ADSORPTION OF DODECAHYDROXYLATED-FULLERENE MONOLAYERS AT THE AIR WATER INTERFACE

by

W. -J. Liua, U. Jenga and T. -L. Lin **Department of Engineering and System Science** National Tsing Hua University Hsinchu 30043 Taiwan and S.-H. Laib and M. C. Shih **Department of Physics** National Chung-Hsin University Tai-Chung 402 Taiwan and C.-S. Tsao Division of Nuclear Fuel and Materials **Institute of Nuclear Energy Research** Lungtan 325 Taiwan and L. Y. Wangd and L. Y. Chiang **Center for Condensed Matter Sciences** National Taiwan University Taipei 106, Taiwan and **Li-Piin Sung Building and Fire Research Laboratory** National Institute of Standards and Technology Gaithersburg, MD 20899-8621 USA

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Adsorption of dodecahydroxylated-fullerene monolayers at the air-water interface

W.-J. Liu^a, U. Jeng^a, T.-L. Lin^a, *, S.-H. Lai^b, M.C. Shih^b, C.-S. Tsao^c, L.Y. Wang^d, L.Y. Chiang^d, L.P. Sung^e

^aDepartment of Engineering and System Science, National Tsing Hua University, 101, Sec. 2, Kvang Fu Road Hsinchu 30043, Taiwan ^bDepartment of Physics, National Chung-Hsin University, Tai-Chung 402, Taiwan

> ^eDivision of Nuclear Fuel and Materials, Institute of Nuclear Energy Research, Lungtan 325, Taiwan ^dCenter for Condensed Matter Sciences, National Taiwan University, Taipei 106, Taiwan ^eNational Institute of Standards and Technology, Gaithersburg, MD 02899, USA

Abstract

We study the adsorption behaviors of dodecahydroxylated-fullerene $C_{60}(OH)_{12}$ at the air-water interface. With the hydrophilicity imposed by the 12 hydroxy groups randomly bounded on the C_{60} cage, $C_{60}(OH)_{12}$ can dissolve in water slightly. Surface pressure-area isotherms, Brewster angle microscopy, and neutron reflection results for the aqueous solutions of $C_{60}(OH)_{12}$ provide consistent evidence of adsorbed $C_{60}(OH)_{12}$ monolayers at the air-water interface. A Langmuir-Blodgett film of $C_{60}(OH)_{12}$, prepared from the sample solution with the vertical dipping method, is examined using atomic force microscopy. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Langmuir films consisting of fullerenes or fullerenederivatives attract attention both for their potential applications and as model two-dimensional thermodynamic systems [1]. These two approaches are based on, essentially, the unique physical characteristics of fullerenes [2] and the high coherent scattering for X-ray or neutron from a single fullerene molecule. The latter is a special advantage in characterizing two-dimensional surface structures using grazing incidence X-ray and/or neutron scattering [3].

In the spreading of C_{60} or C_{70} fullerenes on aqueous surfaces, multilayered films are often obtained due to the strong aggregation of fullerenes [4,5]. In an attempt to reduce the high hydrophobicity of fullerenes to facilitate the formation of a molecular monolayer at the air-water surface, fullerene-derivatives functionalized with various polar groups have been synthesized. These C_{60} -derivatives have varying degrees of success in the Langmuirmonolayer formation, depending on their enhanced amphiphilicity [4,6,7]. In comparison with these C_{60} derivatives, the fullerene derivative $C_{60}(OH)_{12}$ which we synthesized has a considerably improved hydrophilicity due to the 12 hydroxy groups randomly bounded on the C_{60} cage, and can dissolve in water slightly [2]. We expect that $C_{60}(OH)_{12}$ molecules may form stable Langmuir monolayers on water surfaces as well [8,9]. Furthermore, the spherical shape of $C_{60}(OH)_{12}$ may be advantageous in depositing Langmuir–Blodgett (LB) films of well-organized multilayers of fullerene-derivatives.

Polyhydroxylated- C_{60} (fullerenol) has many other potential applications due to the physical and chemical properties of the C_{60} cage and the hydroxy groups chemically bonded on the cage [2]. With the variation of the hydroxy number, fullerenols can be selectively dissolved in water or organic solvents for biochemical researches or polymer engineering. In synthesizing the

^{*} Corresponding author.

E-mail address: tllin@mx.nthu.edu.tw (T.-L. Lin)

fullerenol-cross-linked poly(urethane-ether) elastomers [10], a good solubility of $C_{60}(OH)_{12}$ in an organic solution containing prepolymers can facilitate an isotropic distribution of fullerenol-cross-linkers in an elastomer cast from the solution [11]. In another direction of application fullerenols of a high hydroxyl number, for instance $C_{60}(OH)_{18}$, have a high water solubility and can serve as free radical scavengers or antioxidants in biological systems [12,13].

In this report, we study the adsorption of $C_{60}(OH)_{12}$ at the air-water interface from bulk solutions using surface pressure-area ($\pi - A$) isotherms [14], neutron reflection [15], and Brewster angle microscopy (BAM) [3]. An LB film of $C_{60}(OH)_{12}$, prepared with the Langmuir technique, is also examined using atomic force microscopy (AFM) [9,14].

2. Experimental

The preparation of dodecahydroxylated-fullerenes was described in Ref. [2]. Sample solutions of 0.22 mM $C_{60}(OH)_{12}$ in H_2O , a concentration few times higher than the solubility, were made and sonicated thoroughly for π -A isotherms, BAM, and neutron reflection measurements, respectively. The neutron reflectivity measurement was performed on the NG7 reflectometer at the Institute of Standards and Technology, Gaithersburg, USA [16]. An LB film of two $C_{60}(OH)_{12}$ layers was deposited on a mica substrate, of size of 1×3 cm², from the sample solution. The 100% and 30% transfer ratios for the first and second layer, respectively, were achieved by vertically dipping the mica substrate in and out of the sample solution subsequently at a constant surface pressure of 5 dyn/cm (see Fig. 1) and an ambient temperature of 25°C [14].

3. Results and discussion

Although the π -A isotherm measured immediately after the fill of the sample solution into the Langmuir trough showed a featureless flat line, the isotherm remeasured few hours later (squares in Fig. 1) displayed similar characteristics as that for other fullerene-derivatives monolayers mentioned previously [6,7,17], and was reproducible. This result demonstrates clearly the adsorption characteristics of C₆₀(OH)₁₂ to the air-water interface from the bulk solution, which, is likely, a slow thermodynamic equilibrium process between the surface and the bulk [18]. The adsorption behaviors were also observed using BAM, which exhibited images of numerous blinking points on the sample surface right after filling the sample solution into the Teflon trough for BAM. These blinking points diminished gradually, im-



Fig. 1. The isotherm (squares) measured for the aqueous solution of $C_{60}(OH)_{12}$ at 25°C. A linear extrapolation (dashed line) of π , in the region corresponding to a condensed phase of the surface monolayer [14], intercepts zero surface pressure at 70 cm² where $C_{60}(OH)_{12}$ in the monolayer are close to packed [4,9,18]. Inset shows the relaxation of π at a surface area of 50 cm².

plying, presumably, the reaching toward an equilibrium state.

The inset in Fig. 1 shows the relaxation of π at a surface area $A = 50 \text{ cm}^2$, after A being compressed to 50 cm^2 from 500 cm^2 at a compression rate of $2 \text{ cm}^2/\text{min}$. Rapidly dropping below 20 dyn/cm within the first few minutes, the measured surface pressure relaxed in a form of $\pi \propto \exp(-t/\tau)$ (solid curve) with a relaxation time $\tau \approx 40 \text{ min}$, and stabilized at 5 dyn/cm.

Using neutron reflection, we also detected a sign of an adsorbed $C_{60}(OH)_{12}$ layer at the air-water interface. In Fig. 2, we show the neutron reflection data (squares) measured for the sample solution without surface compression. The data elevate from that for pure water (circles) gradually as Q increases, indicating the existence of a thin surface layer on water [19]. Here, Q is the wave vector transfer of neutrons. A standard model fitting algorithm [20] for multilayer structures, where a continuous transition between successive layers of different scattering-length-density (ρb) being accounted by the Debye-Waller factor, was used to extract the information of the thin surface layer. It is obvious that the thickness and ρb for the layer are difficult to be determined unequivocally from the limited Q-ranged data measured. Nevertheless, encouraged by the characteristics of the π -A isotherms and BAM observed previously for the sample solutions, we fit the measured reflectivity R with a model consisting of a $C_{60}(OH)_{12}$ layer on water. Considering the partial coverage effect [21], we have $R = fR_{\rm m} + (1 - f)R_{\rm s}$ where f is the fraction for the surface



Fig. 2. Neutron reflection data (squares) for the $C_{60}(OH)_{12}$ solution in H_2O are fitted (long dashed curve) using the scattering-length-density profile shown in the inset. The reflection data (circles) for H_2O are fitted (short dashed curve) by an H_2O Fresnel reflectivity modified with a surface roughness effect of 3 Å.

covered by the layer, R_m the reflectivity for the layer on the H₂O substrate, and R_s the reflectivity for the substrate.

Taking into account, the data-smearing effect due to the instrumental resolution (the divergence and wavelength resolution of the monochrome beam used), we can fit (long dashed curve) the data reasonably well using the ρb profile shown in the inset of Fig. 2 [19]. The thickness of the surface layer $d = 12 \pm 2$ Å fitted corresponds well to a monolayer of $C_{60}(OH)_{12}$ whose thickness (the dimension of the molecule) is approximately 13 Å [22]. The corresponding ρb value obtained for the layer is 1.65×10^{-6} Å⁻². Whereas the f value fitted, 0.64, implies that the monolayer only covers the water surface partially. For neutron reflection, this is equivalent to patches of monolayers on the water surface, a picture that is more close to the observation of BAM. Since the interfacial widths for the surface layer are not sensitive parameters, we have assigned a roughness of 2.1 Å to the air-C₆₀(OH)₁₂-layer and C₆₀(OH)₁₂-layer-water interfaces, respectively, in the fitting process. Thus, the total roughness contributed by the thin $C_{60}(OH)_{12}$ -layer is 3 A, which is a typical value for air-liquid interfaces of a high surface tension (\sim 70 dyn/cm) [23].

From the structural parameters obtained above for the $C_{60}(OH)_{12}$ layer, we have the following deductions. (1) From the ρb value $1.65 \times 10^{-6} \text{ Å}^{-2}$ obtained for the monolayer, we deduce $a = 190 \text{ Å}^2$ for the area per $C_{60}(OH)_{12}$ molecule in this monolayer using



Fig. 3. (a) AFM image of the $C_{60}(OH)_{12}$ film on mica. The darker regions (for instance the one on the line AB) are the defects of the film, which contrast out clearly the existence of the $C_{60}(OH)_{12}$ layer. (b) The depth profile for the $C_{60}(OH)_{12}$ layer along the line AB shown in Fig. 3a. The dip around $X = 12 \mu m$ corresponds to the defect spot on the line. The depth of the dip, of a size of $\approx 13 \text{ Å}$, reflects the characteristic thickness of a $C_{60}(OH)_{12}$ monolayer.

 $\rho b = b_{tot}/ad$. In the above calculation, $b_{tot} = b_c + b_w$ is the total scattering length in the volume of ad, with the scattering lengths $b_c = 427 \text{ fm for } C_{60}(OH)_{12}$ and $b_{\rm w} \approx (a - a_0) d (\rho b)_{\rm s}$ for the water molecules in the volume. Here, $a_0 \approx 133 \text{ Å}^2$ is the cross-section for $C_{60}(OH)_{12}$, and $(\rho b)_s = -0.56 \times 10^{-6} \text{\AA}^{-2}$ is the scattering-length-density for H_2O_2 (2) From the f value (≈ 0.6) obtained, we presume that the adsorbed monolayer of C₆₀(OH)₁₂ becomes macroscopically uniform with the uncovered surface ($\approx 40\%$) being expelled by surface compression. For further compression, a rise of π may be expected. This deduction is roughly consistent with the isotherm measurement (Fig. 1) which shows a gradually increase of π after $A \approx 300 \text{ cm}^2$, namely, 60% of the original surface area. (3) X-ray reflection measurement using a brilliant X-ray source from synchrotron radiation should provide reflection data of a wider Qrange for a better determination of the structural parameters, for instance d, ρb , and f, of the C₆₀(OH)₁₂ layer. (Note, according to an estimation using the structural parameters obtained above, the scattering contrast for neutrons between the $C_{60}(OH)_{12}$ layer and the H_2O substrate, $2.21 \times 10^{-6} \text{ Å}^{-2}$, is about two times larger than that for X-rays.)

Another indirect evidence for the adsorbed monolayer of $C_{60}(OH)_{12}$ is provided by an LB film of two $C_{60}(OH)_{12}$ layers prepared from the sample solution. The AFM images for the LB film (Fig. 3a) manifest a relatively homogeneous texture for most of the film. The depth profiles (Fig. 3b) probed show that the undulation of the film surface can be characterized by occasional dips of a depth of 13 Å, which reveals clearly the $C_{60}(OH)_{12}$ monolayer characteristic. These AFM images reflects that the $C_{60}(OH)_{12}$ layers of the LB film are inherited from the adsorbed $C_{60}(OH)_{12}$ monolayers at the air-water interface.

4. Summary and conclusion

We have studied the adsorption of $C_{60}(OH)_{12}$ at the air-water interface from bulk solutions. The results obtained from π -A isotherms, BAM, neutron reflection, and AFM provide consistent and/or complementary evidence for the formation of Langmuir monolayers of $C_{60}(OH)_{12}$ via adsorption.

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