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Langmuir and Langmuir-Blodgett films of di-ureasil hybrid compounds containing phosphotungstic acid

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ABSTRACT

The search for new molecular architectures to improve the efficiency of sensors and optoelectronic devices is fundamental to enhance the effectiveness of nanostructured materials. In this present work, a di-ureasil hybrid compound (DUPTS) was spread at the air-water interface in order to form Langmuir monolayers. Phosphotungstic acid, $H_3PW_{12}O_{40}$, PWA inserted in the aqueous subphase stabilized the formation of DUPTS as a stable Langmuir film, as showed with surface pressure and surface potential-area isotherms, rheological measurements, polarization modulation reflection-absorption spectroscopy, and Brewster angle microscopy. The monolayers were transferred to solid supports as Langmuir-Blodgett films and presented different patterns of heterogeneity as observed with atomic force microscopy, with the morphology dependent on the presence of PWA and on the kind of solid support surface.

1. Introduction

Recently, silicon alkoxides have been employed in sol-gel routes for the formation of polymeric electrolytes acting as a host matrix, generating hybrid organic/inorganic compounds with their own characteristics, which can be applied for the production of advanced materials for lasers, luminescent devices and optical amplifiers [1,2]. Among these compounds, di-ureasil DUPTS (structure shown in Fig. 1) has been used as precursor for luminescent materials produced from the sol-gel process [3].

Also, polyoxometalates have been shown as an attractive class of photochromic materials because of their structure and versatility [4,5]. They were also studied in di-ureasil hybrids in the form of monoliths [6]. The importance for application of these materials relies on the fact that they can be employed as commercial catalysts for oxidation of organic compounds [7,8]. For instance they can be used as alternatives to chlorine-based wood pulp bleaching processes [9], and for decontaminating water [10]. Also they can employed in flash memory devices [10], nanocomputer storage devices [11,12], and as a potential antitumor and antiviral drugs [13–15]. Some polyoxometalates are reported to inhibit amyloid β (Aβ) aggregation in a therapeutic strategy for Alzheimer's Disease [16]. When these compounds are structured as ultrathin films, they may exhibit functional and differentiated properties of those obtained in monoliths [17]. These facts make polyoxometalates interesting to be investigated at interfaces and organized in nanometric structures.

As they present low solubility in water and are amphiphilic, presenting some hydrophobic and hydrophilic groups, it is likely that they may form Langmuir films at air-water interfaces. Furthermore, floating monolayers is a powerful tool to investigate interactions at the molecular level as many properties can be controlled using this approach, such as surface density, composition, and surface tension. Langmuir films are molecular films of amphiphiles formed at the gas-liquid interface [18], being widely used as membrane models for enzyme actions [19,20], polysaccharide interactions [21], and incorporation of drugs [22,23]. When these monomolecular films are transferred to solid surfaces by the vertical passage of solid substrates, the so-called Langmuir-Blodgett (LB) films are formed [24]. LB films can be characterized by a variety of techniques and molecular interactions at the molecular level can be deeper investigated.

In this context, in this present work, we have studied DUPTS-type precursors as Langmuir films, and characterized them with surface-area pressure isotherms, surface-area potential isotherms, dynamic surface rheology, infrared spectroscopy and Brewster angle microscopy. The effect of phosphotungstic acid, $H_3PW_{12}O_{40}$, PWA, was investigated by inserting it into the aqueous subphase. PWA is a known type of polyoxometalates (POMs), classified as metal-oxide cluster, presenting interesting characteristics such as high electron density, reduction properties, especially under ultraviolet irradiation, as well as solubility in different kind of solvents. They can be also incorporated in many organic, inorganic and hybrid matrices. This behavior makes it appropriated for many applications in different areas such as biology,

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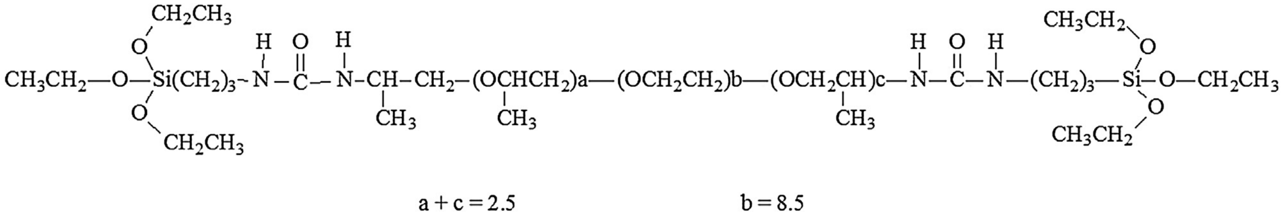

$$CH_3CH_2{-}O{-}Si(OCH_2CH_3)_2(CH_2)_3{-}NH{-}C(=O){-}NH{-}CH(CH_3){-}CH_2{-}(OCH(CH_3)CH_2)_a{-}(OCH_2CH_2)_b{-}(OCH_2CH(CH_3))_c{-}NH{-}C(=O){-}NH{-}(CH_2)_3{-}Si(OCH_2CH_3)_3$$

$a + c = 2.5$ $b = 8.5$

Fig. 1. Structure of DUPTS.

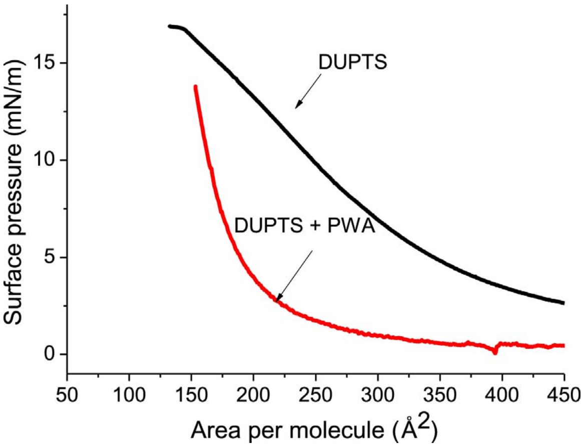

Fig. 2. Surface pressure-area isotherms for DUPTS spread at the air-water interface without or with PWA as indicated through arrows on the graph.

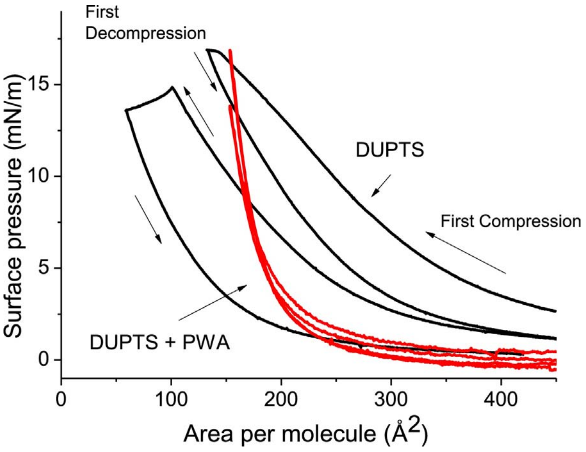

Fig. 3. Surface pressure-area isotherms for cycles of compression-decompression of DUPTS spread at the air-water interface without or with PWA as indicated through arrows on the graph. The surface areas of compression and decompression are in the same interval.

catalysis, and optical [25–28]. PWA was chosen because we intend to form nanostructured hybrid materials with DUPTS aiming a possible application as a sensor and this polyoxometalate may present photochemical and structuring properties [30,31]. The films were then transferred to solid substrates as Langmuir-Blodgett films and characterized by surface techniques (contact angle and specific vibrational spectroscopy), and morphological (atomic force microscopy). The arrangement of these compounds as nanostructured films can provide hybrid matrices for the immobilization of compatible biomolecules for future application as sensors as well as other optoeletronic devices.

2. Materials and methods

The di-ureasil DUPTS hybrid precursor was synthesized by the cross-links between the organic and the inorganic parts reacting the NH_2 groups of a diamine commercially named as Jeffamine-ED600® (where 600 $gmol^{-1}$ is the average molecular weight of the polymer chain) and $-N{=}C{=}O$ group of 3-isocyanatepropyltriethoxysilane, ICPTES in a molar ratio ICPTES: Jeffamine 2:1 in tetrahydrofuran, THF, under reflux and magnetic stirring at 80 °C for 24 h. DUPTS was obtained after the evaporating of the THF solvent [3,19,20]. The compound used in this work was previously characterized by our group [32–34].

DUPTS was dissolved in chloroform (Synth, purity higher than 99%) to give a 0.8 mg/mL concentration solution. This solution was spread drop by drop at the aqueous solution-air interface whose subphase was formed either with ultrapure water or with an aqueous solution of phosphotungstic acid, $H_3PW_{12}O_{40}$, PWA, which was purchased from Sigma-Aldrich. PWA solutions were prepared to give a 10^{-4} mol/L concentration. The films were prepared in a Langmuir trough (model mini KSV instruments), equipped with surface pressure sensor, a Kelvin probe for surface potential, a Polarization-modulation infrared reflection absorption spectrophotometer (PM-IRRAS) (KSV PMI 550 instrument), a Brewster Angle Microscopy (KSV-Nima Instruments, model: micro BAM3), and a dipper that allowed transfer of floating monolayers from the liquid interface to solid supports. The surface area of the Langmuir trough was 36 × 7 cm^2 and total volume of approximately 220 mL. Trough and barriers were made of Teflon®. Surface compression can lead to a decrease of the 10% of the maximum area. Molecular area is calculated by the software informing the molar concentration of the solution, its molecular weight and spread volume at a given surface area determined by the position of the barriers.

After carefully spreading 10 µL of the DUPTS solution on the top of the air-water interface, drop by drop, 10 min were waited for the evaporation of chloroform. The air-water interface was then compressed with two movable barriers at a rate of 10 $mmmin^{-1}$ (5 $Å^2$ $molecule^{-1}$. s^{-1}). Aqueous subphase was constituted of pure water (pH ~6.0). The surface pressure was monitored with a Wilhelmy plate made of filter paper that intercepted the air-water interface, while the surface potential was measured using a Kelvin probe. Surface pressure and surface potential were measured as long as the surface area decreased.

Polarization-modulation reflection-absorption spectroscopy (PM-IRRAS) measurements were done with the monolayers previously compressed to 12 mN/m. For that the air-water interface was compressed at a rate of 10 $mmmin^{-1}$ until the desired surface pressure. This value was kept constant during the obtaining of the spectra due to the action of the barriers. The incidence angle of the infrared beam to the normal was 75° and the detector obtained the reflective beam at the same angle of incidence. A minimum of 6000 scans were obtained for each spectrum and the absorption of the p (R_p) and s (R_s) components of the light was obtained independently. The PM-IRRAS signal is calculated as the rate between $R_p - R_s$ and $R_P + R_p$ eliminating vibrational isotropic absorptions such as from as water vapor and CO2.

Images of the monolayer at desired values of surface pressure were obtained with a Brewster angle microscope. The microscopy is positioned above the air-water interface so that a polarized light source beats the liquid surface at that water's Brewster angle in such a way for the microscope to catch an image of any light reflected from the light source via the liquid surface. Since there is no p-polarized reflection from the surface of pure water, after the spreading of the monolayer, the optical parameters of the reflective surface change and a contrast of