

Inexpensive Wilhelmy balance based in a fiber optic sensor for the study of Langmuir films

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An inexpensive Wilhelmy balance based on a fiber optic sensor capable of sensitive surface tension measurements has been designed and implemented. The system consists of a leaf spring conforming a cantilever structure and a bifurcated optical fiber acting as a laser beam deflection detector. Operated in a static way, it achieves a force measurement sensitivity of 0.154 V by N and a tension surface resolution of 0.1 mN/m. π -A isotherms of Langmuir films from insoluble amphiphiles 5 hexadecanoylamino fluorescein (fluorescein H-110) in water, were followed as a model system to characterize this instrument. © 2005 American Institute of Physics. [DOI: 10.1063/1.1877032]

I. INTRODUCTION

A Langmuir film or a Langmuir monolayer (LM) is basically an insoluble monolayer spreads at the air/water interface, while the term Langmuir–Blodgett (LB) film includes its subsequent transfers onto a solid substrate.^{1–5} The LB technique is a viable route for making active thin films with controllable thickness, uniform surface, and suitable molecular architecture, to be applied in molecule-based electrical and optical devices. A considerable number of surface-sensitive experimental methods have been developed for probing *in situ* the organization of molecules on the water surface, which include spectroscopic and microscopic techniques. As a first and critical step in the LB films production, the study of LM is essential for understanding and exploiting the LB technique. When the area of a LM is varied at constant temperature it exhibits a variety of structural phases and phase transitions. This behavior is analogous to that of a substance in which an isothermal change in volume results in transitions between solid, liquid, and gas phases.⁴ These phase transitions may be followed by measuring a surface pressure Π - A - T isotherm, a plot of the change in surface pressure Π (a measure of the decrease in surface, i.e., two-dimensional analog of pressure) as a function of the monolayer area A available to each molecule on the aqueous subphase surface.^{4,6,7} The phase transitions could be signaled by discontinuities in $(\partial\Pi/\partial A)_T$. Surface pressure Π can be defined as

$$\Pi = \gamma_0 - \gamma, \quad (1)$$

where γ_0 is the surface tension of the uncovered surface and γ is that of the monolayer covered surface.

There are two main methods to measure Π during monolayer compression: the Langmuir balance and the Wilhelmy method.^{2–4} The former is a differential technique, measuring the force acting in the partition that separates clean water or aqueous surface from that covered with a monolayer. The

Wilhelmy method is an absolute method in which the forces acting on a probe, usually made of platinum or filter paper, partially immersed in the subphase are measured. Such forces are the downward forces, such as gravity and surface tension, and upward forces, such as buoyancy due to the displacement of water, and are normally measured with a sensitive electrobalance. Systems to implement the Wilhelmy method are known as Wilhelmy balances. There are a number of available commercial models of Wilhelmy balances, but they are costly and sometime bulky devices. The last problem becomes especially severe in the laboratory because of its relatively small scale.

Different modifications to the original method and different ways to follow film compression have been discussed, as illustrated in Refs. 8–10.

We are interested in the nonlinear optic response from liquid-air interface studies, where particularly elaborated and crowded experimental setups are used. Consequently, we decided to make our own balance, based on a cantilever structure which would be deflected in response to the movement of a Wilhelmy plate, and a fiber optic sensor (FOS) acting as a transducer which would measure the amount of the deflection. There is detailed report in the literature of similar apparatus. In this article we describe the mechanical and optical features of the fiber optic sensor Wilhelmy balance FOS–WB, followed by a description of its calibration. The surface pressure Π was calibrated independently to specific monolayer properties in order to obtain an independent estimate of the sensitivity and accuracy of the balance. The measurement of the equilibrium spreading pressure of insoluble amphiphilic 5 hexadecanoylamino fluorescein (fluorescein H-110) in water was used as a representative demonstration of the performance of the FOS–WB.

II. FOS–WB

The principle of the FOS–WB described in this article is shown in Fig. 1. The design was quite simple; the deflection of a cantilever structure was monitored with a fiber optic lever displacement.^{11–13} It consists in an ultraviolet (UV)-

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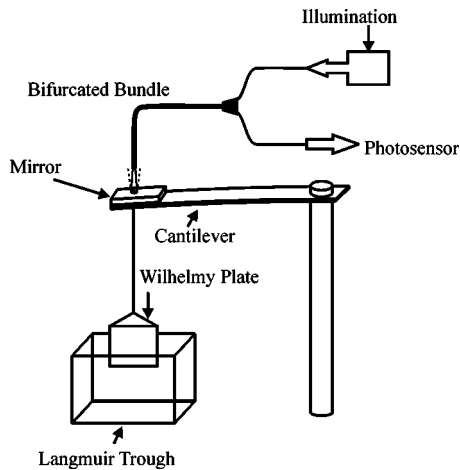


FIG. 1. A schematic of the fiber optic sensor and the cantilever structure, for measuring the surface pressure of Langmuir monolayers.

visible (VIS) bifurcated fiber-optic assembly from Ocean Optics (BIF400-UV-VIS), containing two groups of fiber optics. One set, the transmitting fibers, was coupled to a 670 nm wavelength diode laser from Coherent (FVLM2), delivering 1 mW of power. The other set, the receiving fibers, was attached to a silicon optical power meter from Thorlabs (S20MM), consisting of a photodiode sensor head and a module that allows a standard digital voltmeter to be used as a meter readout. These two groups of fibers are bundled into a common probe and are randomly mixed at the sensing point. The light generated from the source is channeled through the transmitting fibers to the probe tip. The light emerging from the fiber is reflected from a thin mirror glued to the free side of a cantilever structure. This structure consists of a leaf spring fabricated from a thin piece of stainless steel, ($155 \times 12 \times 0.7$ mm), rigidly supported by one end to an optical mount post. Attached to the spring opposite to the mirror is a thin platinum wire, finished as a small hook from which hung the filter paper plate (15×5 mm). Light reflects from the mirror surface back into the fiber sensor and then goes to the power meter where its power is measured. The intensity of the reflected light is a function of distance (gap) between the probe tip and the target surface; with an output function (i.e., light intensity versus distance to target surface) primarily determined by the diameter and the numerical aperture of the fiber.^{12,14} This output function can be divided into three regions: the front slope, the transition, and the back slope. The front slope is more linear and sensitive, while the back slope has a larger effective range. We use the front slope during the performing of this work.

III. FOS-WB CALIBRATION

The displacement of the Wilhelmy plate changes as the force exerted by the surface changes when the surface tension goes from γ_0 to γ . The force F exerted over the plate can be expressed as⁴

$$F = \rho_p g L w t - \rho_L g t w h + 2\gamma(t+w)\cos\theta, \quad (2)$$

where ρ_p , L , w , and t are the density, length, width, and thickness of the plate, g is the standard acceleration of free

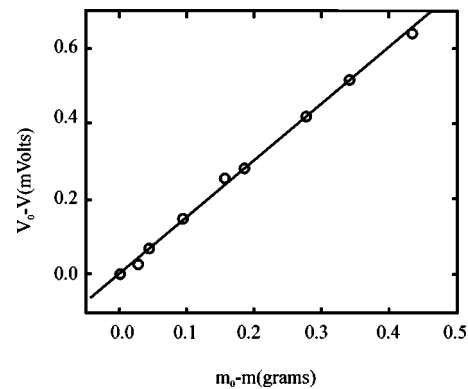


FIG. 2. Fitting of a linear model to describe the relationship between $V_0 - V$ (mV) against $m_0 - m$ (g). The equation of the fitted line is $(V_0 - V) = (1.51 \text{ mV/g}) \times (m_0 - m)$. The response of the balance is linear over the whole range of interest.

fall, ρ_L is the density of the liquid subphase, h is the depth of the plate in the subphase, γ is the surface tension, and θ is the contact angle for the subphase on the plate. Experimentally, we use a small piece of filter paper as a plate, and water as the subphase, hence, we can consider $w > t$ and, because the water completely wets the filter paper, $\theta = 0$. Therefore, the force difference ΔF detected may be attributed to a variation in surface tension

$$\Pi = -\Delta\gamma = -\frac{\Delta F}{2w}. \quad (3)$$

For simplicity we consider the spring leaf as a simple coiled spring so $\Delta F \propto -k(x_0 - x)$ with k as the spring constant and x as the displacement of the spring. We note that $g(m_0 - m) = -k(x_0 - x)$, where m_0 is a mass on the order of that due to the piece of filter paper (Wilhelmy plate) in the uncovered water surface, and m is a smaller mass, thus

$$\Pi \approx \frac{g(m_0 - m)}{2w}. \quad (4)$$

To obtain Π from Eq (4), we need to put ΔF in terms of the direct current output voltage of the Wilhelmy balance. To calibrate the system response, different pieces of stainless steel wire, previously weighted, were hung at the end of the platinum wire. Figure 2 presents a plot of readout of the voltmeter connected to the power meter in millivolts against mass in g. Table I shows the results of fitting a linear model to describe the relationship between $(V_0 - V)$ and $(m_0 - m)$. The equation of the fitted model is $(V_0 - V) = (1.51 \text{ mV/g}) \times (m_0 - m)$. Since the probabilities values in the analysis of variance table is less than 0.01, there is a statistically significant relationship between $(V_0 - V)$ and $(m_0 - m)$ at the 99% confidence level. The R -squared statistic indicates that the model as fitted explains 99.83% of the variability in $(V_0 - V)$. An estimated of the balance sensitivity can be obtained from the calibration graph slope value and using $g = 9.80665 \text{ m s}^{-2}$, yielding 0.154 V N^{-1} . Substituting the sensitivity value obtained into Eq. (4), we have

TABLE I. Regression analysis: linear model: $y=a+b \times x$.

Dependent variable: $V_0 - V$ Independent variable: $m_0 - m$					
Parameter	Estimate	Standard error	T statistic	P value	
Intercept	0.000	0.005	0.21	0.83	
Slope	1.51	0.02	64.68	0.00	
Analysis of variance					
Source	Sum of squares	D_f	Mean square	F ratio	P value
Model	0.42	1	0.42	4184.44	0.00
Residual	0.00070	7	0.00010		
Total (Corr.)	0.42	8			
Correlation coefficient = 0.999.					

$$\Pi = \frac{6.49 \times (V_0 - V)}{2w} N V^{-1}. \quad (5)$$

An independent estimate of the method accuracy could be obtained through a straightforward propagation of the error treatment of Eq. (5). The accuracy was approximately $\pm 0.1 \text{ mN m}^{-1}$.

IV. MONOLAYER PREPARATION

A home-built Langmuir trough made in Teflon was extensively cleaned and then filled with ultrapure water. The trough was fastened to a vibration isolated optical table. Fluorescein H-110 (Molecular Probes) was dissolved in a mixture of ethanol and chloroform (HPLC grade). Subsequently, 60 μL of this solution was taken with a Hamilton microliter syringe and placed on the water surface, where the chloroform was allowed to evaporate. A Teflon barrier, driven by a motorized translation stage (Newport-Klinger, Irvine, CA), and running linearly along the top edge of the trough was used to control the surface area available to the monolayer.

V. SURFACE PRESSURE—AREA ISOTHERMS

The applicability of our FOS-WB was evaluated by means of a π vs A surface isotherm study. The monolayer

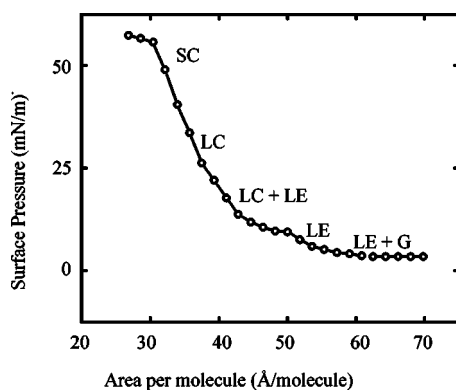


FIG. 3. Surface pressure-area curve of fluorescein H-110 molecules dissolved in water.

was compressed to some surface pressure and area, and then we held the area constant about 3 min, to achieve steady state relaxation. At that moment thermodynamic equilibrium may be considered reached. Π was then recorded against area by molecule. Figure 3 shows a representative isotherm of fluorescein H-110 on water subphase at 25 °C. The features of this isotherm may be interpreted in terms of four monolayer phases: gas, liquid-expanded (LE), liquid-condensed (LC), and solid.^{2,7,15,16} At large available areas ($>70 \text{ \AA}^2$), the monolayer is in the “gaseous” state. The free energy of the aqueous subphase and therefore the surface tension remain unchanged. At further compression there is a gradual onset of surface pressure until an approximately horizontal region is reached. This is the gaseous-liquid expanded (LE) transition in the fluorescein H-110 isotherm. In the horizontal region the hydrophobic tailgroups, which were originally lying almost flat on the water surface, are subsequently being lifted from that surface. For mean molecular areas around 48 \AA^2 the compressibility approaches infinity, indicating a first order phase transition from the LE to the LC phase. At a surface area of just over 38 \AA^2 per molecule there is an abrupt increase of slope. This is due to a phase change and represents a transition to an ordered arrangement of the molecules, known as the solid condensed or solid phase. If this second linear portion of the isotherm is extrapolated to zero surface pressure, the intercept gives the area per fluorescein H-110 molecule that would be expected for the hypothetical state of an uncompressed close-packed layer.

We have presented an extremely simple and inexpensive FOS-WB, consisting in a cantilever structure and a fiber optic displacement sensor system. The experimental results demonstrated that this system design can be used effectively to measure the surface pressure of monolayers.

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