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Louis Bosio, J. J. Benattar, François Rieutord

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X-ray reflectivity of a Langmuir monolayer on water

L. Bosio (*), J. J. Benattar (**), and F. Rieutord (**)

(*) Laboratoire « Physique des liquides et électrochimie » ESPCI,
 10, rue Vauquelin, 75231 Paris, France

(**) DPhG/SPSRM-CEN Saclay, 91191 Gif-sur-Yvette Cedex, France

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Résumé. — Nous avons mis au point une cuve de Langmuir qui permet l'utilisation de la technique de réflexion des rayons X. A l'aide de ce dispositif nous avons pour la première fois étudié le profil de densité d'une monocouche de Langmuir directement sur l'eau. Cette expérience ouvre de nouvelles perspectives en particulier, pour des mesures précises de la rugosité des films solides sur l'eau.

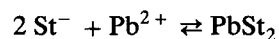
Abstract. — We built a special Langmuir trough allowing the use of X-ray reflectivity. Using the device we studied for the first time the density profile of a Langmuir monolayer directly on water. This experiment opens new prospects in particular to measure the roughness of solid films on water subphase.

Monolayers of amphiphilic molecules on liquids have been studied for many years [1]. Monomolecular Langmuir systems are a field of growing physical interest since they are rather simple and versatile two-dimensional systems. For example the investigation of monolayers of phospholipids has proved a successful approach for the study of the physical properties of membranes. From a theoretical point of view, very interesting systems involving polar molecules with high dipole moments should give rise to complex phase diagrams in which a supercrystal phase is expected [2]. In all cases the knowledge of the structure of the layer will be necessary to help fully understand these systems [3].

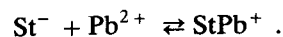
Some new optical X-ray techniques have been developed and applied to the surface studies [4]. Among these techniques the X-ray reflectivity has been previously used to determine the density profile at a liquid-vapour Hg interface [5] as well as the surface roughness of water [6].

In this letter we report the first reflectivity study of a monolayer of lead stearate on a water subphase. Our experiment has been conducted in an attempt to demonstrate that it is possible to determine the structure perpendicular to the film. This investigation is a first step in a direct complete structural determination of the solid phase of a monolayer on liquids. The sensitivity of the method is such that we could operate with a conventional X-ray source. We chose lead stearate as the density of a purely organic

compound is very close to that of the water. Thus to create a density gradient at the film/water interface a heavy sublayer was required. The monolayer was prepared using the chemical process described by B. L. Henke in [7] where the lead stearate forms directly on the water subphase. Pb^{2+} ions are obtained from a 3×10^{-5} M solution of lead acetate in highly purified water (resistivity $> 15 \text{ M}\Omega\cdot\text{cm}$). The pH (~ 7.5) is maintained constant using a buffer of 0.1 M sodium acetate. A few drops of a dilute solution of stearic acid in chloroform are spread on the solution surface. The solvent rapidly evaporates, leaving dispersed molecules of stearic acid at the surface which react with the lead ions to form an insoluble layer of lead stearate. Then the molecules are compressed into a solid-like phase. It is well known [8] that two equilibria can occur :



and



Until now the concentration of the two species has never been directly measured on the monolayer. This point will be examined further below.

Details of our experimental device are schematically represented in figure 1a. The Langmuir trough which was specially designed to be incorporated in the goniometer, is made of teflon. It is rectangular $500 \times 70 \text{ mm}^2$ in size and three millimeters deep.

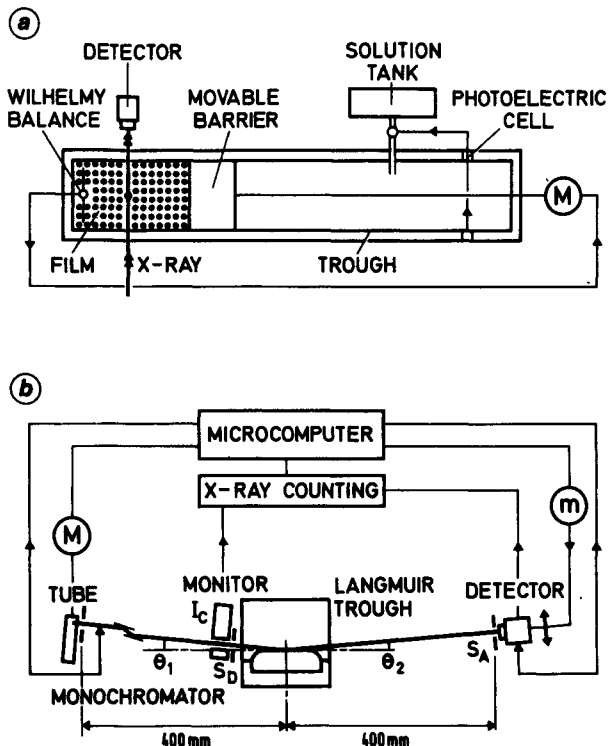


Fig. 1. — (a) Top view of the Langmuir trough. (b) Schematic representation of the experimental geometry.

The surface pressure (i.e. the variation of the molecular area) is provided by a movable barrier whose displacement is controlled by means of a Wilhelmy balance allowing a present surface pressure to be constant.

The liquid level was set to lie 1 mm above the teflon edge on account of the presence of a meniscus. The molecules can be compressed by the movable barrier without disrupting the meniscus. This arrangement allows the X-ray reflectivity to be obtained at glancing angles on the liquid surface. A differential photo-diode device detects any variation of the liquid height and adjusts the liquid level within $\pm 5 \mu\text{m}$ by heating an auxiliary tank which provides the extra solution. The whole device is maintained under a nitrogen flow to avoid any pollution of the Langmuir film. This device is equipped with two mylar windows to allow passage of the incident and reflected X-ray beams.

The goniometer [9] that we have used, is schematically represented in figure 1b. The $\text{CuK}\alpha$ radiation is obtained by a double monochromator equipped with two flat $\text{LiF}(200)$ crystals and a divergence slit S_D which isolates the $\text{K}\alpha_1$ line. With such a device it is possible to use a low divergence, typically 0.2 mrad in the grazing angle range (0-10 mrad), and 0.4 mrad for $\theta > 10$ mrad, depending on the S_D width. The intensity of the monochromated beam is monitored by an ionization chamber I_c while the

intensity of the reflected beam is detected by a scintillation counter placed behind the analysis slit S_A .

The angle scale accuracy is: ± 0.05 mrad; the zero angle and incident beam intensity were directly determined by scanning the direct beam after removing the sample.

Figure 2a shows the experimentally measured reflectivity curve of the lead stearate monolayer in the solid phase on the solution subphase at the pressure of 25 mN/m between 0 mrad and 10 mrad. This part of the reflectivity curve does not exhibit any significant difference with that of the solution or that of pure water [6]. This point can be easily understood knowing that the critical angles θ_c are directly related to the mass density ρ . Indeed in the range of X-ray wavelength (λ) the real part of the

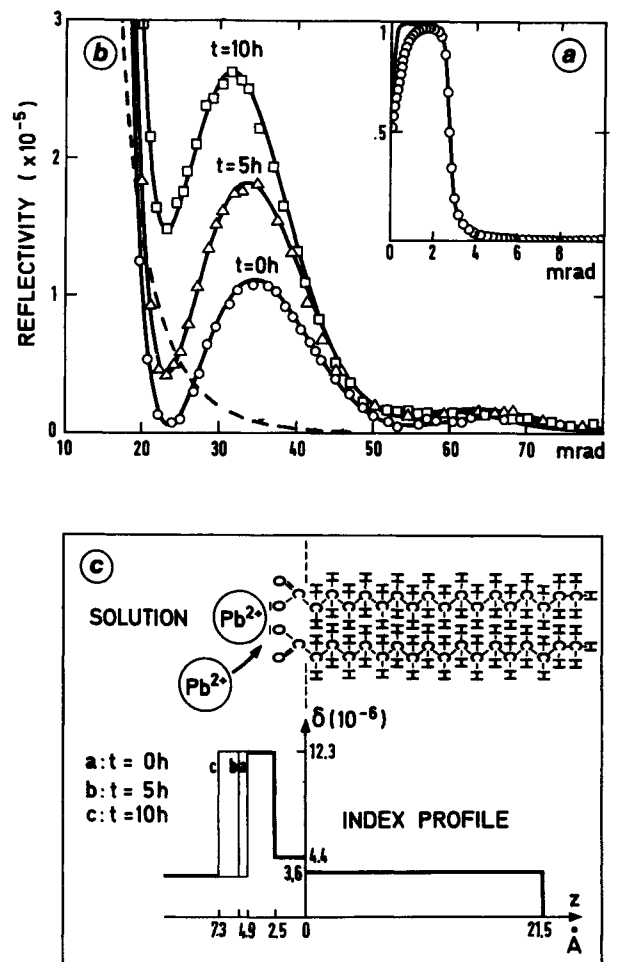


Fig. 2. — (a) The measured X-ray reflectivity from 0 to 10 mrad. The solid line corresponds to the calculated reflectivity including convolution.

(b) The measured X-ray reflectivity from 10 to 80 mrad at 3 different times. The solid line corresponds to the best fit and the dashed line to the reflectivity of the solution.

(c) Index profile of the monolayer at the 3 different times. The values of β are 0.05×10^{-7} for $(\text{CH}_2)_n$, 0.15×10^{-7} for COO^- and 10.8×10^{-7} for Pb.

refractive index n is less than unity: $n = 1 - \delta - i\beta$. δ is given by

$$\delta = \frac{e^2 N}{2 \pi m c^2} \frac{(f + \Delta f')}{M} \lambda^2 \cdot \rho .$$

The term e^2/mc^2 is the classical electron radius, N the Avogadro constant, M the atomic mass, f the atomic scattering factor and $\Delta f'$ the real part of the anomalous dispersion. β is proportional to the linear absorption coefficient μ ($\beta = \frac{\mu \lambda}{4 \pi}$). From the Fresnel equations and when $\beta = 0$, then for a glancing angles lower than θ_c , the incident beam is totally reflected ($\frac{I(\theta)}{I_0} = 1$). The critical angle θ_c is approximately given by $\sqrt{2 \delta}$. It should be pointed out that running the experiments overnight has allowed the elimination of almost all the mechanically excited ripples on the liquid surface as demonstrated by water reflectivity which reached $\sim 98 \%$ below the critical angle θ_c (2.64 mrad). Note that a small difference between the reflectivity of the water (or the solution) and that of the monolayer has been observed below θ_c ; this is due to the lead absorption. The reflectivity measurements between 10 and 80 mrad are reported in figure 2b. These measurements were recorded at three different times and at a constant pressure (25 mN/m). The most striking feature of these data consists in the time increase of the reflectivity. This clearly indicates a time dependence of the chemical composition of the film.

The whole set of curves exhibits two orders of diffraction which are remarkably well defined. They correspond roughly to interference phenomena between the reflected beams at the two interfaces film/air and film/solution. A similar set of experiments has been performed at a different pressure (45 mN/m) in the solid phase, and no significant change of the reflectivity has been detected. This means that, in the solid phase, the structure does not strongly depend on the pressure.

The evaluation of the specularly reflected intensity was directly obtained by subtracting the intensity measured at $\theta_2 = \theta_1 \pm \Delta\theta$, $\Delta\theta = 1$ mrad from that measured at $\theta_1 = \theta_2$. This intensity measured outside the specular reflection corresponds to a diffuse intensity due to the bulk scattering. This procedure was checked by determining the reflectivity of the pure solution (Fig. 2b) which was found to be identical to that of pure water.

The treatment of the experimental curves has been performed using the optical formalism for stratified media [10]. In this formalism the layer is broken into a series of laminae corresponding to chemically different parts of the system. Each lamina is defined by a characteristic transfer matrix which takes into account the refractive index, thickness

and incident angle. The characteristic matrix of the overall system is obtained by successive multiplication of the different matrices and the reflection coefficient is then given in terms of the matrix elements. This optical method is particularly well suited to machine calculation [11].

In order to build a model of the electronic density perpendicular to the layer, we have used standard chemical data for the aliphatic chain and the COO^- group. Moreover, the knowledge of the film area and of the number of molecules directly gives the molecular area.

On the pressure-molecular area isotherm of lead stearate film which is represented in figure 3, we found for 25 mN/m corresponding to our case, a value of about 19 \AA^2 . The adjustable parameter was mainly the lead ions concentration at the film-solution interface. The best fits of the experimental reflectivity curves reported in figure 2b, correspond to the index profiles shown in figure 2c. The refined density profile shows that the molecular axis is perpendicular to the liquid surface. Thus a hexagonal lateral packing can be expected.

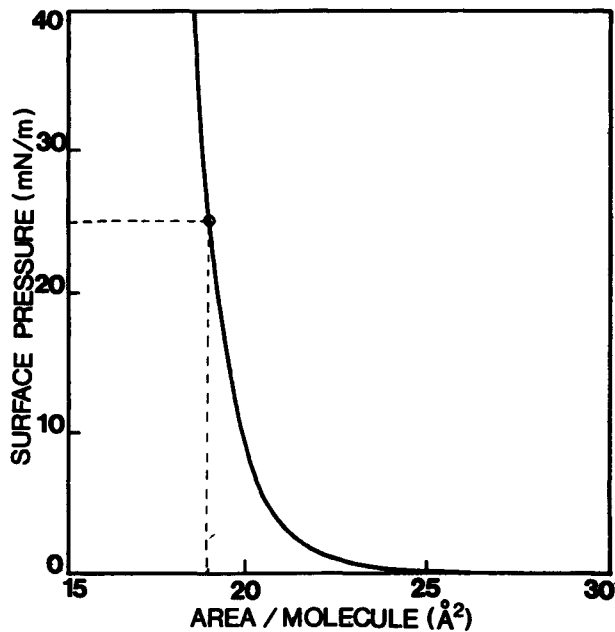


Fig. 3. — Pressure-molecular area isotherm. The open circle indicates the experimental conditions.

The evolution of the lead lamina shown in figure 2c may simply correspond to a change in chemical species. This transformation can be interpreted as a time increase of the StPb^+ concentration. Indeed, the size of the peak is related to the area of the lead lamina (thickness e) in the profile (Fig. 2c) i.e. the product $e \times (\delta_{\text{Pb}} - \delta_{\text{CH}_2})$. Our best fits correspond to an increase of the thickness of the lead lamina rather than an increase of the δ value. Nevertheless, a more complex profile involving an

interfacial roughness (solution/film) is also possible but cannot be directly determined with our experimental data. In the initial state after deposition ($t = 0$), the film is only composed of the PbSt_2 species whereas at $t = 5$ h we found about 75 % PbSt_2 and 25 % PbSt^+ . Finally, at $t = 10$ h the only remaining species is PbSt^+ . To our knowledge this time effect on Langmuir films has not been described until now.

Note that the fit of the reflectivity curve required the introduction of a roughness. Assuming a Gaussian distribution, the mean square roughness of the

layer was found to be rather small ($\langle z^2 \rangle = 2 \text{ \AA}^2$ for $t = 0$ and 5 h and $\langle z^2 \rangle = 4.5 \text{ \AA}^2$ for $t = 10$ h) compared to that of pure water [6].

In conclusion we have shown that using a conventional X-ray source, it is possible to measure the reflectivity of a Langmuir monolayer. The analysis of the data provides interesting and direct structural information. One can expect that the use of synchrotron radiation will allow similar investigations on lighter compounds. We wish to thank G. Folcher for competent technical assistance, M. Dupeyrat, P. Robin and J. Hodges for helpful discussions.

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