



Properties of Langmuir monolayers from semifluorinated alkanes

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Abstract

The aim of this study was to characterize several semifluorinated alkanes (SFA), of the general formula $F(CF_2)_m(CH_2)_nH$ (in short $FmHn$), containing 25 carbon atoms in total (pentacosanes) differing in the m/n ratio, as Langmuir monolayers at the free water surface. The following compounds have been studied: F6H19, F8H17, F10H15 and F12H13. Surface pressure (π) and electric surface potential (ΔV) isotherms were recorded in addition to quantitative Brewster angle microscopy results. The negative sign of ΔV evidenced for the orientation of all the investigated semifluorinated pentacosanes, regardless the length of the hydrogenated segment, with their perfluorinated parts directed towards the air. As inferred from apparent dipole moment values and relative reflectivity results, the fluorinated pentacosanes with shorter perfluorinated fragment (F6H19 and F8H17) were found to be vertically oriented at the air/water interface, while those with longer perfluorinated moiety (F10H15 and F12H13) remain tilted even in the vicinity of the film collapse.

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1. Introduction

Perfluorinated alkanes and hydrocarbons are known to have limited mutual solubility and tend to segregate. A very different physicochemical characteristic of alkanes and their perfluorinated analogues have stimulated efforts to synthesize a new group of

compounds containing within one molecule two opposing moieties namely: perfluorinated and hydrogenated, covalently bound together. These chemicals of the general formula $F(CF_2)_m(CH_2)_nH$ (in short $FmHn$) called semifluorinated alkanes (SFA), were originally synthesized by Brace in the 60s of the preceding century [1], whereas their physical properties in solution and in the solid state were first investigated by Rabolt et al. [2]. Turberg and Brady [3] showed that SFA are surface active both in hydrocarbon and perfluorinated liquids solutions, and called them “primitive surfactants”. SFA are known to

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decrease the interfacial tension between hydrocarbons and fluorocarbons [4], thus causing emulsion formation. They also reveal surface activity in supercritical CO₂ [5] and were tested, alone and in mixtures with other fluorinated substances, as stabilizers of water in supercritical CO₂ emulsions. Some of SFA, especially F6H8, were clinically applied in ophthalmology as so-called endotamponades in retinal surgery [6,7]. Other SFA were tested as components of blood substitutes [8,9].

SFA form Langmuir monolayers when spread at the water/air interface. This phenomenon, first reported by Gaines [10], was a breakthrough as regards floating monolayers, which were previously believed to be formed only by amphiphilic molecules having a polar “head” group and a hydrophobic “tail”. Research on Langmuir monolayers from SFA was continued by Acero and coworkers [11] and later by El Abed et al. [12–14].

Studying the papers which have appeared so far on Langmuir monolayers formed by SFA one may infer that the investigated compounds were chosen for research randomly. No systematic studies have been performed to be able to conclude how the ratio of the perfluorinated to the hydrogenated chain length of a SFA molecule affects its film forming properties. To shed light on this problem, we have synthesized four different semifluorinated alkanes, namely F6H19, F8H17, F10H15 and F12H13. All of them possess 25 carbon atoms in total, and thus can be treated as derivatives of *n*-pentacosane, differing in the degree of its fluorination. Mechanic properties of Langmuir monolayers formed by the above mentioned compounds are characterized herein by the π -*A* isotherms and stability measurements, while electrical properties are investigated by surface potential measurements and dipole moment calculations. In addition, optical properties of the monolayers are studied applying Brewster angle microscopy in its quantitative aspect (relative reflectivity measurements).

2. Experimental

SFA were synthesized according to the procedure described previously [2]. The purity of obtained products (>99%) was corroborated by ¹H and ¹³C NMR, mass-spectroscopy and elemental analysis. The

spreading solutions for Langmuir experiments were prepared by dissolving the compound in freshly distilled chloroform (Aldrich, HPLC grade) with a typical concentration of ca. 1 mg/ml. In a typical experiment, 50–100 μ l of chloroform solution was spread with a Microman Gilson microsyringe, precise to $\pm 0.2 \mu$ l. After spreading, monolayers were left for 10 min to enable the solvent to evaporate, after which the compression was initiated with a routine barrier speed of 25 cm²/min. Ultrapure water (Milli-Q water purification system, resistivity = 18.2 M Ω cm) was used as a subphase. Its temperature was controlled to within 0.1 °C by a circulating water system from Haake. Monolayer experiments were performed with a single barrier trough (NIMA 601, Coventry, UK) (total area = 550 cm²) placed on an anti-vibration table. Surface pressure was measured with the accuracy of ± 0.1 mN/m using a Wilhelmy plate (made from chromatography paper, Whatman Chr1) as the pressure sensor. Surface potential measurements (reproducible to ± 10 mV) were carried out using the Kelvin probe (model KP2, NFT, Germany) mounted on a NIMA trough. Relative intensity measurements were performed with BAM2 plus (NFT, Germany), equipped with a 30 mW laser emitting *p*-polarized light at 690 nm wavelength. The incident light was reflected off the air/water interface at approximately 53.1° (Brewster angle). At these conditions:

$$I = |R_p|^2 = Cd^2 \quad (1)$$

where *I* is the relative intensity, *C* the constant, *d* the film thickness and *R_p* is the *p*-component of the light.

3. Results

All the synthesized here SFA were found to be capable of Langmuir monolayer formation at the free water surface. Their π -*A* isotherms are shown in Figs. 1–3 at three different subphase temperatures. It is rather difficult to find any regular tendencies analyzing the π -*A* isotherms of the investigated molecules. The onset of surface pressure is observed at molecular areas ranging from 0.3 to 0.40 nm², and the film collapse occurs between ca. 10 and 16 mN/m. For a more precise analysis, plots of the compression modulus, *C_s*⁻¹ [defined as *C_s*⁻¹ = -*A*(d π /d*A*)] as a

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