Advances in Colloid and Interface Science xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Advances in Colloid and Interface Science

journal homepage: www.elsevier.com/locate/cis

# Langmuir monolayers as models to study processes at membrane surfaces

Cristina Stefaniu, Gerald Brezesinski, Helmuth Möhwald *

*Max Planck Institute of Colloids and Interfaces, Science Park Potsdam-Golm, Am Mühlenberg 1, D-14476 Potsdam, Germany*

ARTICLE INFO

Available online xxxx

*Keywords:*
Monolayers
Bilayers
GIXD
IRRAS
Interactions
Lipids
DNA
Peptides
Nanoparticles
Interfacial reactions

ABSTRACT

The use of new sophisticated and highly surface sensitive techniques as synchrotron based X-ray scattering techniques and in-house infrared reflection absorption spectroscopy (IRRAS) has revolutionized the monolayer research. Not only the determination of monolayer structures but also interactions between amphiphilic monolayers at the soft air/liquid interface and molecules dissolved in the subphase are important for many areas in material and life sciences. Monolayers are convenient quasi-two-dimensional model systems. This review focuses on interactions between amphiphilic molecules in binary and ternary mixtures as well as on interfacial interactions with interesting biomolecules dissolved in the subphase. The phase state of monolayers can be easily triggered at constant temperature by increasing the packing density of the lipids by compression. Simultaneously the monolayer structure changes are followed in situ by grazing incidence X-ray diffraction or IRRAS. The interactions can be indirectly determined by the observed structure changes. Additionally, the yield of enzymatic reaction can be quantitatively determined, secondary structures of peptides and proteins can be measured and compared with those observed in bulk. In this way, the influence of a confinement on the structural properties of biomolecules can be determined. The adsorption of DNA can be quantified as well as the competing adsorption of ions at charged interfaces. The influence of modified nanoparticles on model membranes can be clearly determined. In this review, the relevance and utility of Langmuir monolayers as suitable models to study physical and chemical interactions at membrane surfaces are clearly demonstrated.



**Contents**



* Corresponding author.
*E-mail address:* Helmuth.Moehwald@mpikg.mpg.de (H. Möhwald).

http://dx.doi.org/10.1016/j.cis.2014.02.013
0001-8686/

## 1. Introduction

Since the early days of the membrane model of Singer and Nicholson [1], phospholipid monolayers have been considered good models of biomembranes, as they represent half of a membrane (Fig. 1). But the early work with amphiphile monolayers was largely hampered by the absence of tools to investigate liquid interfaces with molecular and microscopic resolution. This has changed drastically in the last 30 years since many interface sensitive techniques have become applicable to fluid interfaces (X-ray [2,3] and Neutron scattering [4,5], ellipsometry [6], fluorescence [7] and Brewster angle microscopy [8,9], Reflection–absorption FTIR-spectroscopy [10], nonlinear optical spectroscopy [11]). Therefore studies of Langmuir monolayers have encountered a drastic increase in activity, although they are not directly relevant for any applications. Yet, due to their high definition they are excellent models for many areas with application potential. They are the precursors for Langmuir–Blodgett films [12,13], organized monolayers possessing potential for coatings and organic electronics. They present the interfaces in emulsions, a basic structure in colloid science. Here we concentrate on their value as 2D models of biological membranes (phospholipid monolayers at the air/water interface). In the first part we will focus on general aspects, comparing monolayers and bilayers, whereas in the second part we will present modern examples on their real strengths, studies of interactions at the membrane surface.

One major difference between monolayers and bilayers concerns thermodynamics. Condensed phases of monolayers are in many cases metastable states whereas bilayers in multilamellar systems represent thermodynamically stable states. Moreover, the lipid polymorphism is richer in liquid crystals in three-dimensional systems than in 2D systems. The 3D structure of a collapsed monolayer is less hydrated than the corresponding fully hydrated bilayer in the LC phase [14]. The dynamics within monolayers and bilayers constitutes an additional difference. As concerns the structure, the recent works of Ziblat et al. [15] showed that the interactions between leaflets of ceramide/cholesterol and phospholipid/cholesterol systems led to phase separation, changes in molecular tilt angle or formation of cholesterol crystals. The structures are similar but the unit cell dimensions depend on the number of juxtaposed layers (monolayers, single hydrated bilayers, and multilayers).

The in-plane fine structure in multilayers and monolayers of lipid mixtures is in many cases different (not the tilt angle of the chains but the direction and rate of lattice distortion) [16]. As a consequence, employing one or the other physical model to describe real biological membranes could give different information regarding in-plane structures and the influence of other biological molecules as peptides or proteins on lipid structures.

In this review, we concentrate on results obtained in the last years with 2D model systems (Langmuir monolayers at the soft air/liquid interface). Our intention is to highlight the usefulness of monolayers in studies of interfacial interactions in model systems well suited to answer important questions in material and life sciences.

## 2. General comparison of monolayers and bilayers

### 2.1. Lateral intermolecular interactions

Inspecting the cartoons in Fig. 1 it is obvious that the lateral interactions in monolayers and bilayers are similar, and therefore also theoretical models are comparable. In the bilayer, the neighboring monolayer is expected to provide a weak additional interaction, and for the case of the biomembrane, where the membrane is fluid, this may be approximated by an oil with very low interfacial energy. Of course the monolayer may undergo drastic changes in density and hence exhibit phase transitions from gaseous to condensed phases [17], whereas the bilayer does not exhibit gaseous phases but only

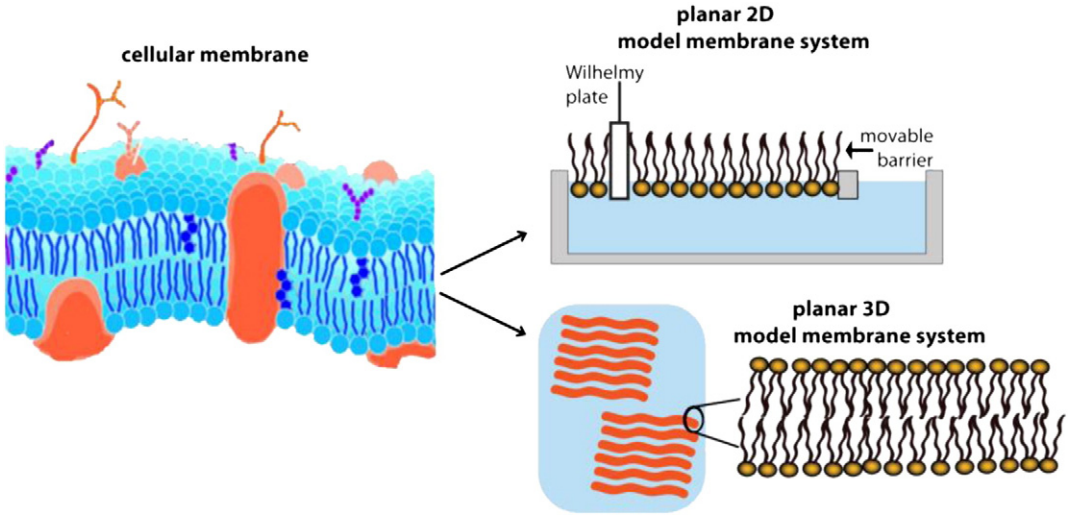


**Fig. 1.** Representation of a biological membrane as a multicomponent system (left). The two most used models are: Aqueous dispersions of lipid bilayers (right bottom) and planar lipid monolayers on an aqueous subphase (right top).

Please cite this article as: Stefaniu C, et al, Langmuir monolayers as models to study processes at membrane surfaces, Adv Colloid Interface Sci (2014), http://dx.doi.org/10.1016/j.cis.2014.02.013