16 on the ID10B beamline. We used a monochromatized x-ray beam of energy 8keV ($0.154nm$). The beam was deflected downwards to impinge on the water surface with an incident angle of $1.98mrad$. In the way to reaches smallest Q vectors, we limit the beam size to $300\mu m$ horizontally and to $100\mu m$ vertically. Scattered photons was detected by a vertical PSD ($150mm$ height) located at $835mm$ from the center of the goniometer (COG). As collimator, we used two verticals slits of horizontal gap of $300\mu m$ and $500\mu m$ and located respectively at $272mm$ and $803mm$ from the COG. The sample was deposited in a home built gas tight Langmuir through adapted to the goniometer and flushed by Helium gas. The Surface pressure measurement accuracy was $0.1mNm^{-1}$.

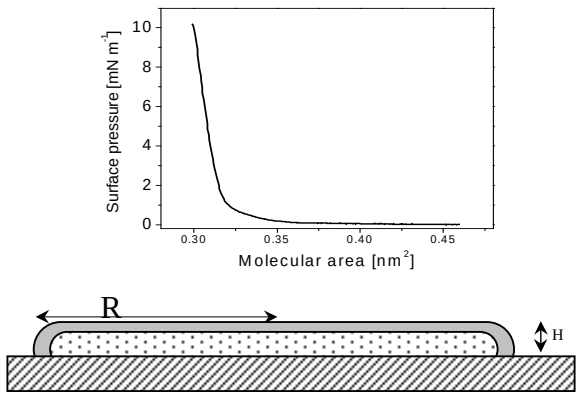

Figure 1: top: Surface pressure vs. Area isotherm of F8H16 monolayer on pure water surface. Bottom : Schematic representation of the cross-section of a surface micelle of F8H16 (disc-like model). The gray area represents the fluorinated segment F8 region and the dotted area represents the hydrogenated segment H16 region

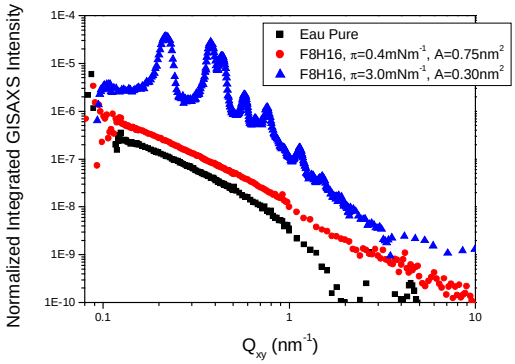

Figure 2 : GISAXS spectra measured on pure water surface and on a monolayer of F8H16 diblock at two different surface pressure, at $\pi = 0.4mN.m^{-1}$ *on the "plateau region" (red dots), and at* $\pi = 3.0mN.m^{-1}$.

Figure 1-top gives the surface pressure vs. area per molecule isotherm of a F8H16 monolayer deposited at the air water interface. The compression of such monolayer results in a "plateau" region at high area per molecule followed by a pressure rise at $0.36nm^2$. The collapse pressure is rather low at $10mN.m^{-1}$ due to the absence of a polar head in the molecule. Figure 2 gives the Grazing Incidence x-ray Small Angle Scattering (GISAXS) of F8H16 monolayer measured for two different surface density. First on the "plateau" region at $0.4mN.m^{-1}$ and at an area per molecule of $0.75nm^2$, area of the deposition of the monolayer. At such surface density, the curve is featureless, and the evolution of the scattered intensity with the scattering wave vector appears only determined by capillary wave fluctuations and surface pressure[5]. However, compressing the monolayer at $3mNm^{-1}$, one observe at least 12 diffraction peaks (figure 2, some peaks are not visible due to the scale needed for the first peaks). They can be indexed in a hexagonal lattice of $33nm$ parameter, as presented in Table 1. This dimension is very good agreement with the size of the micelle observed by AFM[4]. Thus these experiments demonstrate unambiguously the presence of surface hemimicelles of semifluorinated alkanes at the at water interface prior Langmuir Blodgett deposition. Moreover these experiment evidences an hexagonal packing of the hemimicelles on the liquid surface. Up to our knowledge, this is the first time that organized surface micelles are evidenced at the air water interface using GISAXD.

Q (nm^{-1})	W (nm^{-1})	L (nm)	Indexation (hexagonal lattice)	Q (nm^{-1})	W (nm^{-1})	L (nm)	Indexation (hexagonal lattice)
0.2159	0.0249	250	1 0	0.8478	0.0222	280	40
0.3772	0.0303	210	1 1	0.939	0.044	140	32
0.4333	0.0307	200	2 0	1.113	0.0524	120	33
0.575	0.033	190	2 1	1.172	0.0362	170	42
0.6509	0.0299	210	3 0	1.293	0.068	90	60
0.747	0.0467	130	22	1.482	0.0438	140	44

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