Langmuir and Langmuir-Blodgett films revisited

(A Review)

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Abstract

The Langmuir and Langmuir-Blodgett (LB) technique has been applied for a long time. It exist several books and reviews on the subject. Also, a big number of works and papers have been made. This work only intends to afford a revision of the subject under the point of view of the author, and centered mostly in new references.

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A.- Introduction

Antecedents and actual applications

Nanometric films (NF) are systems with one dimension, the thickness, in the nanometric scale (between few nanometers and decades of nanometers). Organized NF (ONF) are those films where molecules place in an organized or structured way, with a certain translational or orientation order. This organization can be spontaneous, self-organization, or forced. Films may be monolayer (monomolecular layer) and multilayer. Several techniques exist to obtain ONF, as: self-assembled monolayers (SAM) [Ulman 1990], Langmuir films, Langmuir-Blodgett (LB) films [Petty 1996; Ulman 1990] and Layer-by-Layer (LbL) films [Decher 2003]. ONF can also be obtained by adsorption, drop-casting o spin-coating, even their organization degree is lower. ONF have applications in basic and applied fields: nanoelectronics, cellular biology (biomembranes), sensors and biosensors, solar cells, interfacial physicochemistry, lubricants, surface modification, molecular electrochemistry, modified electrodes, nanoparticles, etc.

The Langmuir and Langmuir-Blodgett (LB) techniques have been applied for a long time. It exist several books on the subject (Ulman 1990; Petty 1996) and reviews (Dynarowicz 2001; Knobler 1999; Stefaniu 2014; Giner-Casares 2014). Stefaniu et al. [Stefaniu 2014] discuss the relation between the behavior of a substance in a Langmuir film with its physicochemical properties, aggregation in different solvents, micelle or vesicle formation, etc. Also, a big number of works and papers have been made. Some featured articles are those of Mazur 2009 and Monkman 2000. This work only intends to afford a revision of the subject under the point of view of the author, and centered mostly in new references.

The description and application of the Langmuir-Blodgett technique has been reported in literature by several authors [Petty 1996; Ulman 1990; Mazur 2009]. The properties of LB films are dependent on the organization, the relative orientation and distance of the molecules from each other. Furthermore, applications of LB films in devices usually require good mechanical properties, which are related to molecular organization in the film [Mazur 2009]. Thus, the determination of the film structure is of primer importance.

Between the systems of interest it can be cited those films with non-covalent π-π interactions (phthalocyanines, porphyrins, thiophenes) [Tang 2007], those with van der Waals interactions between hydrocarbon chains (fatty acids,..) and those driven primarily by H-bonding and polar interaction (proteins and peptides, polysaccharides, galactolipids, charged phospholipids,..). Langmuir and LB films find applications in molecular electrochemistry, modified electrodes, sensors and solar cells, artificial photosynthesis, biomimetic membranes, and to the study of the lipid layer of the tears.

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Abstracts

Langmuir monolayers as unique physical models
Juan J. Giner-Casares, Gerald Brezesinski, Helmuth Möhwald
Current Opinion in Colloid & Interface Science 19 (2014) 176–182

Physico-chemical processes at air/liquid interfaces are of paramount importance in nature. The Langmuir technique offers the possibility of forming a well-defined monolayer of amphiphilic molecules under study at the air/liquid interface, with a unique control of the area per molecule and other experimental conditions. Despite being a traditional technique in Colloid and Interface science, there is an ever growing interest in Langmuir studies. Herein, recent developing fields of research currently taking advantage of the Langmuir technique are reviewed, comprising the interfacial structure of: water, biomolecules and inorganic/organic hybrids. The good state of the Langmuir technique at present and the foreseeable increase of its usage are discussed.

Langmuir-Blodgett Films
Ursula Mazur
Dekker Encyclopedia of Nanoscience and Nanotechnology, Second Ed, 1:1, 1738-1748

Highly ordered LB films show great promise as supermolecular assemblies for molecular electronics applications. As the dimensions of molecular based devices shrink toward the nanometer scale a new approach is required for designing Langmuir–Blodgett films with predictable performance characteristics. In this approach, the mechanical properties of thin film systems need to be systematically evaluated in terms of their relationship to the physical structure and the chemistry of the film. Furthermore,generalized models for the interplay of structural, mechanical, and Optical and electronic properties have to be developed. With these models, new LB thin film structures can be designed and fabricated with optimized optical, electronic, and magnetic properties and great strength and durability.

Monomolecular Langmuir-Blodgett films tomorrow's sensors?
Gareth Monkman
Sensor Review, Volume 20 . Number 2 . 2000 . pp. 127-131

Langmuir Monolayers as models to study processes at membrane surfaces
Cristina Stefaniu, Gerald Brezesinski, Helmuth Möhwald
Advances in Colloid and Interface Science 208 (2014) 197–213

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 anoparticles 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.

B.- Principles

The principles and fundamentals of the Langmuir and Langmuir-Blodgett technique have been explained in several references [Dynarowicz 1999; Dynarowicz 2001; Dynarowicz 1995; Kaganer 1999]. In the following sections more references will be done for specific subjects.

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B.1 Film formation: Langmuir and LB films

Briefly, films or Langmuir monolayers are formed by extension of an amphiphilic substance, insoluble in water, on the surface of the water or an aqueous solution. The film formed on the air-water interface can be transferred to a substrate, resulting in a Langmuir-Blodgett (LB) film, and the process can be repeated to form multilayer LB films. The air-water interface enables nanoscale molecular organization in films, as Langmuir or Gibbs monolayers. Their interaction and molecular structural order can be controlled with external factors such as compression (lateral pressure, area per molecule). These monolayers permits to establish models and the study of interfacial phenomena and membranes. Monolayers of fatty acids present several phases with different orders and directions of the hydrocarbon chains [Kaganer 1999].
When films incorporate functional molecules (dyes, molecular recognition, redox) open the way to the fields of molecular machines and sensors. The transfer process to substrates, resulting in LB films, allows the applied design of these devices, and even leading to molecular architectures. On one hand, the transfer depends on the characteristics of the substrate, hydrophilic or hydrophobic, and various dispositions can be obtained, known as X, Y or Z. Furthermore, the technique allows for alternate LB multilayers, in which alternate layers of molecules with different characteristics can be deposited.
Some aspects related to Langmuir film formation have been published. Aspects related to errors in properties measurement have been exposed in Welzel 1998. Aspects related to nucleation during film formation have been treated in Vollhardt 2006. The role of subphase chemistry in controlling monolayer behavior has been treated in Lendrum 2009, Turshatov 2008 and Giner 2007. Recent progress in the study of organized monolayers and the techniques applied can be found in Imae 2007 and Möbius 2000.

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B.2 Π-A isotherms. Compressibility. Film (monolayer) state. Phase transition. Phase diagram

The physical states in Langmuir film formation are called in different names.

LE: L1 LC: tilted condensed S: untilted condensed

G: gas LE: liquid expanded LC: liquid condensed S: solid

The record of the surface pressure ($\Pi=\gamma_o-\gamma$) versus the area or area per molecule constitutes the Π-A isotherm. From the isotherms information on the system can be obtained (phases or states of the monolayer, compressibility) and for mixed films information about miscibility of the components (see section B.4).

Thermodynamics of films can be resumed in some equations:

$\Delta S=(d\Pi c/dT)\,\Delta A$ $\Delta Q=T\Delta S$ 1st order phase transition

Compressibility coefficient

$\beta=C_s=-1/A\,(dA/d\Pi)$

Inverse of the compressibility coefficient, elastic modulus or Young modulus

$\beta^{-1}= C_s^{-1}= -A\,(d\Pi/dA)$

Vitovic, 2006, reported the relation between the values of β^{-1} and the film physical states.

A paper devoted to the contribution of viscoelastic and compressibility in surface pressure-area isotherms is that of Verwijlen 2014. In references Volhardt 2006 and Su 2007 the compressibility is also treated. In Volhardt 2015 a historical perspective on phases and phase transition in insoluble and adsorbed monolayers of amide amphiphiles is done.

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Abstracts

Separating viscoelastic and compressibility contributions in pressure-area isotherm measurements
T. Verwijlen, L. Imperiali, J. Vermant
Advances in Colloid and Interface Science 206 (2014) 428–436

Monolayers of surface active molecules or particles play an important role in biological systems as well as in consumer products. Their properties are controlled by thermodynamics as well as the mechanical properties of the interface itself. For insoluble species forming Langmuir monolayers, surface pressure-area isotherms are typically used to characterize the thermodynamic state. A Langmuir trough equipped with aWilhelmy plate is often used for such measurements. However, when Langmuir interfaces are compressed and become more structured, the elastic response of these interfaces can interfere with the measurement of the surface pressure-area isotherm, even when the compression speed is slow. Recent reports of compression data for highly elastic interfaces revealed a dependence of the apparent surface pressures on the geometry of the measurement trough. In the present work, this dependence is investigated by considering adequate constitutive models. Since deformations in such compression experiments can be large, linearized versions of the Kelvin–Voigt model do not suffice. We develop a framework for quasi-linear constitutive models by choosing suitable non-linear strain tensors, adequately separating the shear and dilatational effects in a frame invariant manner. The proposed constitutive models can be used as building blocks to describe viscoelastic behavior as well. The geometry dependence in isotherm measurements is then shown to be a consequence of varying contributions of the isotropic surface pressure and extra shear and dilatational elastic stresses. Using these insights, an approach is proposed to obtain the intrinsic Surface pressure-area isotherms for elastic interfaces. As a case study, experimental data on graphene oxide sheets at the air–water interface is investigated to evaluate the proposed model.

Phases and phase transition in insoluble and adsorbed monolayers of amide amphiphiles: Specific Characteristics of the condensed phases
D. Vollhardt
Advances in Colloid and Interface Science 222 (2015) 728–742

For understanding the role of amide containing amphiphiles in inherently complex biological processes, monolayers at the air-water interface are used as simple biomimetic model systems. The specific characteristics of the condensed phases and phase transition in insoluble and adsorbed monolayers of amide amphiphiles are surveyed to highlight the effect of the

chemical structure of the amide amphiphiles on the interfacial interactions in model monolayers. The mesoscopic topography and/or two-dimensional lattice structures of selected amino acid amphiphiles, amphiphilic N-alkylaldonamide, amide amphiphiles with specific tailored headgroups, such as amide amphiphiles based on derivatized ethanolamine, e.g. acylethanolamines (NAEs) and N-,Odiacylethanolamines (DAEs) are presented. Special attention is devoted the dominance of N,O-diacylated ethanolamine in mixed amphiphilic acid amide monolayers. The evidence that a first order phase transition can occur in adsorption layers and that condensed phase domains of mesoscopic scale can be formed in adsorption layers was first obtained on the basis of the experimental characteristics of a tailored amide amphiphile. New thermodynamic and kinetic concepts for the theoretical description of the characteristics of amide amphiphile's monolayers were developed. In particular, the equation of state for Langmuir monolayers generalized for the case that one, two or more phase transitions occur, and the new theory for phase transition in adsorbed monolayers are experimentally confirmed at first by amide amphiphile monolayers. Despite the significant progress made towards the understanding the model systems, these model studies are still limited to transfer the gained knowledge to biological systems where the fundamental physical principles are operative in the same way. The study of biomimetic systems, as described in this review, is only a first step in this direction.

B.3 Monocomponent systems

Many monocomponent systems have been studied with the Langmuir technique, mainly fatty acids and fatty amines, fatty alcohols, phospholipids, polar lipids, but also other molecules with a not well-defined amphiphilic molecular structure. The bibliography on the subject is wide, and a review of previous studies can be found in Petty 1996, Ulmann 1990, Möbius 2002 and Imae 2007. Specific studies by the author's group are Torrent-Burgués 2010, Oncins 2006, Torrent-Burgués 2006, Oncins 2008, Torrent-Burgués 2012, Hoyo 2012, Hoyo 2013, Torrent-Burgués 2014, Hoyo 2015a, Hoyo 2015b. In these works, more bibliographic references can also be found, as well as in previous reports of the author [Torrent 2011, Torrent 2004].

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B.4 Multicomponent (mixed) systems: miscibility

In the work of Dynarowicz and Kita [Dynarowicz 1999] a brief revision on mixed monolayers is presented, with reference to the criteria used to see if miscibility is present, to the thermodynamic and to the state equations, using the 2D model of gas as well as the model of 2D solution. The model 2D is studied in deep to obtain parameters for the molecular

interactions by Dynarowicz et al. [Dynarowicz 1995], and applied to the stearic acid with 1-octadecanol system.

Thermodynamic of mixed monolayers

For the study of mixed monolayers the collapse pressure can be analyzed or the excess properties (A^E, G^E, ..) can be determined, which give useful information about the molecular interactions, volume effects, phase separation, packing, aggregate formation, etc.

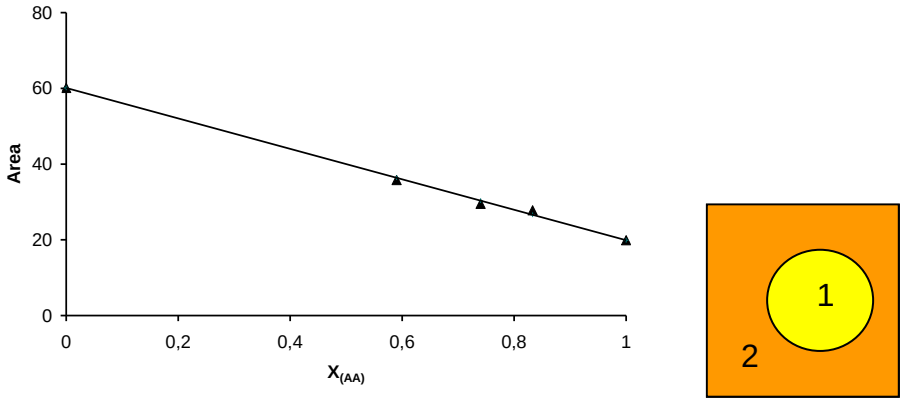
The excess area is defined as the difference between the real area of the mixture and the ideal area. The excess Gibbs energy is calculated from the excess area.

$$A^E = A_{12} - (\chi_1 A_1 + \chi_2 A_2)$$

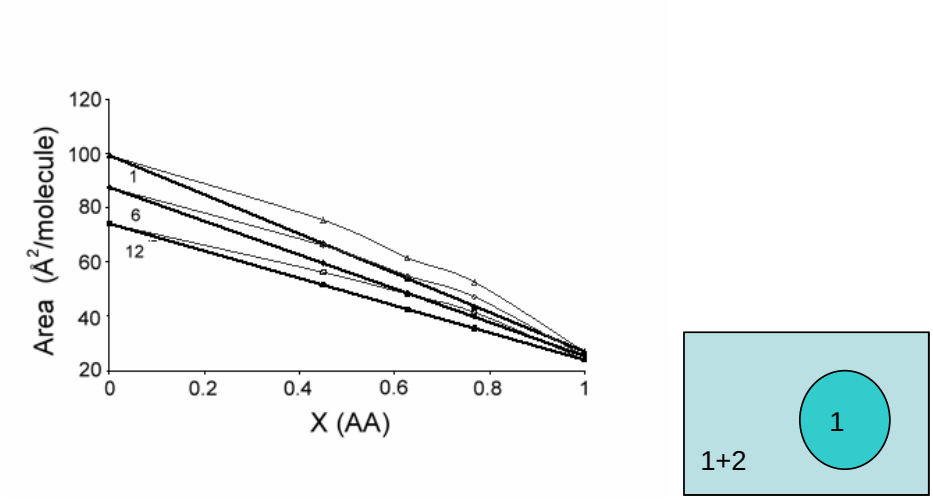
$$G^E = \int_0^{\pi} \left[A_{12} - (\chi_1 A_1 + \chi_2 A_2) \right] d\pi$$

A linearity between the area per molecule and the molar fraction indicates ideal behavior or immiscibility of the components in the monolayer. If no linearity exists, thus a certain miscibility between the components occurs.

For instance, the linearity observed in the figure (corresponds to a mixture of AA+ phthalocyanine) can indicate ideal mixture or immiscibility. To discern between both an AFM study is needed [Torrent 2008].



In the other situation of the figure below (corresponds to a mixture of AA and a thiomacrocyclic compound) no linearity is observed, and this indicate total or partial miscibility. An ulterior study by AFM allows deciding the correct option [Torrent 2012].



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B.5 Film stability. Collapse. Equilibrium spreading pressure

Du and Liang [Du 2004] studied the improvement of thermal stability of LB films through an intermolecular hydrogen bond and metal complex. Wurlitzer et al [Wurlitzer 2002] studied relaxation dynamics of domains in Langmuir monolayers. Haycraft 2007 studied the reversible collapse. Hu et al 2003 studied the film stability on a sealed minitrough for microscopy.

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B.6 Equations of state

The physical description and behaviour of the film can be done using state equations, such as in 3D systems. Several equations or isotherms have been proposed: Isot Henry, Isot virial, Isot Langmuir, Isot Frumkin, Eq Volmer, Isot Temkin, Eq van der Waals, Eq Szyskowski-Langmuir, Eq Butler.

In the following a resume of them, and its linearization, is presented.

$\pi a = kT$ (1) Eq Henry

$\pi a = \alpha kT$ (2) Eq Henry corrected

$\pi(a-a_o) = kT$ (3) Eq Langmuir

$\pi(a-a_o) = \alpha kT$ (4) Eq Langmuir corrected

$\pi a/kT = 1 + \pi a_o /kT$ o $\pi a/kT = \alpha + \pi a_o /kT$

$kT/\pi = a - a_o$ o $kT/\pi = (a - a_o)/\alpha$

$(\pi-\pi_o)(a-a_o) = kT$ (5) Eq Volmer

$(\pi+(b/a^2))(a-a_o) = kT$ (5'). Eq van der Waals

$a = b_o + b_1 \pi + b_2 \pi^2 + \ldots.$ (6)

$\pi = b_o + b_1 /a + b_2/ a^2 + \ldots.$ (7)

$\pi a = kT \ (b_o + b_1 \pi + b_2 \pi^2 + \ldots.)$ (6')

$\pi a = kT(b_o + b_1 /a + b_2/ a^2 + \ldots.)$ (7') Eq virial corrected

$\pi a = kT \ (1 + b_1 \pi + b_2 \pi^2 + \ldots.)$ (6'')

$\pi a = kT(1 + b_1 /a + b_2/ a^2 + \ldots.)$ (7'') Eq virial

$(\pi a/kT - 1)/\pi = b_1 + b_2 \pi$ o $a(\pi a/kT - 1) = b_1 + b_2 /a.$

$$\left(\pi + \frac{n\varepsilon Ao}{2A^2}\right)\left[A\left(1-\frac{Ao}{2A}\right)^2\right] = kT \qquad (8)$$ Ref Chattoraj-Birdi; Adamson

$$\left(\pi + 400n/A^{3/2}\right)(A - Ao) = kT) \qquad (9)$$

$$\sigma = \sigma_n + \frac{\alpha\sum_0^l l'\exp\left[-(\pi a l' + \varepsilon')/kT\right]}{\sum_0^l \exp\left[-(\pi a l' + \varepsilon')/kT\right]} \qquad (10)$$

$\pi a = kT(1 + B(1/a - 1/a_o))$ (11) Eq Weis et al $\pi a/kT = (1-B/a_o) + B/a$

$\pi a(1-\omega/a)^2 = kT$ (12) Eq Lebowitx; Meinders et al $(kT/\pi a)^{1/2} = 1-\omega/a$

$a=b_o - b_1 \pi$ (13)

Note: The Eq virial leads to Eq Henry or to the Eq Frumkin ($\pi a=kT(1 + b_1 /a)$) neglecting terms of higher order. Exist another version of the Eq Langmuir (we are going to call Eq Langmuir logarithmic): $\pi a=-kT \ln(1-A_m/a)$. This eq also reduces to the Eq Henry when $A_m/a<<1$.

These equations can be classified as function of the number of parameters:

Eq without parameter: ec (1)

Note: also, theoretical eq has no adjustable parameters, but if the parameters are not known then they become adjustable.

Eq with 1 parameter: eq (2), eq (3), eq (12)

Eq (2): α Eq (3): a_o Eq (12): ω Eq (6'') truncada: b_1

Eq (7'') truncada: b_1 (Eq Frumkin)

Eq with 2 parameters: ec (4), ec (5), ec (5'), ec (6''), ec (7''), ec (11)

Eq (4): α, a_o Eq (5): π_o, a_o Eq (5'): b, a_o Eq (6'') truncada: b_1, b_2

Eq (7'') truncada: b_1, b_2 Eq (11): B, a_o Eq (13): b_0, b_1

Eq with more parameters: ec (6), ec (6'), ec (7), ec (7')

Ec (6): b_0, b_1, b_2 Eq (6'): " Ec (7): " Ec (7'): "

Ec (6''): b_1, b_2, b_3 Ec (7''): "

In the works of Dynarowicz 1999 and Dynarowicz 1995 a study and application of state equations to mixed systems is done. Vollhardt et al. [Volhardt 2000; Volhardt 2006] make a thermodynamic study and state equations of DPPG phospholipid monolayers at different temperatures. They also make BAM observations. A state equation of 4 parameters is proposed (equation of Volmer generalized) in order to describe all the π-A curve, indicating that the equation of Volmer simple can be applied to describe the phase of liquid expanded (LE). Gurkov et al. [Gurkov 2003] proposed that a state equation simple such as that of Volmer or that of Langmuir, can be used to describe monolayers of globular proteins, instead of more complex equations such as that of Lebowitz. Weis et al. [Weis 2000] describe a state equation and its applications to the study of phospholipids POPX (POPC, POPG, POPS). In Chou 2000 a thermodynamic treatment of mixed monolayers of DPPC/cholesterol is done, as well as the de relaxation processes. Pogorzelski and Kogut [Pogorzelski 2003] use an equation of virial in order to study films of marine surfactants. They also present the calculation of thermodynamics parameters, such as enthalpy and entropy of phase change. Sánchez-González et al. [Sánchez-González 1998, 1999] use different state equations, particularly the virial eq, to study the interaction between lipids and the protein γ-globulin. Yu et al. [Yu 2002] present a brief treatment of the compressibility curves for characterization of the transition LE-LC of DPPC. Liu [Liu 2002] does a modelization of non-ideal mixtures of amphiphilic substances and its application for ionic surfactants, which do not follow the behaviour of regular solutions.

On the other hand Lin et al. [Lin 2003] have studied the state equations for surfactants non-ionic such as CmEn. These surfactants present adsorption, which is treated to obtain the state equation. Gochev et al [Gochev 2013] studued the adsorption isotherm and equation of state for β-lactoglobulin at the air/water interface. Other works are those of Chattoraj 2006, Rusanov 2007, Fainerman 2008, Hossain 2007. Fainerman et al [Fainerman 2003] made the description of the adsorption of proteins in the framework of a 2D solution model. Fainerman et al [Fainerman 2000] studied the effect of surfactant interfacial orientation/aggregation on adsorption dynamics. Fainerman et al [Fainerman 2002] studied the adsorption of single and mixed ionic surfactants at fluid interfaces. The work of Ni et al can also be viewed [Ni 2006].

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B.7 Penetration in monolayers

Penetration of molecules in monolayers is a very interesting subject, with biological and pharmaceutical implications. Penetration systems at the air-water interface in which a dissolved amphiphile (surfactant, protein) penetrates into a Langmuir monolayer are interesting models for a better understanding of various technological and biologic processes. This subject has been treated in Vollhardt 2000, Feinerman 1999.

This phenomenon can be studied using the surface pressure or surface potential techniques, Brewster Angle Microscopy and Atomic Force Microscopy (Ohtsuka 2005).

Examples of penetration of proteins or peptides into phospholipid monolayers are Clifton 2008, Sanchez-Martin 2010, Maget-Dana 1997, Ronzon 2002, Lahdo 2004, Polverini 2003, Dynarowicz-Latka 2005, Phillips 1975, Zhao 2000, Quinn 1970, Saraga 1986, Fainerman 1999.

Recently the penetration of rhodopsin have been reported [Sanchez-Martin 2013].

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Key terms: competitive adsorption; contraction of the Langmuir film, formation of condensed domains; by compressing the protein is not removed from the interface layer; GOx, PDA; Isoterms, Microscopy fluorescence.

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Key terms: protein binding to lipid membrane; DSC, CD, fluorescence, PC liposomes; b-Galactosidase; unfolded state more active than the native form.

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Key terms: Pulmonary surfactant; AFM, SE on ITO, LB

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Key terms: Polyunsaturated fatty acids: oxidation, effect of protein binding; DDHA-PC; RP2, recoverin; MIP maximum insertion pressure, Langmuir monolayer.

S Yu Zaitsev et al. Adv Colloid Interf Sci 183-184 (2012) 14. Thin films and assemblies of photosensitive membrane proteins and colloid nanocrystals for engineering of hybrid materials with advanced properties.

Key terms: membrane proteins: bacteriorhodopsin bR, bacterial photosynthetic RC; light harvesting, energy transferring; Langmuir, LB, LbL; Colloidal nanoparticles with bR.

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Key terms: Isotherms p-A; x-ray reflectivity; complex DPPC-BSA pH-sensitive.

M Marti et al. J Biophys Chem 3 (2012) 81. Laccases stabilization with PC liposomes.

Key terms: Enzyme-textile fibre; protein 3D stability; microencapsulation, liposomes.

P Toimil et al. COLSUB 92 (2012) 64. Monolayer and BAM study of HSA-DPPC mixtures at the air-water interface.

Key terms: p-A isotherm, BAM; Pressure exclusion.

Abstracts

Biochem. J. (1970) 119, 21-25 21
The Penetration of Serum Albumin into Phospholipid Monolayers of
Different Fatty Acid Chain Length and Interfacial Charge
P. QUINN AND R. M. C. DAWSON

The highest sturface pressure of phosphatidylcholine monolayers allowing penetration of delipidated serum albumin decreased in the order dibehenoyl> distearoyl>dipalmitoyl = dimyristoyl. This pressure was not related to the area occupied or to the space available between the phospholipid molecules at the interface. 2. Penetration of albumin into yeast phosphatidylcholine monolayers was increased by adding a small percentage of long-chain anions (phosphatidic acid, dicetylphosphoric acid) to the film but only when the protein was below its isoelectric point (i.e. positively charged). 3. Stearylamine added to phosphatidylcholine monolayers had no effect on albumin penetration even when the protein was oppositely charged to that of the phospholipid/water interface. 4. The results are discuissed in relation to the activation of certain phospholipases by anionic amphipathic suibstances.

Penetration into insoluble monolayers. 3. Surface potential study with soluble vinblastine sulfate and spread egg lecithin

Lisbeth. Ter-Minassian-Saraga
Langmuir, **1986**, *2* (1), pp 24–29, **DOI:** 10.1021/la00067a004

Colloids and Surfaces A: Physicochemical and Engineering Aspects
Volume 171, Issues 1-3, 10 October 2000, Pages 175-184

doi:10.1016/S0927-7757(99)00567-1 | How to Cite or Link Using DOI

Effect of protein penetration into phospholipid monolayers: morphology and structure

J. Zhao[a, b], D. Vollhardt [a], G. Brezesinski[a], S. Siegel[a], J. Wu[b], J. B. Li[a, b] and R. Miller[a]

Abstract

Phase transition and phase properties of dipalmitoylphosphatidylcholine (DPPC) monolayers penetrated by bovine β-lactoglobulin dissolved in a buffered aqueous subphase are experimentally studied. The phase transition during the penetration dynamics is indicated by a break point in the $\Pi(t)$ transients. The condensed phase domains formed during the β-lactoglobulin penetration are visualized by Brewster angle microscopy (BAM). The lattice structure of the condensed phase is characterised by grazing incidence X-ray diffraction (GIXD). Experiments on the penetration kinetics of β-lactoglobulin into DPPC monolayers are performed, starting from different monolayer states and using different protein concentrations. The condensed phase formed after the main phase transition point, consists only of DPPC. The β-lactoglobulin penetration occurs without any specific interaction with the DPPC molecules. Number and growth of the domains depend on the area per DPPC molecule at which the β-lactoglobulin penetration takes place. A first-order main phase transition can be induced when the protein penetrates into a fluid (gaseous) DPPC monolayer. β-Lactoglobulin cannot penetrate into a condensed DPPC monolayer at a surface pressure above the equilibrium penetration pressure. Conformational changes and squeezing out of protein from the penetrated monolayer are studied by compression of penetrated monolayers in equilibrium.

Nature **254**, 154 - 156 (13 March 1975); doi:10.1038/254154a0

Lateral compressibility and penetration into phospholipid monolayers and bilayer membranes

M. C. PHILLIPS, D. E. GRAHAM & H. HAUSER

THE phospholipid bilayer[1] in certain biological membranes is maintained so that the range of temperature over which the gel-to-liquid crystal transition occurs includes the environmental temperature[2]. As a result, clusters of phospholipid molecules in crystalline and liquid-crystalline states[1] coexist in the membrane and the isothermal lateral compressibility of the membrane lipids is enhanced[3]. Any increase in compressibility should facilitate insertion of foreign molecules into the bilayer thereby affecting transport across the membrane. Indeed, there is evidence that transport of ions[4,5] and sugars[3], and penetration of an enzyme[6] is increased when the chain-melting transition of the lipids occurs. The lateral compressibility of phospholipid bilayers has not been measured, however, and there is no direct evidence for an increase in compressibility at the point where the gel-to-liquid crystal phase transition occurs. In order to measure lateral compressibility, compression solely in the plane of the bilayer is required. Such directed compression of bilayers will be difficult but it can be readily achieved with monolayers at the

air−water interface. Since the molecular packing in such monolayers of phospholipids is equivalent to that in bilayers dispersed in excess water[1,7], this model system is particularly convenient for exploring the role of lateral compressibility. Here we show (1) how the compressibility of lecithin mono-layers varies with packing density and changes at the chain-melting transition, and (2) how penetration of a hydrophobic protein is dependent on the compressibility.

BAM studies on the penetration of amphotericin B into lipid mixed monolayers of cellular membranes

Dynarowicz-Łątka, P.; Miñones, J.; Conde, O.; Casas, M.; Iribarnegaray, E.

Applied Surface Science, Volume 246, Issue 4, 2005, p. 334-341. DOI: 10.1016/j.apsusc.2004.11.037

The penetration of the antifungal antibiotic amphotericin B (AmB) into Langmuir monolayers formed by cholesterol and ergosterol has been investigated by measuring the overpressure (Δπ) in the film after the injection of AmB into water subphase. In addition, the penetration of AmB into sterol monolayers was studied at the microscopic level with Brewster angle microscopy (BAM) by recording BAM images simultaneously with the surface pressure increase. The obtained results show that monolayers formed by cholesterol are more penetrable for AmB molecules while rigid and closely packed films of ergosterol are less accessible for the antibiotic. This does not imply that the interactions between AmB and ergosterol are weaker than those between AmB and cholesterol, but indicates that the extent of AmB penetration is related to a different space accessibility. To get insight into the role of phospholipids in the interactions between AmB and sterols, the penetration of the antibiotic into mixed ergosterol dipalmitoyl phosphatidylcholine (DPPC) and cholesterol DPPC monolayers have also been investigated. The extent of AmB penetration into mixed monolayers was found to be dependent both on AmB bulk concentration and DPPC sterol proportion in the mixed film.

Langmuir **2003,** *19,* 872-877

Interaction of Myelin Basic Protein with Phospholipid Monolayers: Mechanism of Protein Penetration
Eugenia Polverini,† Simona Arisi,† Paolo Cavatorta,† Tatiana Berzina,† Luigi Cristofolini,† Anna Fasano,‡ Paolo Riccio,§ and Marco P. Fontana*,†

The myelin basic protein (MBP) is the second most abundant protein in the myelin sheath of the central nervous system and is believed to be important for the compactness and integrity of the membrane. We investigated the mechanism of the interaction of lipid-free MBP with phospholipid monolayers at the air/water interface; in particular, we studied the process of MBP adsorption onto monolayers made up either of neutral dipalmitoylphosphatidylcholine (DPPC) or of negatively charged dipalmitoylphosphatidylserine (DPPS) monolayers. They are natural constituents of the myelin membrane, and sharing an identical hydrophobic chain, they differ only in headgroup composition. The MBP-lipid interaction is investigated for the first time by means of nullellipsometric measurements, monitoring in real time the effect of adsorbed molecules in the insoluble monolayer at different monolayer conditions, such as

surface pressure and molecular area. The different behavior of monolayer thickness and surface pressure confirmed the hypothesis of a different interaction mechanism of MBP with the two kind of lipids. While in the presence of neutralDPPCthe protein seems to penetrate among the lipid domains, in the case of negatively charged DPPS the electrostatic interaction appears to be the driving force, because protein intimately associates with the headgroups and binds to the Langmuir layer as a specific lipid-protein complex. Results with DPPS were confirmed by FTIR spectroscopy measurements, performed after transferring phospholipid multilayers onto a solid substrate by the Langmuir-Schaefer method.

Insertion of the amyloid protein precursor into lipid monolayers: effect of cholesterol and apolipoprotein E

Raghda Lahdo and Laurence de La Fournière – Bessueille*
Biochemical Journal Immediate Publication. Published on 15 Jun 2004 as manuscript BJ20040777

SUMMARY
The amyloid protein precursor (APP) has been linked to Alzheimer's disease (AD) together with cholesterol (Chol) and apolipoprotein E (ApoE). We have examined the hypothesis that interaction of APP with the lipid membranes is modulated by Chol and ApoE. The insertion of APP into lipid monolayers was first evidenced as an increase of the surface pressure. APP injected into a subphase induced a substantial increase of the surface pressure of monolayers prepared from phosphatidylcholine (PC), cholesterol (Chol), sphingomyelin (SPM) and phosphatidylserine (PS), the major lipids present in the plasma membranes of brain cells. At a given initial pressure, the insertion of APP in expanded monolayers is higher than in condensed monolayers, in the order Chol > PC > SPM > PS. The membrane insertion capacity of APP was also measured from surface pressure vs area (π-A) isotherms of APPlipid monolayers. The increase in the mean area per molecule in protein-lipid monolayers, in the order PC > Chol > PS > SPM, provides further evidence for protein-lipid interactions. These interactions occurred at salt and pH optima close to physiological conditions (150 mM NaCl and pH 7.4). In addition, ApoE4 affected the insertion of APP into lipid films. APPApoE complexes showed a decreased ability to penetrate lipid monolayers at constant area. APP-ApoE complexes expanded surface pressure – area isotherm of a Chol monolayer to a lesser extent than APP alone. These experiments demonstrate the role of Chol and ApoE in the modulation of membrane insertion of APP.

Penetration of Bovine Serum Albumin into Dipalmitoylphosphatidylglycerol Monolayers: Direct Observation by Atomic Force Microscopy
Isao OHTSUKA and Shoko YOKOYAMA*

The penetration of bovine serum albumin (BSA) into dipalmitoylphosphatidylglycerol (DPPG) monolayers was observed using atomic force microscopy (AFM) and surface pressure measurements. The effects of surface pressure, amount of BSA and the addition of ganglioside GM1 (GM1) were investigated. The surface pressure of the DPPG monolayer was increased by the penetration of BSA, and the increase in surface pressure was greater in the liquid-expanded film than that in the liquid-condensed film. The AFM images indicated that BSA penetrated into the DPPG monolayer. The amount of BSA that penetrated into the DPPG monolayer increased with time and with the amount of BSA added. On the contrary,

the AFM image showed that BSA penetration into the mixed DPPG/GM1 (9 : 1) monolayer scarcely occurred. GM1 inhibited the penetration of BSA into the DPPG monolayer.

Penetration of a GPI-anchored protein into phospholipid monolayers spread at the air/water interface

Authors: Ronzon F.[1]; Desbat B.; Chauvet J.-P.; Roux B.

Source: Colloids and Surfaces B: Biointerfaces, Volume 23, Number 4, February 2002 , pp. 365-373(9)

Biophysical Journal, Volume 73, Issue 5, 2527-2533, 1 November 1997
doi:10.1016/S0006-3495(97)78281-X

Penetration of the insect defensin A into phospholipid monolayers and formation of defensin A-lipid complexes

R. Maget-Dana and M. Ptak

Defensin A is an inducible cationic protein secreted in the hemolymph of fleshfly Phormia terranovae larvae in response to bacterial or septic injuries. Defensin A is known to permeabilize the bacteria cell membranes by forming voltage-dependent channels. The penetration of this small protein into lipid monolayers was studied as a function of the polar head and acyl chain length of phospholipids. The extent of penetration by defensin A is higher in monolayers made of anionic phospholipids than in monolayers made of zwitterionic phospholipids (phosphatidylcholines), because of electrostatic interactions. From the analysis of the compression isotherm parameters of mixed defensin A/phospholipid monolayers, it appears that defensin A interacts with phospholipid by forming 1:4 complexes. These complexes are not miscible in the lipid phase and induce microheterogeneity in the lipid membrane. These clusters might be related to the ion-channel structures responsible for the biological activity of defensin A.

J Phys Chem B. 2010 Jan 14;114(1):448-56.

A Langmuir monolayer study of the interaction of E1(145-162) hepatitis G virus peptide with phospholipid membranes.

Sánchez-Martín MJ, Haro I, Alsina MA, Busquets MA, Pujol M.

E1(145-162), a peptide corresponding to the structural protein E1 of the GB virus C, has been shown earlier to bind at pH 7.4 to vesicles containing 1,2-dimyiristoyl-sn-glycero-3-phospho-rac-(1-glycerol)] (DMPG) and 1,2-dimyiristoyl-sn-glycero-3-phosphocholine (DMPC) phospholipids. To deepen the understanding of the interaction of E1(145-162) with the lipid membrane, in this paper, we report a detailed study of the surface properties of peptide, miscibility properties, and behavior of mixed monomolecular films of it and three phospholipids DMPG, DMPC, and 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine (POPG). These studies were performed using the Langmuir balance by means of surface adsorption studies, surface pressure-mean molecular area compression isotherms, and penetration

kinetics. The Brewster angle microscopy (BAM) was used to study the morphological properties of pure peptide and the mixed monolayers. The results show us that the peptide showed surface activity concentration dependent when injected beneath a buffered solution (HEPES/NaCl, pH 7.4). This tendency to accumulate into the air/water interface confirms its potential capacity to interact with membranes; the higher penetration of peptide into phospholipids is attained when the monolayers are in the liquid expanded state and the lipids are charged negatively maybe due to its negative electric charge that interacts with the positive global charge of the peptide sequence. The area per molecule values obtained suggested that the main arrangement structure for E1(145-162) peptide is the alpha-helical at the air-water interface that agreed with computational prediction calculations. Miscibility studies indicated that mixtures become thermodynamically favored at low peptide molar fraction.

J Phys Chem B. 2008 Dec 11;112(49):15907-13.

Interfacial structure of wild-type and mutant forms of puroindoline-b bound to DPPG monolayers.

Clifton LA, Green RJ, Hughes AV, Frazier RA.

The interaction of wild-type puroindoline-b (Pin-b+) and two mutant forms having single residue substitutions (G46S or W44R) with L-alpha-dipalmitoylphosphatidyl-dl-glycerol (DPPG) as a Langmuir monolayer at the air/water interface was investigated by neutron reflectivity (NR) and Brewster angle microscopy (BAM). NR profiles were fitted using a three-layer model to enable differences in penetration of protein between the lipid headgroup and acyl regions to be determined. The data showed similar surface excesses for each of the three proteins at the interface; however, it was revealed that the depth of penetration of protein into the lipid region differed for each protein with Pin-b+ penetrating further into the acyl region of the lipid compared to the mutant forms of the protein that interacted with the headgroup region only. BAM images revealed that the domain structure of the DPPG monolayers was disrupted when Pin-b+ adsorption had reached equilibrium, suggesting protein penetration had led to compression of the lipid region. In contrast, the domain structure was unaffected by the W44R mutant, suggesting no change in compression of the lipid region and hence little or no penetration of protein into the lipid layer.

C.- Characterization techniques

It exists several techniques to study the behaviour and for the characterization of Langmuir monolayers and LB films. These techniques are:

Measurement of the surface pressure: isotherm Π-A

Optical techniques: BAM, ellipsometry

Diffraction techniques: grazing X Ray and of electrons

Spectroscopic techniques: IR, Raman, UV-Vis

Measurement of electric properties: surface potential

SPM techniques: AFM, FFM, STM, NSOM

Other techniques (QCM, SEM, TEM, contact angle)

These techniques afford information on molecular orientation and domain structure, and furthermore about coverage, thickness, density, atomic composition, chemical composition, chemical structure, order and defect content. To obtain several of these parameters, several techniques are needed. Recent progress son the study of organized monolayers and on the applied techniques can be found in references [Imae 2007; Möbius 2002; Dynarowicz 2001].

Measurement of the surface pressure during monolayer compression affords information on the molecular area, phases and states of the monolayer, collapse, compressibility, stability, interaction with the subphase or the miscibility degree in mixtures.

Among the optical techniques, the most usual are Brewster angle microscopy (BAM), microscopy of fluorescence or epifluorescence, ellipsometry, dichroism.

Among the X Ray techniques we have the X Ray diffraction in low angle (GIXD o GIXRD: grazing incidence X-ray diffraction) (and GIXRD of synchrotron) or the reflectivity of X ray and of neutrons, or the dispersion of X ray (X-ray scattering).

Among the spectroscopies we have that of infrared (IR, FTIR) or Raman, ultraviolet-visible (UV-Vis) or fluorescence. Furthermore the transmission techniques, also exist the variants of reflection: IRRAS (o RAIRS) and that of UV-Vis.

Measurement of the Surface potential affords information on changes in this magnitude due to the monolayer presence and to changes in its structure and organization, orientation of dipoles. Also informs on interactions of especies from the subphase with the monolayer.

The properties of the LB films transferred can differ from those of the correspondents Langmuir films, nevertheless the comparison is still possible whether the interface change is considered and its possible influence on the film structure. For the study of phases and domains using the LB films, the techniques of local probe microscopy (SPM) can be used.

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C.1 Π-A, ΔV-A isotherms

Surface Potential

The measure of the surface potential affords information on changes in this magnitude due to the presence of the monolayer and to changes in its structure and organization, and dipole orientation. Also informs on interactions between the subphase and the monolayer. The technique uses a vibrating Kelvin probe that measures the potential difference between two faces of a condenser, where one of them is forced to vibrate giving a current. Then, an external potential is applied, the surface potential, in order to null such current,

Some models have been proposed in order to relate the measured values and the structure of the monolayer and the subphase [Dynarowicz].

Model condenser of parallel plates (equation of Helmholtz):

La monolayer is a surface of dipoles distribute uniformly.

$$\Delta V = \frac{\mu_n}{A\varepsilon_r\varepsilon_o} + \Psi_o \qquad \mu_n = \mu_\perp$$

Ψo: contribution of the double layer in ionized monolayers.

$$\Psi_o = \frac{2kT}{e}\sinh^{-1}\left[\frac{e\alpha}{A\left(5.88\times10^{-7}c\varepsilon T\right)^{1/2}}\right] = \frac{2kT}{e}\sinh^{-1}\left[\frac{e\alpha}{A\sqrt{8\varepsilon_r\varepsilon_o kTc}}\right]$$

Model Demchak-Fort : Model of three-layer condenser

$$\Delta V = \frac{1}{A\varepsilon_o}\left(\frac{\mu_1}{\varepsilon_1} + \frac{\mu_2}{\varepsilon_2} + \frac{\mu_3}{\varepsilon_3}\right) + \Psi_o$$

1: contribution reorientation water

2: region hydrophilic of the group

3: region hydrophobic of the group

Demchak-Fort: ε_3=5.3, ε_2=7.6, μ_1/ε_1=+0.04 D

Oliveira et al: ε_3=2.8, ε_2=6.4, μ_1/ε1=-0.065 D, μ_3=0.33 D,

μ_2=0.99, 1.00, 1.1, 0.15 D for acidic groups, alcohol, ester, amine

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C.2 UV-Vis, IR spectroscopies

Between spectroscopic techniques we can include those of infrared (IR, FTIR) o that of Raman, the ultraviolet-visible (UV-VIS) or that of fluorescence. Furthermore the transmission

techniques, also exist the variants of reflection: IRRAS (o RAIRS) and that of UV. Also the attenuate total reflection (ATR) and the SERS (surface enhanced Raman scattering) [Ozaki 2007].

Spectroscopy of reflexion UV-Vis

Investigation of the orientation, association, adsorption and chemical change of chromophores in monolayers at the air-water interface.

Applications from protein to dye-containing monolayers, including tensides, fatty acids, LB films on solid substrates, liposomes.

In dissolution $\varepsilon = \frac{A}{c \cdot l}$ ε: absorptivity molar ($cm^{-1}mol^{-1}L$), A: absorbance,

c: concentration ($mol \cdot L^{-1}$), l: length of the cell (cm)

On the interface air-water $\varepsilon = \frac{\Delta R}{2.303 \cdot 10^3 \Gamma R_w^{1/2}}$ R_w: reflectivity of water

Γ: surface density ($mol \cdot cm^{-2}$)

Considering a distribution homogeny of the moments of transition respected the normal

$f_{orient} = \frac{3}{2}\sin^2\theta$ θ: angle of moment dipole of transition respected the normal

(non symmetrical molecules)

$f_{orient} = \frac{3}{4}(1+\sin^2\theta)$ θ: angle between the plane of moments of transition and the normal

(symmetrical molecules)

In dissolution the strength of the oscillator is

$f = \frac{4\varepsilon_0 2.303 m_e c_0}{N_A e^2} \int_{banda} \varepsilon \cdot d\nu = 1.4410^{-19} \int_{banda} \varepsilon \cdot d\nu$ units 1.44 10^{-19}: $mol \cdot L^{-1} \cdot cm \cdot s$

ε_0: vacuum permittivity, m_e: electron mass, e: electron charge, c_0: vacuum light velocity

In the monolayer $f_{app} = 2.610^{-12} \int_{banda} A \cdot \Delta R \cdot d\nu = 2.610^{-12} \int_{banda} \Delta R_n \cdot d\nu$

$f_{orient} = \frac{f_{app}}{f}$ and together the former equation the θ can be obtained.

IR spectroscopies

PM-IRRAS (Polarization modulation-infrared reflection absorption spectroscopy)

800-4000 cm-1

For interface analysis, monolayers floating on aqueous subphases or deposited on metal substrates.

Molecular orientation, adsorption/desorption in mono and multilayers, phase transitions, hydration/hydrogen bonding, surface reactions, chemical composition.

Applications: lipid films, membrane proteins, nanoparticles, surfactants.

Works that use spectroscopic techniques are Matsumoto 2003 and 2004, Cheng 2007, Haro 2005, Martín 2004, Martín 2007, del Caño 2003.

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Abstracts

UV–Vis Reflection–Absorption Spectroscopy at air–liquid interfaces
Carlos Rubia-Payá, Gustavo de Miguel, María T. Martín-Romero, Juan J. Giner-Casares , Luis Camacho

Advances in Colloid and Interface Science 225 (2015) 134–145

UV–Visible Reflection–Absorption Spectroscopy (UVRAS) technique is reviewed with a general perspective on fundamental and applications. UVRAS is formally identical to IR Reflection–Absorption Spectroscopy (IRRAS), and therefore, the methodology developed for this IR technique can be applied in the UV–visible region.
UVRAS can be applied to air–solid, air–liquid or liquid–liquid interfaces. This review focuses on the use of UVRAS for studying Langmuir monolayers.We introduce the theoretical framework for a successful understanding of the UVRAS data, andwe illustrate the usage of this data treatment to a previous study fromour group comprising an amphiphilic porphyrin. For ultrathin films with a thickness of few nm, UVRAS produces positive or negative bands when p-polarized radiation is used, depending on the incidence angle and the orientation of dipole absorption. UVRAS technique provides highly valuable information on tilt of chromophores at the air–liquid interface, and moreover allows the determination of optical parameters. We propose UVRAS as a powerful technique to investigate the in situ optical properties of Langmuir monolayers.

C.3 X-ray diffraction

The technique of grazing incidence X-ray diffraction (GIXD or GIXRD) and the technique of total reflection X-ray fluorescence have been applied for the determination of the structure of Langmuir monolayers [Stefaniu 2014; Bang 2000]. Other techniques are synchrotron GIXRD, X-ray reflectivity, neutron reflectivity [Penfold 2007], or X-ray scattering. The GIXD affords information on the positional order and molecular orientation, the network structure in the plane or the different phases of the monolayer. The X-ray reflectivity affords information on the nanostructure of the surface and interface, monolayer reactions, thickness or monolayer-counterions interactions.

The group of Möhwald and Brezesinski in Germany [Kaganer 1999], has used the X-ray diffraction techniques widely. Pignat 2007 studied the tilted phases of Langmuir films using GIXD.

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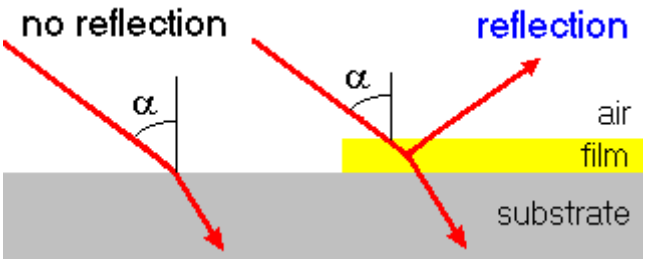
C.4 BAM, ellipsometry, Brewster angle autocorrelation spectroscopy

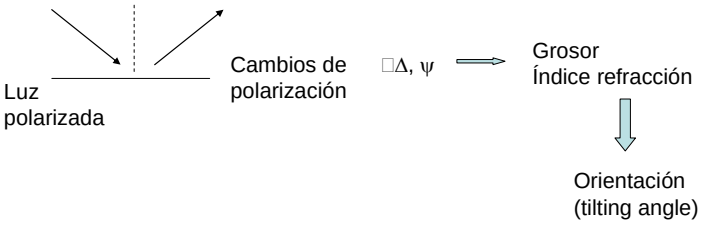
The Brewster Angle Microscopy (BAM) is an optical technique allowing the observation and detection of films of a few nanometers thick. The technique is very useful for the characterization of oil films on water or an aqueous environment, as is the case of lipids (fatty acids, phospholipids, acylglycerols) and other compounds, and for extension can be applied to the lipid layer of the tear film. Although the vertical resolution of BAM is in the nanometric scale, the lateral resolution is only in the micrometric scale.

The Brewster angle microscopy (BAM) uses the phenomenon of the annulation of reflection when a beam of p-polarized light reaches with a defined angle, the Brewster angle, on the water surface. Such angle is of 53º. When a film of an amphiphilic substance forms on the water surface, thus a certain reflection takes place and an optical image of the film can be obtained. With this technique, we get information on the 2D organization of the monolayer, topography of molecules at the interface air-water, on its heterogeneity and domain presence, phase coexistence, aggregation or collapse. Dendritic shapes in domains are related with an increase in anisotropy. BAM is sensible to differences in thickness of the layer as well as differences in orientations of the aliphatic chains in respect to the incidence plane. Works on BAM are those of Chen 2007, Wojciechowski 2006, Martín 2004 and 2007, Haro 2005. Roldan et al. [Roldan-Carmona 2012] review the BAM technique and the relevance of the polar headgroup.



If ellipsometry is used, thus the thickness of the film can be obtained. Works on ellipsometry are Wojciechowski 2006, Zeng 2008.

Elipsometria



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C.5 Fluorescence microscopy (FM), polarization fluorescence microscopy (PFM)

The technique of FM has been applied to observe domain structure in condensed monolayer phases [Qiu 1991]. This technique affords structural information, as domain formation, phases and its coexistence, and allows the study of dynamics of reactions and structural changes. The solubility of the fluorescent probe depends on the monolayer state, for that contrast are generated with the phase changes. Nevertheless, fluorescence results should be corroborated by other techniques.

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C.6 AFM and related SPM (FS, LFM). STM. SNOM

The technique of AFM and related (FS, LFM) has been applied by the author on several studies with LB films of a thiomacrocyclic compound [Oncins 2006; Torrent-Burgués 2006], fatty acids [Oncins 2008; Torrent-Burgués 2008; Torrent-Burgués 2011; Torrent-Burgués 2012a], calixarenes [Torrent-Burgués 2012b], phthalocyanines [Torrent-Burgués 2014a] and phospholipids [Hoyo 2012a; Hoyo 2012b; Hoyo 2013; Hoyo 2015a, b, c] and also to the study of contact lenses [Torrent-Burgués 2014b; Abadias 2015].

More works using AFM are those of Imae 2000, Ozaki 2007, Matsumoto 2003 and 2004, Qi 2011. Works using LFM (or FFM) are that of Matsumoto 2003. Works using NSOM (Near-field Scanning Optical Microscopy) are that of Flanders 2007.

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C.7 Electrochemical techniques

Applications of LB films as sensors is a field in exploration, but the la miniaturization of sensor devices, cost lowering and the conception of an only use, open the way to the research of nanometric films deposited on suitable supports (modified electrodes) [Petty 2002; Goldenberg 1994; Dong 2006; Monkman 2000; Valli 2005; Osada 2000; Mallouk 1994].

Cyclic voltammetry is a classical technique used to the study of confined species on electrodes [Compton 2007; Savéant 2006; Finklea 1996; Marcus 1985].

The impedances' technique or electrochemical impedance spectroscopy (EIS) [Bard 2001; Southampton 2001; Barsoukov 2005; Eckermann] is a powerful technique for analyzing the different elements of partial processes that occur on a global process. On an electrode o in a cell, the different components and processes can be assimilate to resistances and condensers of an electric circuit, building a circuit equivalent.

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Reversible cyclic Voltammetry (CV)

If the scanning velocity is sufficient low, thermodynamics' factors, more than the electron transfer velocity, lead the shape of the CV.

$$i = \frac{4 i_p e^{\theta}}{\left(1 + e^{\theta}\right)^2} \qquad i_p = \frac{n^2 F^2 A \Gamma v}{4RT} = \frac{nFAQv}{4RT} \qquad (Q = nF\Gamma)$$

$$\theta = \frac{nF\eta}{RT}$$

$$i_p \propto v \qquad surface\text{-}confined\ faradaic\ reactions$$

$$\Delta E_p = \left| E_p^a - E_p^c \right| \qquad E^{o'} = \frac{E_p^a + E_p^c}{2}$$

Formal potential of redox center is close to the value in solution.

Reversible ideal process:

$$\Delta E_p = \left| E_p^a - E_p^c \right| = 0 \qquad E^{0'} = E_p^a = E_p^c \qquad \Delta E_{fwhm} = 3.53\frac{RT}{nF} = \frac{90.6}{n} mV\,(25^o C)$$

Reversible no-ideal process:

$\Delta E_p \neq 0$ Oxidation and reduction peaks are close, no coincident, but independents of the scanning velocity, due to several factors: changes in the state of solvation, aggregation, or monolayer structure, with different states of oxidation of the center redox.

$\Delta E_{fwhm} \neq \frac{90.6}{n} mV\,(25^o C)$ due to: existence de several formal potentials (several environments of the redox centre); existence of a high concentration of redox centres, that interact; variations on the surface charge during the process that provoke changes on the surface potential.

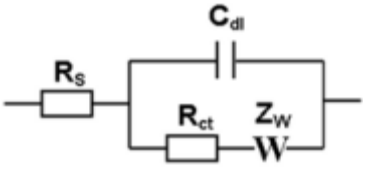
La double layer has effects on the CV reversible. In general, el peak wide and gets asymmetric. If the charge of the redox center or if the electrolyte concentration is high, the effect is lower. If the coverage of the redox center increases, the E_p moves to positive (if z +) or to negative values (if z -). The E_p depends on the concentration of electrolyte (perm selective membrane for counter ions).

Impedances

$Z=Z_{Re}-jZ_{Im}$

If the circuit is R—C then $Z=R-j/(\omega C)$ and representation of Z_{Im} vs Z_{Re} (Nyquist plot) is a vertical line.

In a circuit of Randles:



$$Z_w = \frac{\sigma}{\omega^{1/2}} + \frac{j}{\sigma\omega^{1/2}}$$ Impedance Warburg

$$\sigma = \frac{RT}{n^2F^2A\sqrt{2}}\left(\frac{1}{D_O^{1/2}C_O^*} + \frac{1}{D_R^{1/2}C_R^*}\right)$$

$R_S=R_\Omega$ Ohmic resistance of the solution.

When $\omega \rightarrow 0$ (impedance of Warburg important)

$Z_{Re}=R_{\Omega}+R_{ct}+ \sigma\omega^{-1/2}$

$Z_{Im}= \sigma\omega^{-1/2} + 2\sigma^2C_d$

$Z_{Im}=Z_{Re}- R_{\Omega}-R_{ct}+ 2\sigma^2C_d$ and the Nyquist plot is a straight line of unit slope.

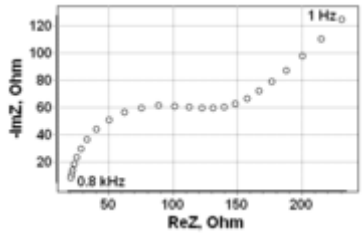
When $\omega \rightarrow \infty$ (Warburg no important)

$$Z_{\mathrm{Re}} = R_{\Omega} + \frac{R_{ct}}{1+\omega^2 C_d^2 R_{ct}^2}$$

$$Z_{\mathrm{Im}} = \frac{\omega C_d R_{ct}^2}{1+\omega^2 C_d^2 R_{ct}^2}$$

$$\left(Z_{\mathrm{Re}} - R_{\Omega} - \frac{R_{ct}}{2}\right)^2 + Z_{\mathrm{Im}}^2 = \left(\frac{R_{ct}}{2}\right)^2$$ and the Nyquist plot is a semicircle

In the general case, the Nyquist plot is a semicircle when $\omega \rightarrow \infty$ and a straight line when $\omega \rightarrow 0$.



An element de phase constant CPE is

$1/Z=T(i\omega)^p$ with p=1 for a pure capacitance, and p=0.5 for a diffusion.

C.8 Others (solar cells)

The self-assembling techniques and the formation of organized films have an important rol in the modern chemistry and technology, with potential applications in the design of nano-devices [Liu 2006; Huang 2004].

Between the possibilities for the design of components photoelectric, there is the possibility to use molecular systems that mimic photosynthesis [Sakomura 2002], using molecules photosensibles (S), and molecules acceptors (A) and donors (D) of electrons, constituent models for photosynthetic reaction centers (RC). It has been observed that using a pool of D, a simile of what succeed with plastoquinone (PQ) in the natural photosynthesis, a higher efficiency in the process is reached.

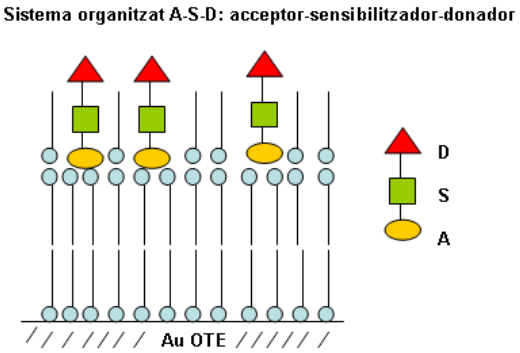


Figure. Model of a photosynthetic reaction center (RC) ASD

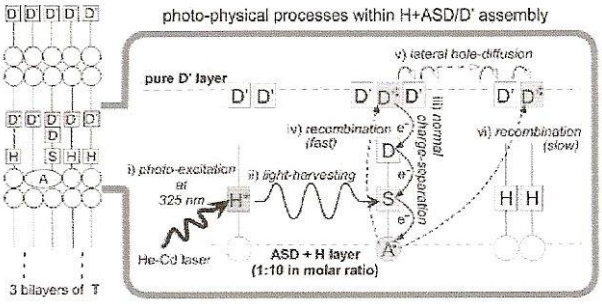


Figure. Processes in a model of a photosynthetic RC

To this goal, organized films with implied molecules in the processes should be obtained. These molecules, as occurs in natural systems, must have an amphiphilic character, with hydrocarbon chains (hydrophobic) and hydrophilic groups for anchorage, at the same time that reactive groups or phototosensibles, whether it does not coincide with the formers.

The formation of Langmuir-Blodgett(LB) films offer this possibility, sometimes in combination with the formation of SAM. With the LB technique multilayers of a unique molecule or alternate multilayers of different molecules can be obtained. Thus, molecules organize as function of its molecular structure and the conditions of preparation, arising different orientations, packings, phases and domains, which influence on the electron transfer processes and charge separation. Danos et al [Danos 2009] remarks the interest for studying the orientation effects of the layer of dyes in a DSSC on the efficiency of the charge separation, being convenient for that to use LB films. Furthermore, the no presence of a covalent bond between molecules and substrate in a LB, in contrast with a SAM, is an interesting factor to

consider since allows to study as this non-covalent character affects the electron transfer, a simile of what occurs in biological systems where the interactions usually are non-covalent.

Several aspects of the dye-sensitized solar cells (DSSC) are still not well understood. Complex interrelations between kinetic and thermodynamic factors hinders the full theoretical description of them. Relevant aspects are interfacial electron transfer, electron transport and trapping on the potential and current in the DSSC [Peter 2007]. With the goal to obtain high efficiencies on solar radiation, is important to incorporate the kinetic asymmetry inside the design of the DSSC, with a fast electron transfer in the side of the regenerator electrode and slow at the side of the transparent electrode.

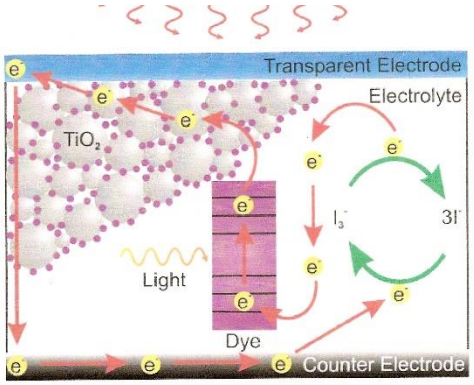


Figure. Schema of a dye sensitized solar cell (DSSC)

The Grätzel DSSC [Grätzel 2006] use a dye (a substance absorbent) adsorbed or deposited on the anode as material S.
Between the parameters to control of a cell there are the short-circuit current J_{CC} and the voltage in open circuit V_{CO}, as well as the efficiency η and the fill factor FF.
For the determination of the mechanism that occurs in the electrode or in the device of solar cell, is important to use the EIS technique.

FF: fill factor

$$FF = \frac{V_{PPM}\, j_{PPM}}{V_{CO}\, j_{CC}}$$

V_{CO}: fotovoltage in open-circuit

J_{CC}: current density in short-circuit

PPM: point of maximum potential

η: total efficiency of the cell

$$\eta = \frac{P_{\text{maxcel·la}}}{P_{llum\ \ incident}} = \frac{V_{PPM}\, j_{PPM}}{P_{llum\ \ incident}}$$

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D.- Studied systems

D.1 Fatty acids

The study of fatty acids have been the subject of a large number of works, the earliest ones have been referred in Petty 1996 and Ulman 1990. The author has shown the results of his studies in a report [Torrent 2011a].

The orientation of the chains of fatty acids or their salts has been studied by X-ray diffraction in Langmuir monolayers (Kenn 1991; Dutta 2002; Ropers 2002) as well as in LB films (Outka 1987). Other study by the author using SPM is [Oncins 2008], the study about oleamide is reported in [Torrent 2011b] and the study of a thiomacrociclic compound with alkyl chain is reported in [Torrent 2006]. The assembly of hybrid films AA/LDHs has been reported by Wang 2008. Fatty acid Langmuir films on Hg have been studied by Kraack 2004.

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D.2 Phospholipids

Biomembranes and biomimetic films: tear film

D.2.1 Biomembranes

The research in biomimetic membranes and films is an active filed, and many works appear each year. The author has published in the field, and in its works, many references are given. A report about the behavior of several mixed phospholipids is [Torrent 2004]

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D.2.2 Tear film

Recent works [Millar 2006; Tragoulias 2005; Mudgil 2006, 2008; Millar 2009; Flanagan 2008] have modelized the adsorption of some lacrimal proteins (lactoferrina, lipocalina, lisozima i Inmunoglobulina A) on the lipid layer of the tear film, observing that have surface activity and that could contribute to the descend of the surface tension of the tear film, and to its stability.

In the formation of the lipid layer, the presence of ions must be also considered [McCulley 2001] since its presence can stabilize the formation of the monolayer of polar lipids. The effect of anionic phospholipids (PS, PI, cardiolipina) should be investigated, since it has been pointed that its presence in small amounts is necessary [McCulley 2001].

A recent work has been done by the author on lípid-containing artificial tears [Torrent 2016]. Recent reports are those of Svitova 2016 and Millar 2015.

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D.3 Proteins, peptides, drugs and antimicrobials in lipidic monolayers

D.3.1 Proteins in lipidic monolayers

Langmuir and other surface techniques (Finot 2013) can be used to investigate the protein-lipid interactions by using model lipids like DHA and others. The experimental techniques for the study of molecular monolayers and films at the interface are now well stablished but the fields of application are expanding, and one of the most interesting is that of natural or biomimetic membranes (Kundu 2012). The Langmuir technique allows forming nanometric monolayers or films at the air-water interface and to study their characteristics, complemented with the Brewster angle microscopy (BAM), which gives nanometric vertical resolution but micrometric lateral resolution. More information at the nanometric scale can be obtained with the Atomic force microscopy (AFM) and other scanning probe related microscopies (SPM) as Force Spectroscopy (FS). The influence of insoluble substances on the lipidic films will be determined spreading mixed solutions of these substances with the lipids and recording and treating the isotherms cited formerly, and also from the BAM and SPM images. The influence of soluble substances on the lipidic films will be determined studying the insertion of these substances in the lipidic film. This is done obtaining first the film at a desired state, injecting the soluble substance in the subphase and recording the surface pressure or surface potential variations with time. At the same time, BAM images can be registered. Also, LB films can be obtained at different stages of the process and characterized using SPM techniques. The binding effect of ligands on proteins can be observed through the injection of the ligand in the subphase bellow the lipid-protein film, and recording the changes (using the biophysical techniques cited above) that the former induces on the later.
The structure and function of GPCRs are clearly affected by the lípid composition of the cell membrane (Lee 2008). There is a need to study the receptors in a lipid environment which can modulate the receptor’s function. Thus, one of the approaches of the project will be to investigate the effect of model lípid compounds on the protein stability and insertion into the membrane by means of biophysical methods (Calvez 2009; Ohtsuka 2005).
The insertion of rhodopsin in biomimetic membranes of DDHA-PC has been studied by Sanchez-Martin et al. [Sanchez 2013]. BAM images on the insertion of proteins in lipidic monolayers has been reported by the author [Torrent 2012]. In section B.7 more references can be found on the subject.

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D.3.2 Peptides, drugs and antimicrobials in lipidic monolayers

The field about the influence of antimicrobials, drugs and peptides on biomembranes is of great interest. The effect of chitosan on model membranes has been studied [Fernandes 2013, 2014]. Several works on the influence of peptides are reported with their abstracts.

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Abstracts on Peptides in phospholipid monolayers and membranes

A Langmuir Monolayer Study of the Interaction of E1(145-162) Hepatitis G Virus Peptide with Phospholipid Membranes

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J. Phys. Chem. B **2010,** *114*, 448–456

E1(145-162), a peptide corresponding to the structural protein E1 of the GB virus C, has been shown earlierto bind at pH 7.4 to vesicles containing 1,2-dimyiristoyl-*sn*-glycero-3-phospho-rac-(1-glycerol)] (DMPG) and1,2-dimyiristoyl-*sn*-glycero-3-phosphocholine (DMPC) phospholipids. To deepen the understanding of theinteraction of E1(145-162) with the lipid membrane, in this paper, we report a detailed study of the surfaceproperties of peptide, miscibility properties, and behavior of mixed monomolecular films of it and threephospholipids DMPG, DMPC, and 1-palmitoyl-2-oleoyl-*sn*-glycero-3-phosphocholine (POPG). These studieswere performed using the Langmuir balance by means of surface adsorption studies, surface pressure-meanmolecular area compression isotherms, and penetration kinetics. The Brewster angle microscopy (BAM) wasused to study the morphological properties of pure peptide and the mixed monolayers. The results show usthat the peptide showed surface activity concentration dependent when injected beneath a buffered solution(HEPES/NaCl, pH 7.4). This tendency to accumulate into the air/water interface confirms its potential capacityto interact with membranes; the higher penetration of peptide into phospholipids is attained when the monolayersare in the liquid expanded state and the lipids are charged negatively maybe due to its negative electriccharge that interacts with the positive global charge of the peptide sequence. The area per molecule values obtained suggested that the main arrangement structure for E1(145-162) peptide is the R-helical at the air-water interface that agreed with computational prediction calculations. Miscibility studies indicated thatmixtures become thermodynamically favored at low peptide molar fraction.

A study on the interactions of Aurein 2.5 with bacterial membranes

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Colloids and Surfaces B: Biointerfaces 68 (2009) 225–230

Aurein 2.5 (GLFDIVKKVVGAFGSL-NH2) is an uncharacterised antimicrobial peptide. At an air/water interface,it exhibited strong surface activity (maximal surface pressure 25mNm−1) and molecular areas consistent with the adoption of _-helical structure orientated either perpendicular (1.72 nm2 molecule−1) or parallel (3.6nm2 molecule−1) to the interface. Aurein 2.5 was strongly antibacterial, exhibiting a mínimum inhibitory concentration (MIC) of 30_M against *Bacillus subtilis* and *Escherichia coli*. The peptide induced maximal surface pressure changes of 9mNm−1 and5mNm−1, respectively, in monolayers mimicking membranes of these organisms whilst compression isotherm analysis of these monolayers showed _*G*Mix > 0, indicating destabilisation by Aurein 2.5. These combined data suggested that toxicity of the peptide to these organisms may involve membrane invasion *via* the use of oblique orientated _-helical structure. The peptide induced strong, comparable maximal surface changes in monolayers of DOPG (7.5mNm−1) and DOPE monolayers (6mNm−1) suggesting that the membrane interactions of Aurein 2.5 were driven by amphiphilicity rather than electrostatic interaction. Based on these data, it was suggested that the differing ability of Aurein 2.5 to insert into membranes of *B. subtilis* and *E. coli*was probablyrelated to membrane-based factors such as differences in lipid packing characteristics. The peptide was active against both sessile *E. coli* and *Staphylococcus aureus* with an MIC of 125_M. The broad-spectrum antibacterial activity and non-specific modes of membrane action used by Aurein 2.5 suggested use as an anti-biofilm agent such as in the decontamination of medical devices.

All-or-none membrane permeabilization by fengycin-type lipopeptides from Bacillus subtilis QST713

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Biochimica et Biophysica Acta 1808 (2011) 2000–2008

The fungicidal activity of Bacillus subtilis QST713 has been utilized for the highly effective and environmentally safe protection of crops against a variety of pathogens. It is based mainly on the production of cyclic lipopeptides of the fengycin (FEs), surfactin, and iturin families. The mixed population of native FEs forms micelles which solubilize individual FEs such as agrastatin 1 (AS1) that are otherwise rather insoluble on their own. Fluorescence lifetime-based calcein efflux measurements and cryo transmission electron microscopy show that these FEs show a unique scenario of membrane permeabilization. Poor miscibility of FEs with lipid probably promotes the formation of pores in 10% of the vesicles at only≈1 μM free FE and in 15% of the vesicles at 10 μM. We explain why this limited, all-or-none leakage could nevertheless account for the killing

of virtually all fungi whereas the same extent of graded vesicle leakage may be biologically irrelevant. Then, crystallization of AS1 and micellization of plipastatins cause a cut-off in leakage at 15% that might regulate the biological activity of FEs, protecting Bacillus and plant membranes. The fact that FE micelles solubilize only about 10 mol-% fluid lipid resembles the behavior of detergent resistance.

Effect of E1(64–81) hepatitis G peptide on the in vitro interaction of HIV-1 fusion peptide with membrane models

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Biochimica et Biophysica Acta 1808 (2011) 2178–2188

One way to gain information about the fusogenic potential of virus-derived synthetic peptides is to examine their interfacial properties and subsequently to study them in monolayers and bilayers. Here, we characterize the physicochemical surface properties of the peptide E1(64–81), whose sequence is AQLVGELGSLYGPLSVSA. This peptide is derived from the E1 structural protein of GBV-C/HGV which was previously shown to inhibit leakage of vesicular contents caused by the HIV-1 fusion peptide (HIV-1 FP). Mixed isotherms of E1(64–81) and HIV-1 FP were obtained and their Brewster angle microscopy (BAM) and atomic force microscopy (AFM) images showed that the peptide mixture forms a different structure that is not present in the pure peptide images. Studies with lipid monolayers (1,2-dimyristoyl-sn-glycero-3-[phospho-rac-(1-glycerol)] (DMPG) and 1,2-dipalmitoyl-sn-glycero-3-phospho-rac-(1-glycerol) (DPPG)) show that both peptides interact with all the lipids assayed but the effect that HIV-1 FP has on the monolayers is reduced in the presence of E1(64–81). Moreover, differential scanning calorimetry (DSC) experiments show the capacity of HIV-1 FP to modify the properties of the bilayer structure and the capacity of E1(64–81) to inhibit these modifications. Our results indicate that E1(64–81) interacts with HIV-1 FP to form a new structure, and that this may be the cause of the previously observed inhibition of the activity of HIV-1 FP by E1(64–81).

Fluorescence study of the dynamic interaction between E1 (145–162) sequence of hepatitis GB virus C and liposomes

Maria Jesús Sánchez-Martín & José Manuel Amigo & Montserrat Pujol & Isabel Haro & M. Asunción Alsina & M. Antonia Busquets
Anal Bioanal Chem (2009) 394:1003‑1010

The physicochemical characterization of the peptidesequence E1(145‑162) corresponding to the estructuralprotein E1 of the hepatitis G virus was done by studying itsinteraction with model membranes. Small unilamellar vesicles (SUVs) of dimyristoylphosphatidylglycerol or dimyristoylphosphatidylcholine were chosen as mimètic membranes. Peptide incorporation and location in the phospholipid bilayer was investigated by fluorescence anisotropy with SUVs labeled with diphenylhexatriene (DPH) or trimethylammonium‑DPH. The addition of the peptide E1 (145‑162) showed significant changes in the anisotropy values of the probe located at the air/water interface. These results indicate that the peptide E1(145‑162) preferably interacts with the lipid surface without penetrating inside the bilayer. A series of fluorescence experiments based on tryptophan peptide fluorescence were modeled by means of multivariate curve resolution-alternating least squares (MCRALS) algorithm to further study the peptide interaction with bilayers at different temperatures. The preliminary results obtained with MCR-ALS showed how the peptide concentration decay is directly linked to the appearance of a new specie, which corresponds to the lipid-peptide binding. These results provide useful information for the design of synthetic immunopeptides that can be incorporated into a liposomal system with potential to promote a direct delivery of the membrane-incorporated immunogen to the immunocompetent cells, thus increasing the immuno response from the host.

Interactions of daunorubicin with Langmuir–Blodgett thiolipid monolayers

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Electrochimica Acta 162 (2015) 45–52

Interactions of daunorubicin (DNR) with thiolipid membranes composed of 1,2-Dipalmitoyl-sn-Glycero-3-Phosphothioethanol (DPPTE) formed both at the air–water interface and transferred onto gold

electrodes were investigated. The drug incorporates into the DPPTE layers during their formation increasing the area per molecule and causing the fluidization of the layers. The interactions of DNR with preformed layers depend on the membrane organization and therefore the dominating type of the driving forces. For less organized layers both electrostatic and hydrophobic interactions take place, while for more condensed layers precompressed to higher surface pressures, electrostatic interactions seem to be prevailing. The drug adsorbs at the layer formed at the air–water interface, which prevents from its further penetration. The DPPTE layers were transferred onto gold electrodes by means of Langmuir–Blodgett and self-assembly method. Cyclic voltammetry experiments revealed that DNR is more easily incorporated into LB layers supported on solid substrate than into SAMs, since the former tend to be less compact and hydrophobic interactions between the acyl chains of the thiolipid and hydrophobic anthraquinone part of DNR is facilitated. The influence of pH changes of the supporting electrolyte on the electrode processes of DNR incorporated into the layers was also investigated in order to verify if the lipid environment affects the mechanism of electron transfer.

Investigations of antimicrobial peptides in planar film systems

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Biochimica et Biophysica Acta 1758 (2006) 1393–1407

Planar systems – monolayers and films – constitute a useful platform for studying membrane-active peptides. Here, we summarize variedapproaches for studying peptide organization and peptide–lipid interactions at the air/water interface, and focus on three representativeantimicrobial membrane-associated peptides—alamethicin, gramicidin, and valinomycin. Experimental data, specifically surface pressure/areaisotherms and Brewster angle microscopy images, provided information on peptide association and the effects of the lipid monolayers on peptidesurface organization. In general, film analysis emphasized the effects of lipid layers in promoting peptide association and aggregation at the air/water interface. Importantly, the data demonstrated that in many cases peptide domains are phase-separated within the phospholipid monolayers,suggesting that this behavior contributes to the biological actions of membrane-active antimicrobial peptides.

Langmuir monolayers as models to study processes at membrane surfaces

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Advances in Colloid and Interface Science 208 (2014) 197–213

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 amphiphilicmonolayers 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 reviewfocuses 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 aswell as the competing adsorption of ions at charged interfaces. The influence ofmodified nanoparticles onmodel membranes can be clearly determined. In this review, the relevance and utility of Langmuirmonolayers as suitablemodels to study physical and chemical interactions at membrane surfaces are clearly demonstrated.

Primary Amphipathic Cell-Penetrating Peptides: Structural Requirements and Interactions with Model Membranes†

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Biochemistry **2004,** *43,* 7698-7706

To identify rules for the design of efficient cell-penetrating peptides that deliver therapeuticagents into subcellular compartments, we compared the properties of two closely related primaryamphipathic peptides that mainly differ by their conformational state. On the basis of a peptide Pâ thatis nonstructured in water and that promotes efficient cellular uptake of nucleic acids through noncovalentassociation, we have designed a peptide [PR] that is predicted to adopt a helical conformation. We showthat [Pâ] undergoes a lipid-induced conformational transition into a sheet structure, while [PR] remainshelical. Penetration experiments show that both peptides can spontaneously insert into phospholipidmembranes. Analysis of compression isotherms indicates that both peptides interact with phospholipidsin the liquid expanded and liquid condensed states. AFM observations reveal that the peptides stronglydisrupt the lipid organization of the monolayers and that the conformational state can influence the uptakeby model membranes.

Study of the inhibition capacity of an 18-mer peptide domain of GBV-C virus on gp41-FP HIV-1 activity

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Biochimica et Biophysica Acta 1808 (2011) 1567–1573

The peptide sequence (175–192) RFPFHRCGAGPKLTKDLE (P59) of the E2 envelope protein ofGBvirus C (GBV-C) has
been proved to decrease cellular membrane fusion and interfere with the HIV-1 infectivity in a dose-dependent manner. Based on these previous results, the main objective of this study was to deepen in the physicochemical aspects involved in this interaction. First,we analyzed the surface activity of P59 at the air–water interface as well as its interaction with zwitterionic or negatively charged lipidmonolayers. Then we performed the same experiments with mixtures of P59/gp41-FP. Studies on lipid monolayers helped us to understand the lipid–peptide interaction and the influence of phospholipids on peptide penetration into lipid media. On another hand, studies with lipid bilayers showed that P59 decreased gp41-FP binding to anionic Large Unilamellar Vesicles. Results can be attributed to the differences in morphology of the peptides, as observed by Atomic ForceMicroscopy. When P59 and gp41-FP were incubated together, annular structures of about 200 nm in diameter appeared on the mica surface, thus indicating a peptide–peptide interaction. All these results confirm the gp41-FP–P59 interaction and thus support the hypothesis that gp41-FP is inhibited by P59.

Surface Active Properties of Amphiphilic Sequential Isopeptides: Comparison Between a-Helical andb-Sheet Conformations

Re´ gine Maget-Dana Dominique Lelie` vre Andre´ Brack

Biopolymers, Vol. 49, 415–423 (1999)

Poly(Leu–Lys–Lys–Leu) and poly(Leu–Lys) are sequential amphiphilic peptide isomers that adopt respectively an a*-helical conformation and a* b*-sheet structure in saline solutions and at the air/water interface. The surface active properties of LKKL and LK sequential isopeptides containing 16, 20, and* n *residues have been compared in order to evaluate the contributions of the* a*-helical and* b*-sheet conformations. Both have a natural tendency to spread at the surface of a saline solution and the values of the equilibrium spreading pressure* pe *lie in the same range. When dissolved in a saline solution,* a*-helical peptides diffuse faster and adsorb faster at the interface than the* b*-sheet isomers. From the compression isotherms of LKKL and LK peptide monolayers it is possible to extract parameters that characterize the behavior of* a*-helical and* b*-sheet conformations:* b*-sheet peptide monolayers are more stable and less compressible than the monolayers formed with the* a*-helical isomers. The LK peptides differ also by their high degree of selfassociation at the air/water interface.*

Surface behaviour and peptide–lipid interactions of the antibiotic peptides, Maculatin and Citropin

Ernesto E. Ambroggio[a], Frances Separovic[b], John Bowie[c], Gerardo D. Fidelio[a,*]

Biochimica et Biophysica Acta 1664 (2004) 31– 37

Surface behaviour of Maculatin 1.1 and Citropin 1.1 antibiotic peptides have been studied using the Langmuir monolayer technique inorder to understand the peptide–membrane interaction proposed as critical for cellular lysis. Both peptides have a spontaneous adsorption atthe air–water interface, reaching surface potentials similar to those obtained by direct spreading. Collapse pressures (P_c, stability to lateralcompression), molecular areas at maximal packing and surface potentials (DV) obtained from compression isotherms of both pure peptidemonolayers are characteristic of peptides adopting mainly a-helical structure at the interface. The stability of Maculatin monolayers dependedon the subphase and increased when pH was raised. In an alkaline environment, Maculatin exhibits a molecular reorganization showing areproducible discontinuity in the P–A compression isotherm. Both peptides in lipid films with the zwitterionic palmitoyl-oleoylphosphatidylcholine(POPC) showed an immiscible behaviour at all lipid–peptide proportions studied. By contrast, in films with the anionicpalmitoyl-oleoyl-phosphatidylglycerol (POPG), the peptides showed miscible behaviour when the peptides represented less than 50% of total surface area. Additional penetration experiments also demonstrated that both peptides better interact with POPG compared with POPCmonolayers. This lipid preference is discussed as a possible explanation of their antibiotic properties.

The importance of bacterial membrane composition in the structure and function of aurein 2.2 and selected variants

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Biochimica et Biophysica Acta 1808 (2011) 622–633

For cationic antimicrobial peptides to become useful therapeutic agents, it is important to understand their mechanism of action. To obtain high resolution data, this involves studying the structure and membrane interaction of these peptides in tractable model bacterial membranes rather than directly utilizing more complex bacterial surfaces. A number of lipid mixtures have been used as bacterial mimetics, including a range of lipid headgroups, and different ratios of neutral to negatively charged headgroups. Here we examine how the structure and membrane interaction of aurein 2.2 and some of its variants depend on the choice of lipids, and how these models correlate with activity data in intact bacteria (MICs, membrane depolarization). Specifically, we investigated the structure and membrane interaction of aurein 2.2 and aurein 2.3 in 1:1 cardiolipin/1-palmitoyl-2-oleoyl-sn-glycero-3-phospho-(1′-rac-glycerol) (CL/POPG) (mol/mol), as an alternative to 1:1 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine(POPC)/POPG and a potential model for Gram positive bacteria such as S. aureus. The structure and membrane interaction of aurein 2.2, aurein 2.3, and five variants of aurein 2.2 were also investigated in 1:1 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphoethanolamine (POPE)/POPG (mol/mol) lipids as a possible model for other Gram positive bacteria, such as Bacillus cereus. Solution circular dichroism (CD) results demonstrated that the aurein peptides adopted α-helical structure in all lipid membranes examined, but demonstrated a greater helical content in the presence of POPE/POPG membranes. Oriented CD and 31P NMR results showed that the aurein peptides had similar membrane insertion profiles and headgroup disordering effects on POPC/POPG and CL/POPG bilayers, but demonstrated reduced membrane insertion and decreased headgroup disordering on mixing with POPE/POPG bilayers at low peptide concentrations. Since the aurein peptides behaved very differently in POPE/POPG membrane, minimal inhibitory concentrations (MICs) of the aurein peptides in B. cereus strain C737 were determined. The MIC results indicated that all aurein peptides are significantly less active against B. cereus than against S. aureus and S. epidermidis. Overall, the data suggest that it is important to use a relevant model for bacterial membranes to gain insight into the mode of action of a given antimicrobial peptide in specific bacteria.

The molecular area characteristics of the HIV-1 gp41-fusion peptide at the airrwater interface. Effect of pH

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Biochimica et Biophysica Acta 1326 _1997. 257–264

The putative fusion peptide of HIV-1 is a highly surface active substance. Relevant measurements with the Langmuirmonolayer technique have been carried out for a broad range of the pH in the aqueous subphase. The data are processedtowards a quantitative analysis of the partitioning equilibrium between the interfacial and aqueous moieties. Our resultsreveal a pronounced decrease of the surface area per peptide molecule upon monolayer compression. This phenomenoncould be interpreted in terms of an orientational transition experienced by an a-helical peptide structure. The arearequirements at any fixed lateral pressure pass through a distinct minimum at a pH of 5.5 _"0.5.. Such an apparentisoelectric point was confirmed by isoelectric focusing of peptide aggregates. Accordingly a drastic drop of the pK-values ofthe two basic amino acid residues in comparison with an aqueous medium is indicated. It can be readily

explained based onan inherent decrease of the effective dielectric constant. The observed low pH in favor of an enhanced surface affinity of thepeptide may be a significant factor concerning its function as a fusion promoting agent.

The monolayer technique: a potent tool for studying the interfacial properties of antimicrobial and membrane-lytic peptides and their interactions with lipid membranes

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Biochimica et Biophysica Acta 1462 (1999) 109^140

Erudites of the antiquity already knew the calming effect of oil films on the sea waves. But one had to wait until 1774 toread the first scientific report on oil films from B. Franklin and again 1878 to learn the thermodynamic analysis onadsorption developed by J. Gibbs. Then, in 1891, Agnes Pockels described a technique to manipulate oil films by usingbarriers. Finally, in 1917, I. Langmuir introduced the experimental and theoretical modern concepts on insoluble monolayers. Since that time, and because it has been found to provide invaluable information at the molecular scale, themonolayer technique has been more and more extensively used, and, during the past decade, an explosive increase in thenumber of publications has occurred. Over the same period, considerable and ever-increasing interest in the antimicrobialpeptides of various plants, bacteria, insects, amphibians and mammals has grown. Because many of these antimicrobial peptides act at the cell membrane level, the monolayer technique is entirely suitable for studying their physicochemical andbiological properties. This review describes monolayer experiments performed with some of these antimicrobial peptides,especially gramicidin A, melittin, cardiotoxins and defensin A. After giving a few basic notions of surface chemistry, thesurface-active properties of these peptides and their behavior when they are arranged in monomolecular films are reported and discussed in relation to their tridimensional structure and their amphipathic character. The penetration of theseantimicrobial peptides into phospholipid monolayer model membranes, as well as their interactions with lipids in mixedfilms, are also emphasized.

D.4 Compounds for sensor applications. Macrocyclic compounds. Redox centers.

LB films for sensor applications is an emerging field, but the miniaturization of the devices, the lowering costs and the tendency to single use, open the way to investigate nanometric films deposited on substrates (modified electrodes) [Petty 2002; Goldenberg 1994; Dong 2006; Monkman 2000; Valli 2005; Osada 2000; Mallouk 1994; Chu 2006; Liu 2007; Kato 2005].

The author on several systems has done electrochemical studies of LB films: a thiomacrocycle compound [Marques 2006; Guaus 2007; Guaus 2008; Guaus 2009], biomolecules such as ubiquinone [Hoyo 2012] and plastoquinone [Hoyo 2015a, b, c] and phthalocyanines [Torrent-Burgués 2014]. Phthalocyanine LB films have also been studied by Gu 2005, Bilgicli 20120, Huo 2000.

Other works devoted to macrocyclic compounds are [Torrent 2006, 2008, 2012a, 2012b], Heck 2002 and Badis 2004.

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D.5 Compounds for optoelectronic applications and solar cells

LB films for photovoltaic applications have been investigated or studied using several substances, such as derivatives of C_{60} [Jin 1999; Tang 2006; Baena 2004], chlorophylls [Desarmeaux 1993, Choi 2001], derivatives of porphyrins of zinc [Desarmeaux 1993], derivatives of carbocianine [Danos 2008; Gao 2008], or merocianine [Kato 2002], melanines [Meredith 2005] or alternate multilayers [Sakomura 2004]. Films of viologens [Cea 2006; Martin 2004] or porphyrins [Perez 2004; De Miguel 2007; Martin 2002] have also been studied. Films of azoderivatives have been reported by Haro 2008, Crusats 2004, Zong 2005, Yamamoto 2007, Giner 2011, Pulido 2010.

Recently the LB technique has been applied to the deposition on ITO of a nanocomposite based on CdSe nanoparticles covered by a thiofene electroactive polymer [Goodman 2009]. Other dyes, such as those based on rhodamine condensed on triphenylamine, able to polymerize and with a high efficiency, could be used. A Ru-biphosphine complex has been studied by Wohnrath 2005.

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