



The interaction between stearic acid monolayers and butane under elevated pressures



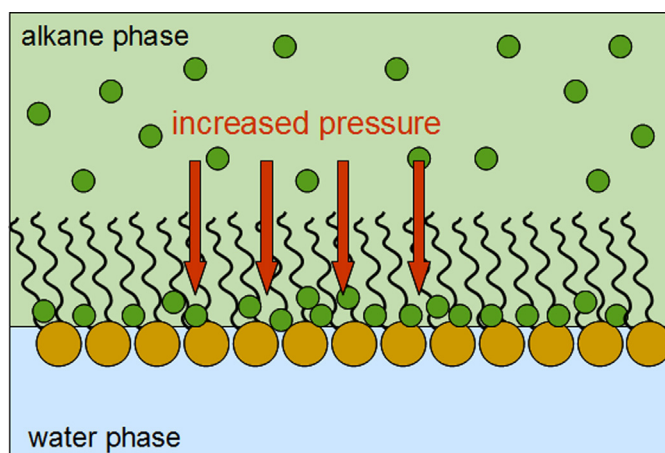
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HIGHLIGHTS

- The interaction between a Langmuir film and butane at increased pressure is studied.
- Gas molecules accumulate between the lipid head groups of the lipids.
- In parallel the long-range lateral crystallographic order of the film is increased.
- At increased pressure, the lipids are dissolved in adsorbed gas molecules.
- Solvent gases have thus a strong impact on the structure of lipid systems.

GRAPHICAL ABSTRACT



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ABSTRACT

A study on the interaction between butane and lipid membranes is presented. Monomolecular films of stearic acid were prepared on a water surface and were exposed to dense gas phases of *n*-butane and isobutane. From X-ray reflectivity measurements and grazing incidence X-ray diffraction, the accumulation of gas molecules at the liquid–gas interface was analyzed. We show that the gas molecules penetrate into the lipid membrane and accumulate between the head group and tail group of the lipids. This process goes in hand with an increase of the long-range lateral crystallographic order within the lipid film. This and the formation of multilayer islands points to an expulsion of lipids by the gas molecules. At higher pressures close to the condensation pressure of the studied gases, the vertical and lateral order is lost, indicating an adsorbed liquid film in which the lipids are dissolved.

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1. Introduction

In the human body, structural and functional units are spatially confined by the cell membrane, which is a lipid bilayer with functional proteins and other constituents. An intact cell membrane is essential for the cell functionality. However, if the cell membrane is exposed to gas molecules, they might diffuse through the membrane or affect the membrane stability and functionality. Thus, the

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question of how harmful substances can modify membranes is of importance for understanding the basic mechanisms of malfunctions. In this context, the effect of anesthesia or narcotics on cell membranes, such as the noble gas xenon, stood in the focus of interest [1]. It was shown that these substances have a significant impact on the phase behavior of lipid systems (for an overview, see e.g. [2]). A well-established model system for complex biological membranes are lipid monolayers. Such Langmuir layers are formed at the water–gas interface. The lipid head group is then oriented to the aqueous phase and the tail group is pointed to the gas phase. These monolayers are very well known and were studied for many years under various conditions. At high surface pressures, they show a lateral crystallographic order that can be disturbed by the insertion of molecules like cholesterol [3,4] or polypeptides [5]. However, also small organic molecules like alkanes might have a degrading effect on lipid membranes.

The behavior of different gases at liquid and solid interfaces was studied extensively in the past [6–13]. Because of the Van-der-Waals interaction between the gas molecules and the liquid phase, thin films can form at the liquid–gas interface even below the condensation pressure of the gases. Depending on the interaction strength between the two liquid phases and the molecules within the respective phase, complete or partial wetting can occur. Also, intermediate states (frustrated-complete wetting) were observed [12]. Furthermore, it was shown that the solvation of water molecules in alkanes has a significant impact on the interaction between the adsorbed alkane layer and the substrate even at low solubilities. Their mutual solubility was successfully modeled via an equation of state that includes association, covering a wide range of pressures and temperatures [14], while the appearance of image-charge forces was identified as one origin of the increased coupling [15,16].

It was shown that below the condensation pressure of the gas, the pressure-dependent film thickness follows a Frenkel–Halsey–Hill isotherm [17–19], which is slightly modified by the capillary wave fluctuations of both the substrate and the adsorption layer [8,11].

The interaction between lipid films and long chained alkanes was studied for a broad range of alkanes with chain length between 12 and 21 carbon atoms [20,21]. The alkanes can arrange within the Langmuir film or can form a top layer, depending on the temperature and chain length. However, the interaction of gases and Langmuir films under elevated pressures was not discussed in literature so far.

For the investigation of the interaction of gas molecules with lipid monolayers, techniques are needed that can resolve the structure of interfaces and thin layers with Ångstrom-accuracy. Furthermore, this technique must be employed *in situ* under a pressurized gas atmosphere. To this end, scattering methods are well established [22–24]. For this study, we used the X-ray reflectivity (XRR) technique and grazing incidence X-ray diffraction (GID).

The XRR technique is sensitive to the vertical electron density contrast along the surface normal of an interface. The specular intensity is measured as a function of the angle of incidence α . Laterally averaged electron density profiles $\rho_e(z)$, where z is the vertical distance to the interface, can be deduced from XRR data by a modeling procedure [25]. The resolution that can be reached is on the order of sub-Ångstrom and depends, besides the experimental setup, on the largest accessible wave vector transfer $q_z = (4\pi/\lambda) \sin(\alpha)$, with the wavelength λ of the X-ray radiation. The reflected intensity I is given by [26]

$$I(q_z) \propto \frac{1}{q_z^4} \left| \int \frac{\partial \rho_e(z)}{\partial z} e^{iq_z z} dz \right|^2. \quad (1)$$

Information on the lateral order of the Langmuir layer can be obtained from GID measurements. In these experiments, the angle of incidence is set to an angle smaller than the critical angle of total external reflection α_c . For $\alpha < \alpha_c$, the penetration of the X-rays into the sample is limited to a few nanometers and only the very top-most part of the sample is probed by detection of the off-specular scattering. In the case of lipid monolayers, conclusions on the lateral order of the molecules, the 2D crystalline structure, and the chain tilt can be drawn by analyzing the position of Bragg reflections in both the q_z and $q_{||}$ direction [28]. Here $q_{||}$ is the wave vector transfer parallel to the sample's interface.

2. Experiment

In order to study the structure of Langmuir films under elevated pressures, a cell sustaining gas pressures up to 5 bar was constructed. The cell is made of stainless steel and contains a circular sample plate (PTFE (polytetrafluoroethylene)) with a diameter of 120 mm. The plate has a 0.5 mm high rim, which allows to prepare a liquid sample of 2 mm depth if water is used. A photograph of the cell is shown in Fig. 1. The cell is mounted on a heat exchanger that is connected to a chiller. The temperature control ($\Delta T = \pm 0.02$ K) is realized by two PT100 sensors, one in the liquid phase, and one in the gaseous phase and a heating foil below the cell. The temperature sensors and the heating foil are connected to a Lake Shore temperature controller. The cell is equipped with two connectors for gas in- and outlet. A small stainless steel holder with a Wilhelmy balance is placed close to the sample plate. The balance allows to monitor the surface pressure during preparation and also under a compressed gaseous phase. One has to keep in mind that a pressure increase causes also artificial changes of the surface pressure because of the changed buoyant force of the Wilhelmy plate. Thus, gas pressure changes cause steps in the course of surface pressure, while monitoring the film stability during the measurements is possible. The cell was equipped with two polyimide windows with a thickness of 0.05 mm, allowing both XRR and GID measurements.

Stearic acid ($C_{18}H_{36}O_2$, Sigma–Aldrich, Taufkirchen, Germany) was used to prepare lipid films on a water phase (MilliA, resistance 18.2 M Ω cm). The lipids were solved in TBME (tert-Butylmethylether, Sigma–Aldrich) at a concentration of 1 mmol/l and spread drop-wise on the water surface until a surface pressure of 15 mN/m was reached. After a waiting time of 5 min to let the TBME evaporate, the cell was closed and flushed with nitrogen. Subsequently, XRR and GID scans of the water–N₂ interface were taken. Afterwards, the cell was flushed with *n*-butane or isobutane (C_4H_{10} , Messer Group, Germany, purity 99.95%) and the pressure was increased. For each pressure, a fresh sample was prepared because of beam damage during a GID scan, causing changes of the surface pressure which were not compensated for since the film was not compressed by barriers.

While *n*-butane has a chain-like structure with a radius of gyration of 2.886 Å, isobutane has a more globular shape with a radius of gyration of 2.948 Å [29]. However, the two gases have similar properties such as the low solubility and a similar condensation pressure of 1.48 bar for *n*-butane and 2.21 bar for isobutane at 10 °C. Due to their structure, they are non-polar and interact with water via hydrophobic and van-der-Waals interactions.

GID measurements were performed at the beamline ID10 of the European Synchrotron Radiation Facility (ESRF) at a photon energy of 22 keV, a beam height of 0.05 mm and a beam width of 2 mm. Photon detection was realized by a position sensitive detector (MBRAUN, Germany). Complementary X-ray reflectivities were recorded with a Bruker AXS D8 advanced diffractometer with a copper anode (photon energy = 8.048 keV). The photon beam was

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