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X-ray investigation of monolayers formed at the soft air/water interface

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ABSTRACT

Gibbs or Langmuir monolayers formed at the soft air/liquid interface are easy to handle and versatile model systems for material and life sciences. The phase state of the monolayers can be modified by lateral compression of the film while the layer structural changes are monitored by highly sensitive surface characterization techniques. The use of high brilliant synchrotron light sources for X-ray experiments is essential for the monolayer research. The present review highlights the recent achievements recorded in the monolayer field with a special emphasis on different synchrotron based X-ray characterizing methods as: grazing incidence X-ray diffraction, X-ray reflectivity and total reflection X-ray fluorescence. Some examples of single-chain surfactants, special sugar lipids, and semifluorinated compounds are given. Additionally, thin layers formed by peptides, polymers or nanoparticles are highlighted.

1. Introduction

Monolayers of amphiphilic molecules can be formed at the air/liquid interface either by adsorption of soluble amphiphiles from aqueous subphases (Gibbs monolayers) or by spreading water insoluble amphiphiles from organic solvent solutions (Langmuir monolayers). The thin layer can be in a fluid-like state or it can exhibit in-plane order (so-called condensed phase with different degrees of crystallinity). In some special cases, the amphiphilic molecules [1] or polymer capped nanoparticles [2,3] can be dissolved or dispersed in water as well as in an organic solvent like chloroform. This gives the unique possibility to compare structures formed in Gibbs and Langmuir monolayers of the same compounds. The striking difference is the very much different coherence length in the in-plane lattice [1]. Since the Gibbs layer is in a dynamic equilibrium, lattice defects can be annealed by adsorption/desorption processes in a much more effective way than by compression of Langmuir layers. Otherwise, very similar lattice parameters have been observed.

In general, thin layers at the soft air/liquid interface are excellent models in material and life sciences. The early work with amphiphile monolayers was largely hampered by the absence of surface sensitive tools to investigate liquid interfaces with molecular and microscopic resolution. This has been drastically changed in the last 30 years. The most important techniques applicable to fluid interfaces are X-ray [4,5] and neutron scattering [6,7], ellipsometry [8], fluorescence [9] and Brewster angle microscopy [10,11], Reflection–Absorption FTIR-spectroscopy [12], and nonlinear optical spectroscopy [13]. The new techniques led to the renaissance of the monolayer research. Because of their high definition, monolayers are excellent models for many areas with high application potential.

Here we concentrate on results obtained in the last years using different synchrotron based X-ray methods. Comprehensive reviews have been published during the last years for describing details of the principles of GIXD and XR [14–19]. Therefore, the present review will only shortly describe the now well established methods and introduce the recently simplified TRXF that is a powerful surface sensitive analytical technique.

The in-plane fine structure in monolayers depends strongly on the chemical structure of the surface active compounds. Herein we give some examples for single-chain surfactants, special sugar lipids, and semifluorinated compounds. The structures of double-chain phospholipids have been described in another review [20]. Then we focus on monolayers of different peptides, polymers and even nanoparticles.

2. Synchrotron X-ray scattering — A brief description of the methods

2.1. Grazing incidence X-ray diffraction (GIXD)

Since more than 25 years GIXD is the primary technique to investigate in situ the structural arrangement of amphiphilic molecules in monolayers at the liquid/air interface. The method is based on the phenomenon of total reflection. A propagating electromagnetic wave striking under a critical angle the boundary between two media is totally reflected from the medium with the lower refractive index. For X-rays with a wavelength λ between 1 and 2 Å, the refractive index of matter is slightly less than unity ($n = 1 - \delta - i\beta$). The term β is related to the linear absorption coefficient. It is much smaller than δ ($\beta \ll \delta$) and can therefore be neglected for hard X-rays. $\delta = 2\pi\rho r_0/(2\pi/\lambda)^2$, with $r_0 = 2.82$ fm and ρ the electron density of the medium, amounts

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to 10^{-6} to 10^{-5} for condensed matter and only 10^{-9} for air. The critical angle can be easily calculated by $\alpha_c = (2\delta)^{1/2}$ and amounts to 0.13° in the case of the air/water ($\rho_w = 0.334\ e^-/Å^3$) interface and a used wavelength of 1.3 Å. In GIXD experiments, a monochromatic X-ray beam with a defined wavelength is adjusted to strike the water surface at an angle α_i which is slightly below the critical angle α_c for total external reflection. The evanescent wave travels almost parallel to the interface and illuminates only the top 8 nm. This particular geometry makes the X-rays highly surface sensitive. The illuminated area is usually in the order of 100 mm^2. The Langmuir trough is placed in a Helium-flushed container with capton windows transparent for X-rays (Fig. 1). In the case of a crystalline monolayer, the evanescent wave may be Bragg scattered from lattice planes oriented by an angle θ_{hk} with the evanescent beam, fulfilling thus the Bragg condition: $\lambda = 2d_{hk} \sin\theta_{hk}$. The diffracted intensity is often monitored by a linear position sensitive detector as a function of the vertical scattering angle α_f and the horizontal scattering angle 2θ. The monolayers formed by spreading a chloroform solution of the amphiphilic molecules on the water surface are composed of 2D crystallites randomly oriented (2D powder). The obtained diffraction patterns are defined by pairs of the scattering vector components (Q_{xy} and Q_z).

Because lattice fluctuations cause the peak intensities to decay rapidly with increasing momentum transfer, the first-order peaks are the most intense and frequently the only observed ones. The observation of only one first-order peak is an indication of hexagonal packing, with equal distances between the lattice points. Two distinct Bragg peaks point to a rectangular unit cell, and three peaks are arising in the case of an oblique one. Usually, the alkyl chains of the amphiphilic molecules are the lattice points. Only in rare cases, the ordering of entire molecules, having more than one chain, has been observed ('subgel phases'). The structural information is extracted by analysis of the obtained diffraction pattern. Thus, the Bragg peaks, obtained by the integration of the scattering intensity (corrected for polarization, effective area, and Lorentz factor) over a certain Q_z window, and the Bragg rods, obtained by the integration of the scattering intensity over a certain Q_{xy} window, give information about the unit cell dimensions, the tilt t of the chains, and the tilt direction $\psi^*_{(hk)}$ by using $Q_z^{(hk)} = Q_{xy}^{(hk)} \cos(\psi^*_{(hk)})tant$. Model peaks taken to be Lorentzians are fitted to the corrected intensities to identify the maximum Q_{xy} values, and model peaks taken to be Gaussians are fitted to the corrected intensities to determine the maximum Q_z values. The full-width at half-maximum (FWHM) of the Bragg peak after correction by the instrumental resolution gives information about the size of the crystalline domains using the Scherrer formula. For many monolayers, values between 100 and 500 Å have been found. The FWHM of the Bragg rod gives information about the thickness of the diffracting layer. Since for most of the amphiphiles investigated the chains are the scattering units, the Scherrer formula allows the determination of the length of an extended chain in all-transconformation in good agreement with calculated values using $L = (n \cdot 1.26 + 1.45)$ Å with n the number of CH_2 groups [21,22]. Using the tilt angle of the chains, the cross-sectional area per chain A_0 can be calculated from the in-plane area per chain A_{xy}: $A_0 = A_{xy} \cos t$.

More detailed information on GIXD is already available in more detailed reviews [17–20].

2.2. Specular X-ray reflectivity (XR)

XR gives information about the vertical structure of the monolayer independent on the phase state, i.e., in contrast to GIXD unstructured liquid monolayers can be also investigated. The X-ray reflectivity is measured with the geometry $\alpha_i = \alpha_f$ (Fig. 1). The data collection can be performed either by a NaI scintillation point detector or a position sensitive linear detector. Using synchrotron radiation, the incidence angle α_i can be varied to allow experiments in a range of 0.01–0.8 $Å^{-1}$ of the vertical scattering vector component $Q_z = (4\pi/\lambda)\sin(\alpha_f)$. The background scattering from the subphase is measured at $2\theta = 0.7°$ and subtracted from the specular signal measured at $2\theta = 0$.

Usually, the reflectivity R is calculated from a given electron density profile by the so-called 'master formula', which uses the Fresnel reflectivity R_F from a perfectly sharp interface calculated from standard optics. The root-mean-square roughness for a bare water surface is

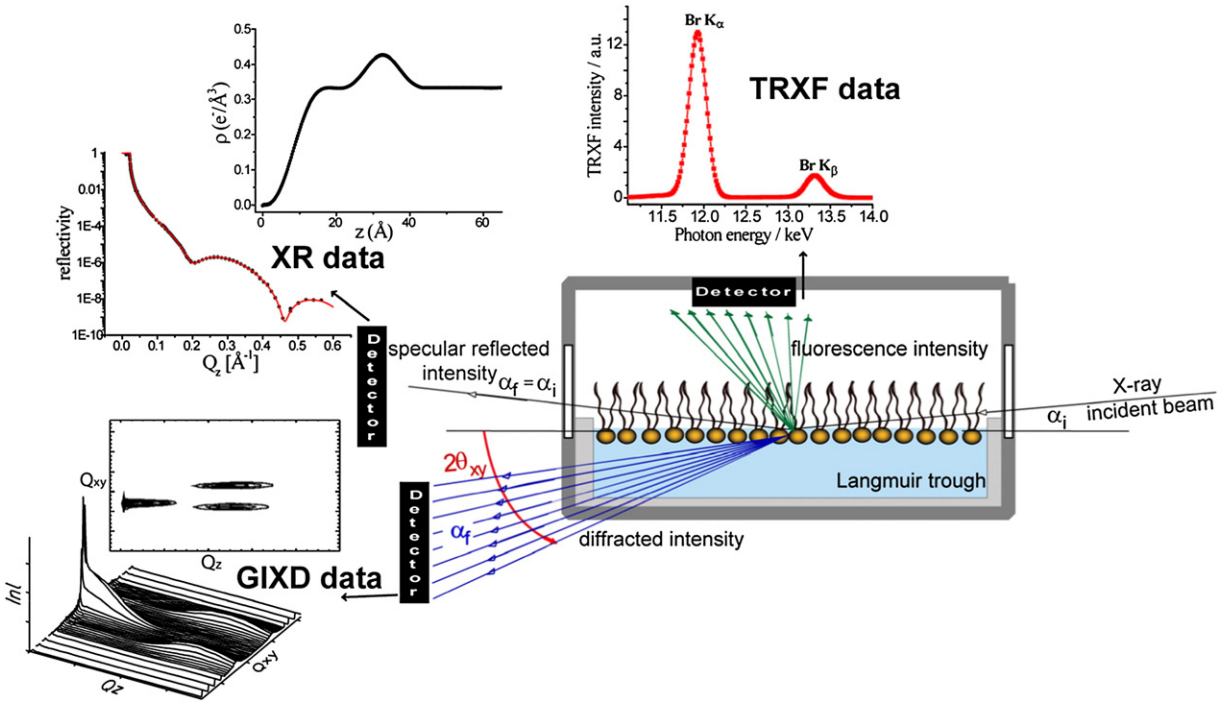

Fig. 1. Working principles of three X-ray methods used for monolayers at the soft air/liquid interface. GIXD and TRXF are performed at an incidence angle below the critical angle for total reflection. The penetration depth of the evanescent wave is only 8 nm. GIXD measures in-plane periodic structures and gives information about the tilt angle and tilt direction of the amphiphilic molecules. TRXF is a surface sensitive elemental analysis technique. Specular XR gives information about the electron density profile perpendicular to the surface.