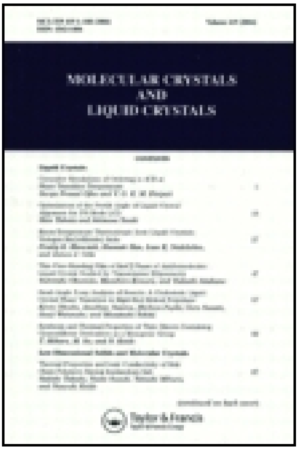

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Molecular Orientation in a Semi-Fluorinated Alkane Monolayer Spread at the Air-Water Interface

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We show that a stable monolayer of $F(CF_2)_8(CH_2)_2$-S-$(CH_2)_{16}H$ molecules can be obtained at the air water interface. The molecular orientation within the monolayer has been determined at the air-water interface by means of surface pressure isotherms, surface charge as a function of the molecular area measurements and fluorescence microscopy. We propose a theoretical model to explain the experimental results. For molecular areas larger than 60 $Å^2$(π = 0 mN/m), half of the molecules extend their perfluorinated chains up and their hydrocarbonated chains down. At molecular areas about 30 $Å^2$, the monolayer exhibits a condensed-like phase for which all the molecules extend their perfluorinated chains up. The transition between these two phases is first order. Eventually, we deduce a value about 4 for the dielectric constant of the monolayer.

Keywords: Langmuir film; semi-fluorinated alkane; dipole moment

INTRODUCTION

One of the main structural features of smectogenic molecules is their amphiphilic character (1). They generally consist of two distinct parts which are non miscible with one another (2). This feature gives rise to the formation of separating alternating sublayers and hence to the well known smectic layering.

Few years ago, structural and thermodynamic properties of semi-fluorinated n-alkanes which chemical formula is $F(CF_2)_n(CH_2)_mH$ (labeled as F_nH_m), have been investigated for their mesogenic properties (3,4). Particularly, based on the non mixing of alkanes and fluoroalkanes (5,6,7), Mahler *et al.* (8) have shown that the $F(CF_2)_{10}(CH_2)_{10}H$ compound exhibits a smectic B bulk phase in the 38-61 °C range.

More recently, Gaines showed that three semi-fluorinated n-alkanes homologues ($F_{12}H_{18}$, $F_{10}H_{12}$ and $F_{12}H_8$), which form mesophases (9), can lead to stable monolayers at the air-water interface (10). Since these molecules consist of two hydrophobic chains, it is surprising to obtain stable monolayers with such kind of hydrophilic headless molecules. In his work, Gaines suggested that due to the low surface energy of perfluorinated chains (18 mN/m for Teflon) the molecules should be oriented normal to the interface with their perfluorinated chains extending up and their hydrogenated chains immersed in water. However, this argument is not persuasive because, on the one hand, his assumption is made only on geometric considerations, and on the other hand, the terminal -CF_3 group of the perfluorinated chains has a strong dipole (1.7 D) and could lead also to hydrogen bonding with water molecules if the perfluorinated chains are put in contact with the water subphase (11).

In the present work, we have been interested in the contribution of the electrostatic interactions in the structure of these systems. The organization of the semi-fluorinated molecules at the air-water interface was studied by surface pressure-molecular area (π-A diagrams) and surface charge-molecular area isotherms and also by means of fluorescence microscopy.

EXPERIMENTAL

The formula of the semi-fluorinated alkane we have used is $F(CF_2)_8(CH_2)_2S(CH_2)_{16}H$, noted in the following F_8SH_{16}. The molecule was synthesized and purified by F. Guittard at Sophia-Antipolis University, Nice, France. The molecule contains a sulfur atom between the fluorinated and the hydrogenated chains which is bound to the fluorinated segment through an ethyl group. The molecule have a permanent molecular dipole moment μ, tilted with regard to the average molecular axis by an angle about 37°, oriented from the fluorinated segment toward the hydrogenated part and whose modulus is about 2.9 Debye. A schematic representation of the molecule is given on the figure 1. The molecule length is about 36 Å. This compound has a clearing point at about 46°C. The bulk polymorphism of this compound has not been studied yet.

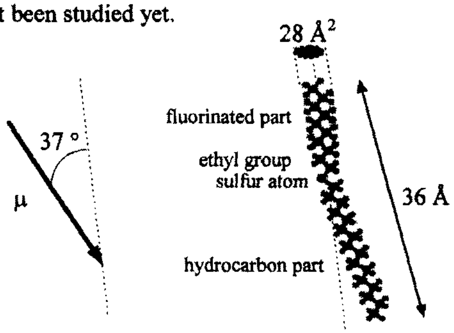

Figure 1 : Schematic representation of the F_8SH_{16} molecule. The dashed line shows the average molecular axis of the molecule. μ is the permanent molecular dipole moment of the molecule, its length is about 36 Å and its cross section is 28 Å^2.

The surface pressure isotherms were obtained with a Teflon Langmuir film balance (Lauda). The experiments were performed at T = 20°C and water pH = 5.7. The trough temperature was controlled by using RM6 Lauda thermostat. The monolayers were obtained by depositing small drops of the semi-fluorinated alkane dissolved in a 2.5×10^{-3} M chloroform solution (Normapur, Prolabo) on the air-water interface. After 15 minutes, the monolayer was compressed with a moving barrier, at a compression rate of 4 Å^2/molecule/mn. The surface pressure was measured continuously with a Wilhelmy plate and with an accuracy of about 0.1mN/m.

The charge measuring device was monitored together with the Langmuir balance. Figure 2 shows the experimental set-up which was described in details elsewhere (12,13). In this technique, two stainless steel electrodes, of rectangular shape, are placed parallel to the air-water interface. Electrode 1 was suspended in air and the electrode 2 was immersed in water. The surface of the electrode 1 was $S_e = 64\ cm^2$. It was electrically shielded by a surrounding metallic box. For all experiments, the distance between the electrode 1 and the air-water interface was adjusted to $d_e = 2 \pm 0.1$ mm by using a micrometer screw. The surface charge flowing through the circuit ΔQ was measured by an electrometer (Keithley 617) connected to a computer. The π-A and ΔQ-A isotherms were recorded simultaneously. The accuracy of the charge measurements was about 0.5 pC.

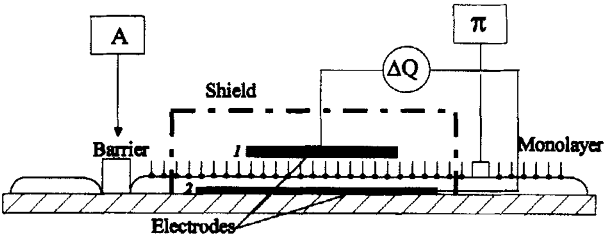

Figure 2 : Schematic representation of the surface pressure π and the surface charge ΔQ versus molecular area A measurements setup. ΔQ is the charge flowing through the circuit during the monolayer compression.

When N molecules carrying a net a dipole moment are at the air-water interface and under the electrode 1, a charge Q is induced on this electrode (14). The charge ΔQ flowing through the circuit during the monolayer compression is given by (14) :

$$\Delta Q = \frac{N}{d_e}\frac{<\mu_z>}{\varepsilon} = \frac{S_e}{A\,d_e}\frac{<\mu_z>}{\varepsilon} \qquad (1)$$

where $<\mu_z>$ is the average vertical component (perpendicular to the interface) of the permanent molecular dipole moment μ and ε is the effective dielectric permittivity of the monolayer. Consequently, a flow ΔQ of charges can be generated from electrode 1 to electrode 2 during the film compression due to variation of N, and due to change of the molecules orientation (*e.g.* change of $<\mu_z>$).

The fluorescence microscopy technique permits to observe two phases coexistence during a first order transition. Indeed, the concentration of the fluorescent dye in the Langmuir film differs from one phase to another and a contrast appears between the coexisting phases. The fluorescence microscopy observations were obtained with an Olympus-BX30 microscope, set on a small Riegler&Kirstein Langmuir trough. An AIS (MXRi2) video camera with an image intensifier which allows for a very high sensitivity (10^{-6} Lux) enabled us to visualize the film and record images. The solution containing 1 % (molar fraction) of the fluorescent dye NBD-cholesterol purchased from Molecular Probes was spread on the water surface. The NBD group has an absorption band in the blue range (470 nm) and a fluorescence band in the yellow range (530 nm). After 15 minutes, the monolayer was compressed with a moving barrier, at a compression rate of 4 Å^2/molecule/mn. The surface pressure was measured continuously with a Wilhelmy plate. The images were recorded at different surface densities, during the compression or after stopping the barrier. The different experiments were carried out at T = 20 °C.

RESULTS

Figure 3 shows the π-A and ΔQ-A isotherms obtained during the compression and the decompression of a F_8SH_{16} film. At molecular areas larger than 32 Å^2, the surface pressure is practically equal to zero. For molecular areas in the vicinity of 30 Å^2, the surface pressure increases abruptly and regularly up to 18 mN/m. The coefficient of compressibility is about 5.7 10^{-3} m.mN^{-1}. The 28 Å^2 molecular area value is equal to the cross section of a fluorinated chain (15). These features are characteristic of the Condensed Liquid phase (LC phase) of the fluorinated chains (16). In this phase the molecules are oriented normal to the interface, and at this stage, we could suppose that the perfluorinated chains of the molecules, respectively hydrogenated chains, are extended either up or down.

The negative sign of the flowing charge ΔQ shows the average vertical component of the molecular dipole moment $<\mu_z>$ is getting oriented downwards (from the air (-) to the monolayer (+)) upon the compression. The surface charge ΔQ remains practically zero for A larger than 60 Å^2. This is clearer in the figure 4 which represents a ΔQ-A isotherm for a monolayer spread at large molecular area (about A = 125 Å^2/molecule).

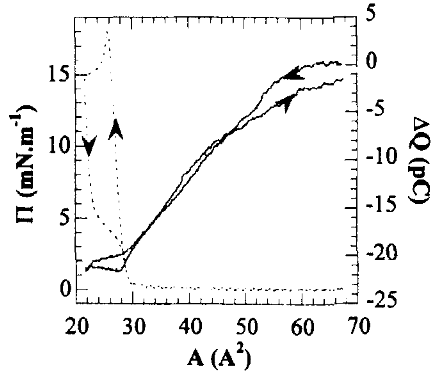

Figure 3 : Surface pressure (π)-molecular area (A) (------) and surface charge flowing through the circuit (ΔQ)-molecular area (A) (——) isotherms obtained during the compression and the expansion of a F_8SH_{16} monolayer spread at the air-water interface. The arrows show the moving direction of the barrier.

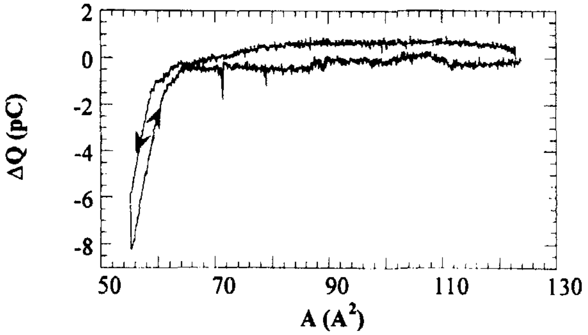

Figure 4 : Surface charge flowing through the circuit (ΔQ)-molecular area (A) isotherm obtained during the compression and the expansion of a F_8SH_{16} monolayer spread at large molecular area. The arrows show the moving direction of the barrier.

Figure 5 shows fluorescence microscopy images of a F_8SH_{16} monolayer at two different molecular areas. The field of view of the microscope remained uniform up to A ~ 60 Å^2/molecule (figure 5-a). Then, brilliant domains appeared (figure 5-b) and grown upon compression. These bright regions correspond to dense domains dispersed in a lower density monolayer. The existence of these domains is a clear evidence of the existence of a first order transition. When the compression reached 30 Å^2/molecule, which corresponds to the LC phase, the field of the microscope became uniformly bright which means the film is homogeneous. Consequently, the transition plateau extends from 60 Å^2/molecule to 30 Å^2/molecule.

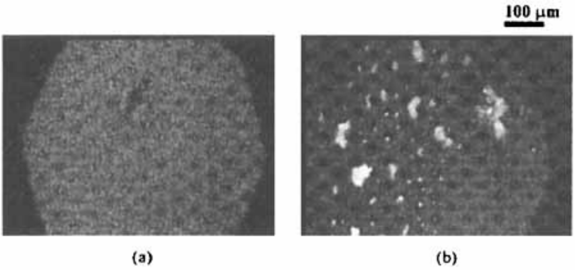

Figure 5 : Fluorescence microscopy images of a F_8SH_{16} monolayer at the air water interface and at different molecular areas : 100 Å^2/molecule (a), 60 Å^2/molecule (b). The dimensions of the images are 700×500 μm^2.

Because of these observations, we concluded the zero surface pressure plateau observed in the π-A isotherm does not correspond, as for the classical amphiphilic molecules, to a transition from a gas phase to a dense phase. Indeed, if it was such a phase transition, the coexistence region of bright and dark domains should extend to molecular areas much larger than 60 Å^2/molecule.

DISCUSSION

Surface charge measurements and fluorescence microscopy results allowed us to show the existence of a transition from A ~ 60 Å^2/molecule downwards.

We cannot see this transition from the pressure surface isotherms because π is practically equal to zero from large molecular areas to about 30 Å^2/molecule.

In principle, zero surface charge ΔQ can be measured either because the molecules density on the water surface is very low or because all the molecules lie on the water surface. For our system, on the one hand, the molecule density is high enough to generate a non zero charge flowing through the circuit at A ~ 60 Å^2/molecule. On the other hand, the area that would occupy a F_8SH_{16} molecule if the molecules were supposed to be lying flat at the air-water interface would be about 180 Å^2 which is three times larger than 60 Å^2. Therefore, molecules cannot lie parallel to the interface at A ~ 60 Å^2/molecule. Consequently, we suggest the following model to explain our results. We suppose the organization of the molecules at the air-water interface is governed by the competition between the non miscibility of the fluorinated and hydrogenated blocks and the dipole interactions. At areas larger than 60 Å^2/molecule, the monolayer is stabilized by anti-parallel dipole interactions. Since ΔQ is equal to zero, we suppose half the molecules are oriented with their fluorinated chain downwards (μ_z) and the other half are oriented with their fluorinated chain upwards ($-\mu_z$). In the dense phase (LC phase), the molecules are close packed and because of the non miscibility of the fluorinated and hydrogenated segments, all the molecules have the vertical component of their dipole moment oriented downwards.

On the transition plateau, ΔQ should be expressed as follows :

$$\Delta Q = \frac{\mu_z}{d_e\,\varepsilon} N_1 - \frac{\mu_z}{d_e\,\varepsilon} N_2 \qquad (2)$$

where N_1 and N_2 are the number of molecules under the electrode 1 for which the normal component of the dipole moment is respectively oriented upwards and downwards.

N_2 can be expressed using the lever rule:

$$N_2 = N_{0_2} + \frac{1}{2} N \left(\frac{A_1 - A}{A_1 - A_2} \right) \qquad (3)$$

where A_1 ~ 60 Å^2/molecule is the molecular area at the beginning of the transition, A_2 ~ 30 Å^2/molecule is the molecular area at the end of the transition and $N_{0_2} = \frac{1}{2}\frac{S_e}{A_1}$ is the number of molecules under the electrode 1 at $A = A_1$ for which the dipole moment is oriented downwards.

Substituting $N_1 = N\text{-}N_2$, N_2 and the A_1, A_2 and N_{0_2} values in equation (2), the surface charge flowing through the circuit can be expressed by:

$$\Delta Q = -\frac{S_e \mu_z}{d_e \varepsilon}\frac{1}{A} + \frac{S_e \mu_z}{60\, d_e \varepsilon} \qquad (4)$$

Figure 6 shows the variation of ΔQ versus $1/A$. This curve is well-fitted by the linear function $\Delta Q = k_1 A^{-1} + k_2$ with k_1 = -1180 pC.Å^{-2} and k_2 = 18.3 pC (regression coefficent R = 0.99). The $\frac{\mu_z}{\varepsilon}$ value can be deduced either from the slope of the curve $\Delta Q(A^{-1})$ or from the extrapolation of the ΔQ value at $1/A = 0$. We find respectively $\frac{\mu_z}{\varepsilon}$ = 1.11 Debye and 1.03 Debye which are very close each other.

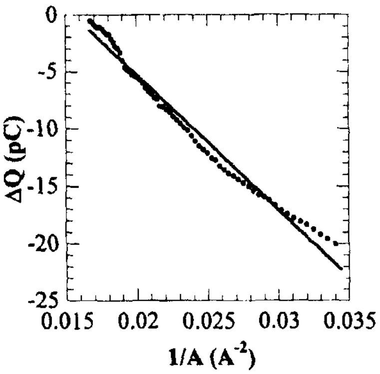

Figure 6 : Variation of the charge flowing through the circuit ΔQ versus 1/A in the transition region (60 Å^2 to 30 Å^2) : experimental curve (•) and theoretical curve (full line).

The ratio $\frac{\mu_z}{\varepsilon}$ is often referred to as an *apparent* dipole moment of the molecule because it contains the dielectric constant ε of the monolayer and also the reorientation of water molecules during the monolayer compression

(17,18). In our case however, we can reasonably neglect the reorientation of water molecules beneath the monolayer due to a lack of strong interactions between monolayer and water molecules. Indeed, it seems that the orientation of the molecules at the air-water interface is governed by semifluorinated-semifluorinated molecules interactions within the monolayer and not by water molecule-semifluorinated molecule interactions. Since in the LC phase the molecules are normal to the interface (16), the average vertical component of the dipole moment should be equal to $\mu_z = \mu \cos 37 = 2.3$ D. Hence, we could deduce from $\Delta Q(A)$ a value of the dielectric constant of the monolayer : $\varepsilon = 4$.

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