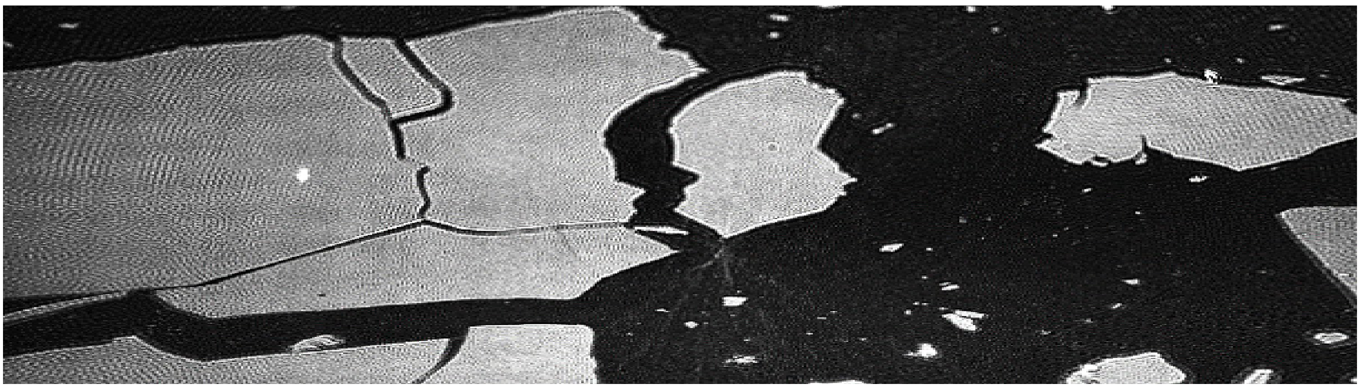
Overview

Brewster Angle Microscopy

Inspect the Quality of the Floating Langmuir Layer



Different materials such as lipids, nanoparticles, polymers, proteins, and many other biomolecules can form a monolayer, called Langmuir (L) layer, on air-water interphase.

These floating monolayers are used to study various different phenomena from biological membranes and their interactions with drugs and toxic compounds to the stability of the oil-water emulsions.

In addition, the monolayers can be deposited to the solid substrates with a Langmuir-Blodgett (LB) deposition technique. This has been especially utilized with different types of nanomaterial thin films, including graphene oxide and nanoparticles, finding applications in various fields such as displays, sensors, and energy storage.

One advantages of the L & LB method is the possibility to check the quality of the floating monolayer [1]. The technique called Brewster angle microscopy (BAM) is used due to its multiple benefits discussed later in this overview.

Brewster Angle Microscopy

When a light beam hits a surface, it usually reflects from it. If a p-polarized light beam is directed on a clean surface at a unique angle, no reflection occurs. If the properties of the interface change, the reflection will happen. This behavior is explained by Brewster's law which describes the use of

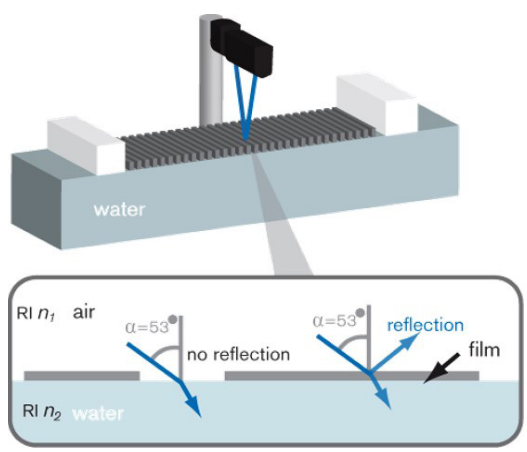


Figure 1: Working principle of Brewster angle microscopy (BAM)

Application	Thin film components	Main findings	Reference
Liquid crystals for displays	Polyhedral oligometric silesquioxanes (POSS) + liquid crystal (LC) 4-octyloxy-4-cyanobiphenyl	New approach for fabrication of LC-based materials. First time to demonstrate hybrid POSS molecules to be mixed with LC.	[5]
Photoluminescence	CdSe quantum dot (QD) + anhydride maleic polymer derivates + gemini surfactant ethylbis	The results together with the previous findings confirm the ability of the LB method to modulate the self-assembly of QDs.	[6]
Transparent conductive film for displays	Graphene oxide	Transfer of graphene oxide sheets onto flexible PET substrate is possible by soft printing method.	[7]
Sensors for antioxidant detection in food industry	Gold nanoparticle + lutetium bisphthalocyanine + dimethyldioctadecylammonium	Thin film components have synergetic effect in terms of improving electrocatalysis for the detection of hydroquinone.	[8]
Advanced, sustainable material development	Cellulose nanofibers (CNF) and CNF/ poly(N-dodecyl acrylamide) (pDDA)	With the help of amphiphilic polymer and formic acid a monolayers with excellent stability were produced and transferred onto various substrates.	[9]
Biosensor	Dipalmitoylphosphatidylcholine (DPPC) + Asparaginase	Mixed enzyme - DPPC Langmuir monolayers could be formed at the air -water interface. The thin film could be transferred on the solid support with LB method. Enzyme activity of mixed layer was lower than in homogeneous environment but presented enhanced stability after 30 days thus demonstrating that the system is suitable for sensing asparagine.	[10]

Table 1: List of selected applications where Langmuir-Blodgett together with Brewster angle microscopy has been utilized

the Brewster angle (α) of the optical media with a refractive index of n. The principle of using the Brewster angle to obtain an image of a monolayer on the water surface is illustrated in Figure 1.

Brewster angle microscopy was first introduced in 1991 [2,3]. Since its introduction, it has become the standard technique for the imaging of thin films on liquid surfaces. When combined with a Langmuir or Langmuir-Blodgett method, it can be used to inspect the quality of the formed (floating) monolayer. Brewster angle microscopy has revolutionized visualization of monolayers at interfaces by allowing label-free real-time images of fully hydrated films. Interactions that result from only minor changes in the area-surface pressure isotherm still result in significant changes in the lateral film organization. The Brewster angle microscopy is thus able to give additional insight to understand the impacts of various parameters (such as the incorporation of nanoparticles or macromolecule, temperature, subphase composition) on monolayer formation [4].

Key Application Areas

Lipid monolayers and molecular interactions. Langmuir films of lipid monolayers are often used as model structures of cell membranes. Brewster angle microscopy images at characteristic phase transitions of the surface pressure - area isotherm give valuable information on the structural and orientational changes in the monolayer. The published data includes BAM images of molecular interactions, lipids in different ionic environments and nanoparticle interactions. Since BAM allows for direct observation of lipid monolayers during compression, it is especially valuable in the imaging of tear fluids and biological liquids [4].

Polymer and nanoparticle monolayers. The Langmuir technique has been shown to be an effective way for fabricating single particle thick layers of lipids, polymers and nanoparticles on liquid surfaces. A Langmuir film can be transferred onto the desired substrate, creating new possibilities for fabricating nanoscale layers and functional surfaces on various materials. Recently, Brewster angle microscopy has been used for finding the optimized transfer conditions of metal nanoparticles and graphene oxide [7, 8].

Petroleum industry. There is an increased interest in understanding the properties and behaviour of asphaltenes and other surface active materials in crude oil. Langmuir troughs are excellent tools for examining the layer formation of such water insoluble surfactants. Brewster angle microscopy has been used to study the layer formation properties of asphaltenes and model compounds.

Case study 1: Graphene Oxide Sheets at Interfaces

Chemical exfoliation of graphite is recognized as one of the most potential methods for producing graphene on an industrial scale. The result of the exfoliation process is graphene oxide, which is known to disperse well in water due to its ionizable –COOH groups. However, the basal plane of graphene is essentially a network of hydrophobic benzene rings. In the following study, the properties of graphene oxide were investigated by examining the amphiphilic nature of the molecule in a Langmuir trough [11].

Methods

Synthesized graphene oxide was examined using a Langmuir trough and Brewster angle microscope. For the CO_2 flotation experiment, graphene oxide was dispersed in carbonated water. The concentration

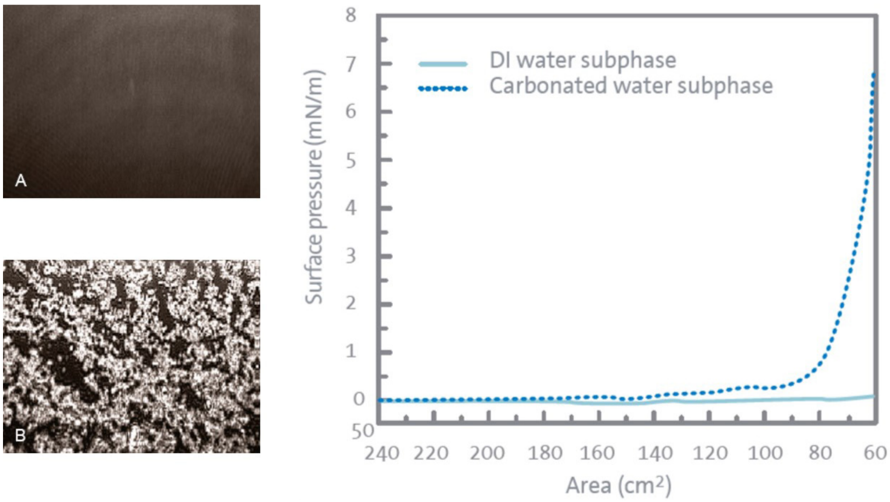


Figure 2: (Left) In situ BAM images of A) a fresly prepared graphene oxide - water solution and B) graphene oxide with flotation. (right) The isotherm of graphene oxide with water subphase and carbonated water subphase. With permission from J. Am. Chem. Soc. 2010, 132 (23), pp 8181-8186. Copyright 2010 American chemical society.

of the solution was optimized for visual observation of the floating graphene oxide sheets.

Results and Discussion

The authors examined the surface activity of graphene oxide using Brewster angle microscopy. If graphene oxide is surface active, the water surface should be covered by a layer of graphene oxide sheets. Figure 2A displays the in-situ BAM image of a freshly prepared graphene oxide - water solution. The image reveals very little surface-active material. After a few hours, graphene oxide sheets started to appear. This was attributed to the slow diffusion of micrometer-sized graphene oxide sheets. To accelerate the migration of graphene oxide to the surface, the authors designed a flotation process using carbonated water. In the process, the graphene oxide sheets adhered to the rising CO_2 bubbles and were transported to the air-water interface. To facilitate the observation, the floating materials were concentrated by compressing the barriers in a Langmuir trough. On the right side of Figure 2 the isotherms of graphene oxide with and without the flotation are presented. It can be seen that the flotation increased surface pressure. At the same time, the Brewster angle microscopy image (Figure 2B) showed a large amount of material on the surface after the flotation process.

Conclusion

Langmuir isotherms and Brewster angle microscopy can be used to examine the properties and observe the formation of graphene oxide sheets at air-water interfaces. The study shows how monolayer imaging can be used to improve solution processing and to help to find the optimal deposition parameters for graphene oxide materials.

Case study 2: Deposition of Magnetic Fe_3O_4 Nanoparticles

Magnetic nanoparticles of iron oxide have gained interest as magnetic storage media. Langmuir-Blodgett technique is one of the most promising methods to deposit magnetic nanoparticles because it enables fine control of the thickness and homogeneity of the monolayer, and ease for multilayer deposition. [12].

Methods

The monolayer of Fe_3O_4 nanoparticles at the air/water interface was obtained in a Langmuir trough. Wilhelmy plate microbalance was used to monitor the surface pressure during the isotherm compression. The monolayer was visualized in situ by using the Brewster angle microscopy. Images at different stages of monolayer compression were taken.

Results and Discussion

The iron oxide nanoparticle isotherm is shown in Figure 3 together with the BAM images taken at different points of compression. At surface pressure of 2 mN/m, the nanoparticles can be considered to be still at the gas phase. With BAM, this is shown as a completely black image (A) since there is no reflection at the air-water interface. This is due to the long distance between the nanoparticles. At 20 mN/m (B), the nanoparticles are already somewhat compressed, and islands of nanoparticles appear in the image. At surface pressure of 35 m/m (C), the nanoparticle monolayer is formed. The deposition of nanoparticles is done at this surface pressure. As the compression is continued, the nanoparticle monolayer will collapse which is again seen in the BAM image as separated nanoparticle clusters (D).

Conclusion

Langmuir-Blodgett technique offers a highly controlled method for nanoparticle monolayer and multilayer deposition. Brewster angle microscopy is used to determine the optimum surface pressure for monolayer deposition.

Case study 3: Oleanolic Acid - Human Serum Albumin Complexes for Biosensing Applications

Oleanolic acids (OLA) is widely known for its anti-inflammatory, anti-viral and anti-diabetic properties, among others. Its bioavailability due to low solubility and dissolution rates is however low. It has been anticipated that the bioavailability can be improved with the help of carrier protein, in this case human serum albumin (HSA). A comprehensive study of oleanolic acid behavior in the presence of its potential carrier, HSA, using the molecular-scale approach based on the Langmuir film technique is presented [13].

Methods

The monolayers of oleanolic acid were formed on water subphase using the Langmuir trough. To study the effect of human serum albumin on the oleanolic acid monolayer, the sample of HSA was injected on the subphase below the monolayer at the desired monolayer surface pressure. The Brewster angle microscope was utilized to visualize the monolayer with and without human serum albumin. The monolayers were deposited on mica for further wettability, surface free energy and topography studies.

Results and Discussion

The results from the isotherm and BAM experiments can be seen in Figure 4. It is clearly seen that the presence of human serum albumin in the subphase changes the isotherm course drastically. There is also a clear impact of the protein concentration on the properties of the interfacial layer. As human serum albumin is also known to be surface active and forms a monolayer at air-water interface. This means that both HSA and OLA may compete for the interfacial area in order to arrange the most thermodynamically favored orientation.

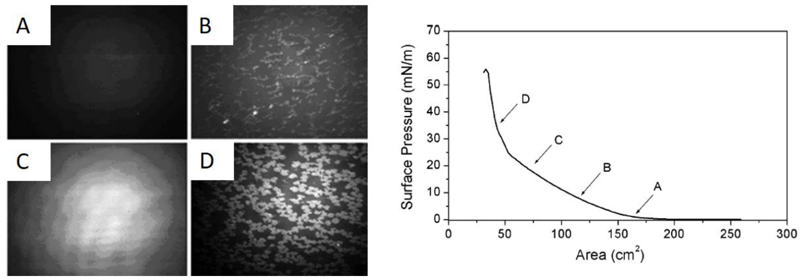


Figure 3: Iron oxide nanoparticle isotherm and Brewster angle microscopy images at different surface pressures. With permission from J. Phys. Chem. B 2007, 111(31), 9288-9293. Copyright 2007 American Chemical Society.

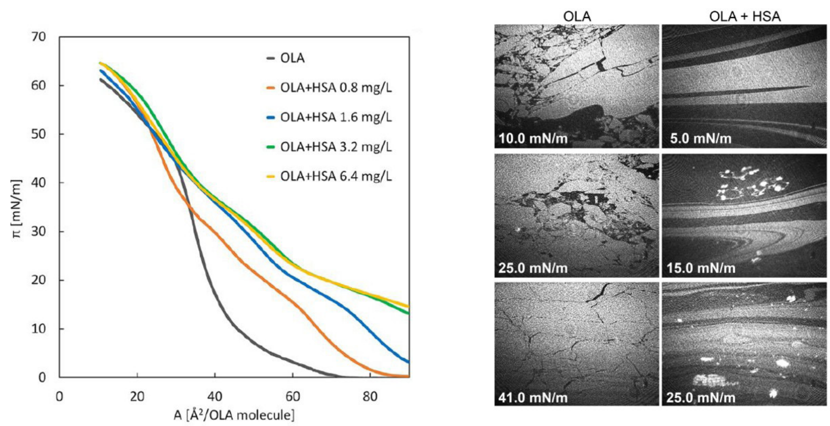


Figure 4: Iron oxide nanoparticle isotherm and Brewster angle microscopy images at different surface pressures. Adapted with permission from Langmuir, just accepted manuscript 2020 Copyright 2020 American Chemical Society. [13]

To determine the morphology of the monolayers, BAM images were captured during the compression of pure OLA film and with the presence of 0.8 mg/l of HSA in the subphase. BAM images reveal a fluidizing effect of the protein on the OLA monolayer especially at 5 mN/m surface pressure.

Conclusion

A detailed physicochemical characterization reveals that oleanolic acid is bound by the adsorbed human serum albumin. It was also concluded that the bounding was irreversible. It is thus concluded that serum albumin may have a significant impact on distribution of oleanolic acid in a human body.

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