Brazilian Journal of Physics, vol. 22, no. 2, June, *1992*

Langmuir-Blodgett Films - Properties and Possible Applications

Osvaldo N. Oliveira Jr.
Instituto de Física e Química de São Carlos, Universidade de São Paulo
Caixa Postal 369, São Carlos, 13560, S.P. - Brasil

Received February 5, 1992

Langmuir-Blodgett (LB) films are ultra thin organic films obtained from the successive deposition of monolayers from the water surface onto a solid substrate. They possess interesting properties such as controllable thickness, surface uniformity and a high degree of orientational order, which make them potential candidates for application in electronic devices and sensors.

I. Introduction

One of the most demanding challenges in materials science today is the development of new materials with tailored properties to suit specific applications. The ultimate goal is the engineering of molecules which would be the building blocks for sensors and electronic devices, in the emerging field of molecular electronics. Such ambitious endeavors will only be achieved if experimental techniques are available which allow the assembling of molecules to form two or three dimensional structures. The Langmuir-Blodgett (LB) technology is perhaps the most promising of such techniques because it allows the fabrication of ultra thin, highly ordered organic films. In the LB method, a one molecule thick layer (Langmuir monolayer) spread at the air/water interface is transferred onto a solid substrate, a process that can be repeated several times with the same substrate to form multilayer films.

In this paper, several aspects of LB films and Langmuir monolayers will be reviewed. In Section II, following a brief historical note the experimental procedures for the film fabrication are described. The most important LB forming materials are discussed in Section III, while Section IV deals with the characterization of Langmuir monolayers as well as LB deposited films. The many possible applications of LB films are discussed in Section V in which a special subsection has been provided for introducing the topic of molecular electronics. Section VI closes the paper with the state of the art. Because literature on LB films and Langmuir monolayers is abundant (see refs.[1-12]), only a few papers will be listed here which may be starting points for those who wish to further their knowledge in the field.

II. Langmuir Monolayer and LB Film Fabrication

Insoluble monolayers are formed on the surface of a clean liquid which has a high surface tension (e.g. water) by the spreading of insoluble, non-volatile substances over the surface. Spreading occurs when the molecules of the substance, generally possessing a hydrophilic head and a long hydrophobic tail (see Section 111), are attracted to the water more than they attract each other. A one molecule thick film, termed Langmuir monolayer, is formed provided that the area of the surface is sufficient to accommodate all the molecules spread. The history of insoluble monolayers can be traced back to ancient times, for Aristotle in ancient Greece was reported to have noted the calming effect of oil on a water surface. Following studies from the end of last century by Agnes Pockels and Lord Rayleigh - the latter was the first to suggest that the oil film could be one molecule thick - Langmuir in 1917 introduced new theoretical concepts and experimental methods which were to prove of major importance to the study of these films. Today, the subject of insoluble monolayers at the air/water interface is a well-established topic addressed in the majority of texts of Physical Chemistry of Surfaces.

The equipment used for the production of Langmuir monolayers and/or LB deposited films has become traditionally referred to as a Langmuir trough (Figure 1). Basically it consists of a container which holds a liquid subphase on which the monolayer is spread, barriers to enable film compression and other measuring apparatus for monolayer characterization. Included in these are a surface pressure sensor and a position detector attached to the barriers to measure the surface area of the film. The container must be made from an inert material such as Teflon which does not contaminate the aqueous subphase. The trough and barrier arrangement must

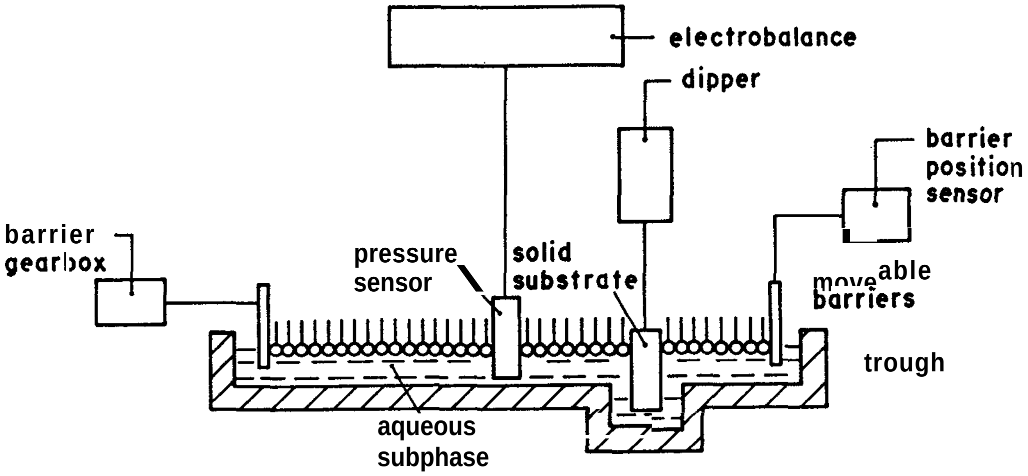

Figure 1: Langmuir trough. The monolayer is spread on the surface of an aqueous subphase, and then compressed by means of moveable barriers. A pressure sensor/electrobalance arrangement measures the surface pressure, and the area per molecule is obtained from the total area given by the barrier position sensor. The dipper controls the immersion and withdrawal of the solid substrate for monolayer deposition.

provide a means for constraining and compressing the monolayer.

The material is dissolved in an appropriate organic, volatile solvent (e.g. chloroform) and dispensed onto the surface of an aqueous subphase. The solvent evaporates within a short time and the molecules then left spread over the whole water surface. The monomolecular layer, so-called Langmuir monolayer, is compressed until the molecules are aligned in a regular arrangement. Langmuir-Blodgett films are fabricated by immersing a clean substrate into the monolayer-covered aqueous subphase, as illustrated in Figure 2. Repeated dippings of the substrate result in the deposition of a multilayer structure, which in some cases can be up to hundreds of monolayers. A good deposition will depend not only on the nature of the monolayer molecules themselves, but also on subphase conditions such as pH, temperature, and ionic contents, on the speed of immersion and withdrawal of the substrate (dipping speed) and on whether the substrate is hydrophilic or hydrophobic.

LB films usually deposit in a symmetrical mode, referred to as Y-type films, in which the molecules in successive layers adopt a head-to-head and tail-to-tail arrangement as shown in Figure 3a. In the Y-type deposition on a hydrophilic substrate, a monolayer is not picked up by the substrate during the first immersion of the substrate (downstroke), but in subsequent trips deposition always occurs both in the downstrokes as well as in the upstrokes. There are two other types of deposition, the so-called X and Z-types shown schematically in Figures 3b and 3c, where deposition occurs only in the downstrokes or in the upstrokes, respectively. Super-lattices can also be built in which monolayers of different materials are deposited on the same substrate.

In addition to the commonly used vertical dipping method described above, deposition can also be made by surface contact using the horizontal lifting method. Almost any type of solid substrate can be employed in LB deposition, though deposition will only be successful if a number of requirements are met. The most used materials are glass slides, or metal evaporated-glass slides and semiconductor wafers. Prior to deposition, substrates must be thoroughly cleaned and usually rendered either highly hydrophilic or hydrophobic depending on the specific type of deposition that is aimed at.

It is essential that the most stringent cleaning procedures are adopted in the LB work. The Langmuir trough and its accessories need to be free of surface-active materials and greases. Glassware must be scrupulously washed and rinsed copiously with ultra pure water. High purity solvents must be used to avoid any residues being left on the cleaned surface. Also, the water must be of very high purity and be changed at regular intervals, preferably for each new monolayer spread, to avoid bacterial growth known to occur when water is left in the trough for several days.

Ultra pure water is usually supplied by commercially available purification systems, based on ultra filtration and ion exchange techniques. Though these systems are provided with a resistivity meter which allows continuous assessment of the quality of the water, non-ionizable impurities may still pass undetected which will affect monolayer behavior. Surface potential and lateral conductance measurements have been proven to be extremely sensitive to minor concentrations of impurities and may therefore be used to ensure that only high purity water is employed in Langmuir monolayer and LB film studies.

It is also widely recognized that a dust-free environment is an essential requirement for the production of high quality Langmuir monolayers and LB deposited films. Ideally, the LB apparatus should be housed in a semiconductor clean room with temperature and relative humidity control. To gain access to such a clean room researchers should wear overshoes and special coats and hats aimed at preventing any dust from contaminating the environment.

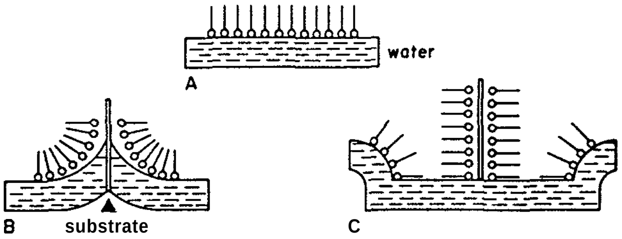

Figure 2: Monolayer deposition. A monolayer is not picked up by the substrate during the first immersion of the substrate (downstroke), but in subsequent trips deposition always occurs both in the downstrokes as well as in the upstrokes.

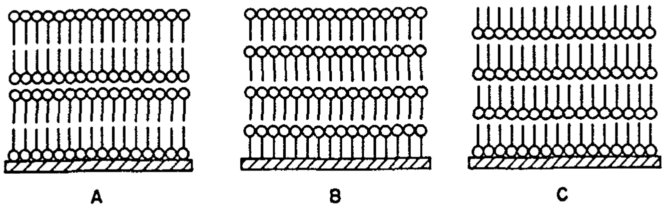

Figure 3: Types of LB deposition. a) Y-type; b) X-type; c) Z-type.

III. LB Forming Materials

The main class of compounds which form stable monolayers on the water surface are those referred to as amphipathic or amphiphilic. Molecules of these compounds possess a highly polar group, which is attracted to the water, and a sufficiently large non-polar moiety (generally a long hydrophobic tail) which prevents the monolayer from dissolving into the water. The polar group is usually located at one end of the molecule so that the molecules can be made to align parallel to each other with the hydrophobic tail protruding from the water surface. The simplest amphiphilic materials are the long chain alkanoic acids, e.g. stearic acid, and their derivatives which have been the most widely investigated compounds. (For a review on LB forming material~see [13]). Chains containing one or more double bonds can replace the alkyl chain of fatty acids yielding monolayers that are amenable to polymerization. A good example of this type of compound is w-tricosenoic acid (a 24 carbon fatty acid with a double bond at the end of the hydrocarbon chain) that has been used in LB resists for electron beam lithography. Aromatic materials such as the long-chain anthracenes and azobenzenes have also been employed in the fabrication of LB films.

LB films of these simple molecules, however, are usually fragile and have poor thermal stability and mechanical properties. This has prompted the study of LB films made from polymerizable materials and also performed polymers in a work pioneered by Tredgold and his collaborators in the United Kingdom[14]. Examples of recent use of polymers for LB film fabrication include films made from polyimides, polyglutamate, polydiacetylene, polyisocyanides, octadecyl esters of polyamic acids, and mixed films of hydrophilic and hydrophobic block copolymers. Polymerizable films of a styrene functionalized surfactant, phospholipids and long-chain derivatives of alpha- amino acids and diynoic, trienoic and acrylic acids have also been reported.

The last 2 or 3 years have seen a spectacular increase in the interest in conducting polymer LB films, as the ability to engineer supermolecular structures of a number of conducting polymers has been demonstrated[15]. The wide variety of possible applications together with their excellent mechanical and electroactive properties make the conducting polymers perhaps the current most important class of materials for fabricating LB films. Three main families of conducting polymers have been used so far, namely the poly-alkyl thiophenes, the polypyrroles and the polyanilines. It is worth mentioning that conducting LB films have also been made from non-polymeric materials such as the tetracyanoquinodimethane (TCNQ) salts and the tetrathiafulvalene derivatives.

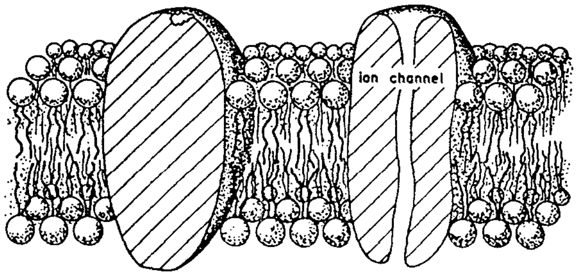

Figure 4: Schematic diagram of a cell membrane. The lipid bilayer is responsible for the structural integrity of the membrane which is traversed by proteins and other constituents. In the picture an ion channel is shown to illustrate how charge transport through the membrane can occur.

Another important class of LB materials comprises those which are relevant because of their biological implications. According to the fluid mosaic model of Singer and Nicholson shown schematically in Figure 4, the structural framework of a biological membrane is formed from a lipid bilayer, or essentially a two-layer LB film: two parallel monolayers with their headgroups on the outside surfaces and the tails pointing inward; and containing a variety of proteins and lipopolysaccharides (LPS). The lipid molecules, such as cholesterol and phospholipids are the most numerous and are responsible for the structural integrity of the membrane. If proteins and other cell membrane constituents are successfully incorporated into LB films, such structures could serve as realistic models of biological systems on which useful devices could be based. For instance, protein LB films have been suggested for biosensors, and the incorporation of Gramicidin A into DPPC (dipalmitoyl phosphatidylcholine) LB films has been used in high spatial resolution of ionic channels using scanning tunneling microscopy.

There has been renewed interest in the synthesis of novel compounds with specifically tailored electrical and optical properties. Accordingly, sulphoxide-containing compounds and organo-ruthenium complexes with a fatty acid have been used in pyroelectric LB films, and dye-impregnated LB films have been fabricated aimed at a variety of applications such as p-n junctions, nonlinear optical films, energy transfer, and coating of optical fibres. The macrocyclic porphyrin and phthalocyanine derivatives have been extensively studied for applications that range from gas sensing devices to electrochromism. Novel materials yielding LB films with unusual, almost unexploited properties have also been studied. Included in these are the ferroelectric side chain polymers, the liquid crystals, and the amphiphilic orthophenanthroline thiocyanato from which magnetic LB films have been deposited.

Some of the materials mentioned in this section are available from chemical suppliers but others have to be synthesized from basic materials. It is often the case that some materials are not suitable for transfer onto a solid substrate because they form monolayers which collapse at relatively low surface pressures. However, in many cases long hydrocarbon chains can be chemically attached to the molecules of interest to improve their stability on the water surface. Some polymer monolayers, on the other hand, are extremely rigid and consequently deposition is not always successful, but this problem can be usually overcome if mixtures of conducting polymers and fatty acids are used, or if appropriate functional groups are added to the polymer molecules.

IV. Characterization

4.1 Langmuir Monolayers

The fabrication and characterization of Langmuir monolayers constitute a field of research in its own right because of the rich variety of electrical, optical, thermodynamical and rheological properties of monolayers which have been under investigation through a variety of experimental techniques. The upsurge of interest in LB films has added a new dimension to the subject of Langmuir monolayers, for the properties of LB films depend on the monolayer characteristics. Important issues in the monolayer characterization are related to the effects of subphase conditions on the monolayer properties, and also its homogeneity and stability on the water surface.

Among the many techniques employed in the characterization of Langmuir monolayers, the surface pressure and the surface potential methods have been the most widespread. After discussing these measurements at some length, other techniques which have also provided relevant information on monolayer behavior will be discussed briefly.

Surface pressure is defined as the decrease in the surface tension of the liquid owing to the presence of the monolayer. It is normally measured using a Wilhelmy plate/electrobalance arrangement that monitors the force required for the sensing plate to be kept stationary against changes in surface tension. The pressure-area (?r-A) isotherm, obtained by compressing the monolayer, is the most commonly used characteristic in the description of a monolayer. Figure 5 (i) shows a typical r-A curve for stearic acid, where A is the average area occupied on the liquid surface by the molecules forming the monolayer. When the monolayer is compressed beyond the steep increase in surface pressure, collapse occurs and the molecules are forced out of the monolayer forming lenses.

The almost featureless *r-A* curve shown in Figure 5 is characteristic of simple, monofunctionalized molecules and can be interpreted unambiguously, at least qualitatively. For more complex molecules, there is usually the formation of expanded monolayers which is dependent upon factors such as the presence of a second polar group which interfere with the tendency of the chains to pack closely. This is illustrated in Figure 6 for a bipolar compound that possesses two hydrophilic groups at each end of the molecule. The carboxylic group (COOH) is anchored to the water surface while the *p*-tolyl sulphoxide group is removed from the water surface as the monolayer compression proceeds.

Although a qualitative explanation for the shape of r-A curves can be offered in many cases, a quantitative analysis is much more difficult to be achieved, even for the simplest long- chain alkanoic monolayers. Theoretical studies have been presented in the literature which have attempted to describe phase transitions in fatty acid and phospholipid monolayers quantitatively. These studies encompass thermodynamical analyses based on statistical mechanics and computer simulation techniques.

The surface potential technique is the secdnd most

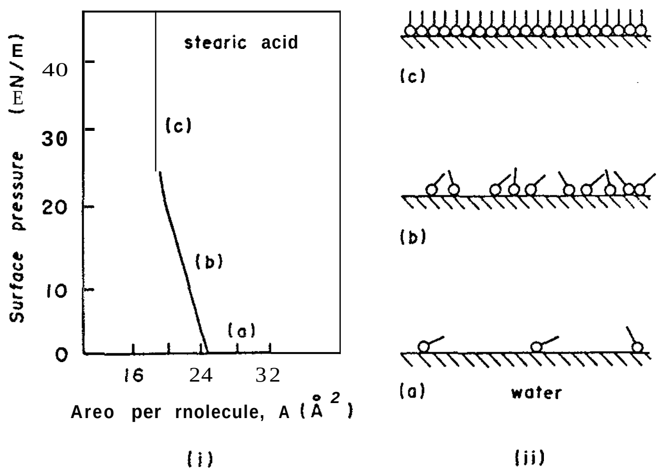

Figure 5: Pressure-area isotherm and molecular configuration. (i) ã-A characteristic for a monolayer of stearic acid on ultrapure water. (ii) molecular configuration in the three regions marked in the π-A curve; (a) gaseous phase, (b) liquid-expanded phase, and (c) condensed phase. From ref. [17].

frequently used method for characterizing floating Langmuir monolayers. The surface potential of a monolayer, AV, is defined as the difference in potential between a monolayer-covered surface and a clean aqueous surface. In most cases, it is measured using a Kelvin probe. The technique provides valuable information on a number of monolayer effects, especially for identifying phase transitions resulting from molecular orientation during monolayer compression.

The interpretation of surface potential measurements, however, has been plagued with two main types of problem. First, although it has long been established that AV arises mainly from the molecular dipoles of the film-forming molecules, discrepancies exist between the measured and the expected values for these dipole moments. Second, the measured monolayer surface potentials for large areas per molecule are usually not reproducible, changing drastically even for consecutive compressions of the same monolayer. Over the last four years these problems have been overcome to a great extent as explained in the following.

The measured AV can now be successfully related to the group dipole moment of individual molecules if the monolayer is treated as a 3-layer parallel plate capacitor. In this so-called Demchak and Fort model[16], the measured surface potential is assumed to arise from three main contributions: a moment μ_1 which is caused by the reorientation of water molecules induced by the presence of the monolayer; a moment μ_2 due to the dipoles of the hydrophilic headgroups; and a moment μ_3 assigned to the hydrophobic tails. Each of the 3 layers has a different relative permittivity to account for the different polarisabilities of the medium immediately surrounding the dipoles (Figure 7). When a monolayer is ionized, an additional contribution to the measured surface potential arises from the Gouy-Chapman electrical double layer.

Quantitative agreement between theory and experiment has now been obtained for condensed monolayers of a number of aliphatic compounds by Taylor and coworkers at Bangor, U.K. [16]. An alternative, slightly different model has been suggested by Vogel and Mobius from Goettingen in Germany, in which a 2-layer rather than a 3-layer capacitor is used, and the local permittivities are not considered explicitly. Despite the success of these models, so far they have been applied only to a limited class of compounds and still contain several arbitrary assumptions whose validity needs to be confirmed.

The non-reproducibility of surface potential data for expanded monolayers was a major problem for a long time. The large fluctuations usually observed in the surface potential was attributed to non-homogeneity in the monolayer with the formation of clusters and islands. This non-homogeneity has been identified as originated from extremely low amounts of impurities present in the water surface, and it has been demonstrated that reproducible results can now be obtained for expanded monolayers provided that adequately purified subphase water is employed. While this may be taken as indicator of a (macroscopically) homogeneous monolayer, it has been unequivocally established, on the other hand, that the monolayers are not homogeneous at the microscopic level. Domains of the order of tens of microns have been observed in monolayers of fatty acids by phase contrast microscope and reflectometry under the Brewster angle, and in monolayers of phospholipids and porphyrin-fatty acids by means of fluorescence microscopy. The existence of domains has also been predicted in molecular dynamics simulations for fatty acid monolayers.

Another recent important finding relating to monolayer structuring has been obtained by measuring directly the lateral conductance of phospholipid and fatty acid monolayers. The conductance was shown to occur only when the molecules are packed at or below a critical area per molecule, and has been suggested to arise from proton hopping through a hydrogen-bonded network at the water/monolayer interface. The existence of a critical area has also been confirmed by surface potential, ellipsometry and microscopy measurements, and appears to be related to the growth of the monolayer domains.

Surface pressure, surface potential, and lateral conductance measurements provide only information on the collective behavior of the assembled molecules, and so do some other measurements like surface viscosity and ellipsometry which have also been used in the characterization of Langmuir monolayers. In recent years,

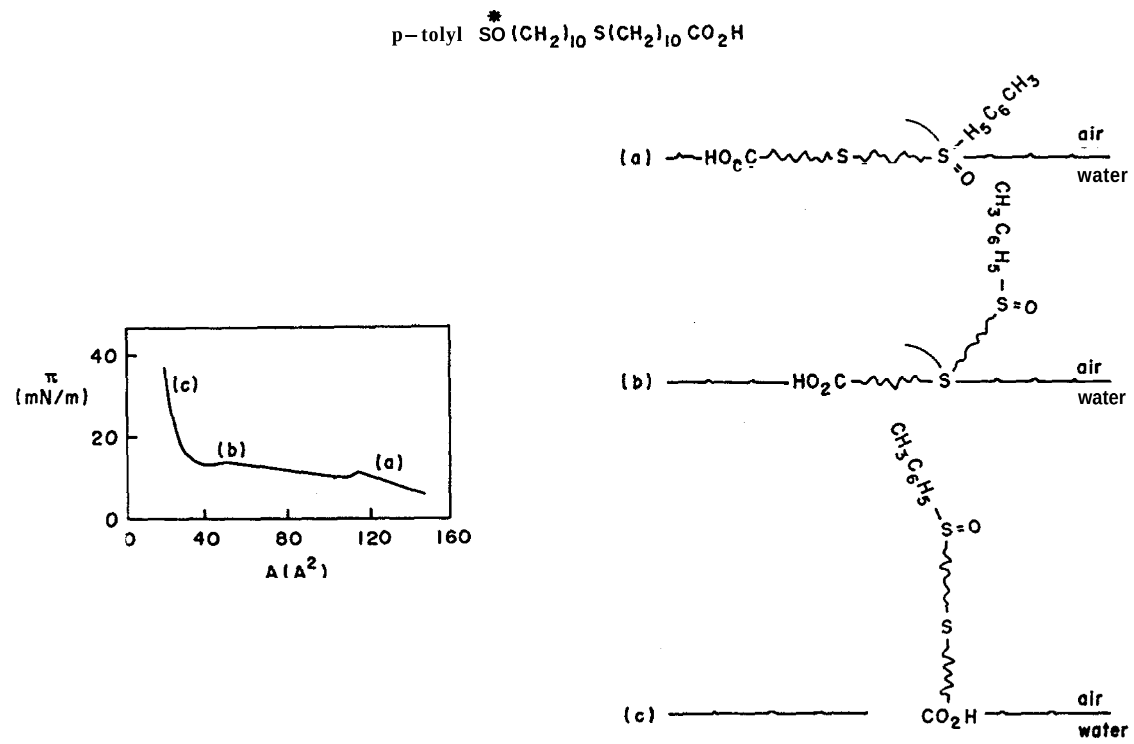

Figure 6: Bipolar compound. (i) π-A characteristic for *a* monolayer of p-tolyl sulphoxide acid (TSA) on ultrapure water. (ii) possible molecular configuration in the three regions marked in the π-A curve. From ref. [17].

molecular ordering has been investigated in which nonlinear optical techniques, synchrotron X-ray diffraction and reflection and neutron reflection have been used. These latter methods provide detailed information on chain orientation and packing characteristics, and allow the thickness of the monolayer to be measured to an accuracy of one Angstron.

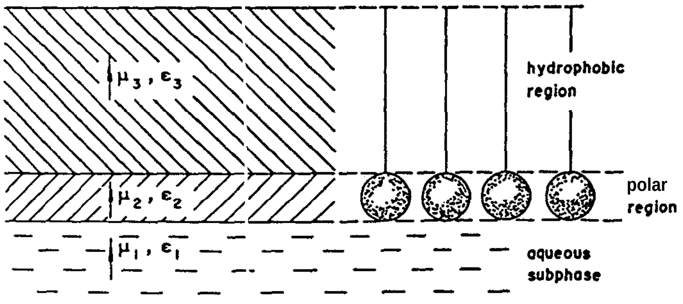

Figure 7: The Demchak and Fort model. The 3-layer capacitor model of a condensed monolayer at the air/water interface. The contribution of the dipoles in each layer, μ_i, to the surface potential, AV, depends on the local permittivity, r, of each layer. From ref. [17].

4.2. Langmuir-Blodgett Deposited Films

There are a number of characteristics which need to be investigated before the properties of LB films can be used in actual applications. First of all, it is necessary to establish whether deposition really took place and whether the film deposited is indeed a genuine LB film or simply a sample prepared using the LB method. By measuring the transfer ratio of a particular monolayer in successive depositions, it is usually possible to know the type of film deposited (Y, X or Z) and also investigate which parameters affect deposition. However, the measurement of the transfer ratio on its own cannot ensure whether the film is uniform or highly ordered. Several other techniques must be used in order to gain such information. The thickness of the LB film and the intermolecular distances may be determined by ellipsometry, surface plasmon resonance, X-ray diffraction and neutron diffraction and reflection, and electron diffraction. Synchrotron X-ray reflection, for instance, allows the thickness to be determined to an accuracy of one Angstrom. The thickness can also be obtained when the film is part of a MIM (metal-insulator-metal) structure by measuring the capacitance of the structure.

Some of the techniques mentioned above can be used to study the orientational order of the molecules in the film, but this can also be investigated by Raman scattering, electron spin resonance, Near Edge X-ray Absorption Fine Structure (NEXAFS), linear dichroism and Fourier Transform Infra Red (FTIR) spectroscopy. Film texture and the presence of defects can be investigated using scanning electron microscopy (SEM), transmission electron microscopy (TEM), scanning tunneling microscopy (STM), atomic force microscopy (AFM) and optical microscopy. Possible reasons for non-homogeneities in LB films are the reorientation of the molecules during deposition or after it, or even non-homogeneity on the monolayer at the air/water interface. At the molecular level, non-homogeneities are bound to exist since domain structures have been reported for fatty acid and phospholipid Langmuir monolayers. Surprisingly, however, regular arrangement (to an accuracy of the order of Angstroms) of fatty acid molecules has been observed in STM measurements.

For conducting LB films, the in-plane conductivity has been measured using mechanically pressed contacts, conducting paste or evaporated gold electrodes, but has also been obtained through Hall effect and surface acoustic wave (SAW) devices. Though some attempts have been made to investigate the mechanisms responsible for the conductivity in LB films, considerable theoretical work is still required for these mechanisms be established.

The characterization of LB films can be a rather complex matter. Structural differences may exist between the first and subsequent layers, including tilt of the chains in relation to the substrate. Some authors have reported that the structural arrangement of fatty acid films may change from hexagonal to orthorhombic at thicknesses greater than a monolayer. These differences probably arise from substrate-film interaction which tend to die off with the increase in the number of layers. Capacitance-voltage measurements, on the other hand, have shown that in some films the thickness is proportional to the number of layers, which would indicate that within the accuracy of the measurements all layers were equivalent.

Stability is a major problem for applications of LB films. In addition to the poor thermostability of films built from aliphatic compounds, there have been reports of changes in film properties with time. The surface potential of sulphur- containing LB films has been shown to decrease by 40% in a month of deposition when they are stored in ambient conditions. Films stored in a dry air atmosphere presented a much smaller decrease which shows that storage conditions are important for film stability[17]. Also, Z and X-type films have been observed to relax to the more stable Y-type, indicating that structural changes may occur as well.

Apart from the experimental methods already mentioned in this section, other techniques which have also been used in the characterization of LB films include thermo and photodesorption measurements, electron spin resonance, Penning ionization electron spectroscopy, surface plasmon resonance, Auger electron spectroscopy, cyclic voltammetry, photoacoustic spectroscopy and Stark spectroscopy.

V. Possible Applications

The multitude of possible applications which have been suggested over many years are a legacy from the pioneering work of Prof. Kuhn and his collaborators in Goettingen, Germany, where charge and energy transfer in LB films were studied. An extensive review of the possible applications of LB films has recently been provided by Petty[18].

The potential applications of LB films stem from their unique blend of features: they are ultra thin films (of the order of nm) and possess a high degree of structural order. Also, some films have interesting optical, electrical and biological properties characteristic of organic compounds. The LB technology offers the possibility of tailoring material properties either by molecular engineering of the individual molecules using modern methods of organic chemistry or the control over the architecture of the films as shown in Figure 8. This latter control permits the observation in LB film form of useful physical properties of organic compounds which is not possible for the same material in its bulk crystalline form because of structural restrictions. For example, most organic materials crystallize with a centre of symmetry and therefore second order nonlinear phenomena such as second harmonic generation and pyroelectricity cannot be observed, but may be present in LB films made from these very materials.

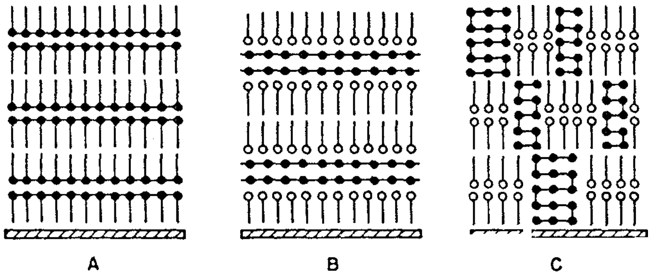

Figure 8: Supermolecular structures. Different possible structures for LB films of conducting polymers. From ref. [15].

A great number of possible applications of commercial interest have been suggested for LB films. The films may be used as passive layers in MIS (metal-insulator-semiconductor) structures, in resists for submicrolitography, in the passivation of n-GaAs surfaces, in surface acoustic wave (SAW) devices, and in the lubrication of thin film magnetic disks to enhance the useful life of high density hard disks. Many other possible applications include non-linear optical devices, pyro- and piezoelectric devices, chemical and biological sensors, photodiodes, conducting films for electrode materials, thermochromic devices, coating of optical fibers for nonlinear optical properties, ultrafiltration membranes and the building of molecular electronic devices. This latter possible application has brought so much excitement to the scientific community that a special subsection has been reserved for molecular electronics in this paper.

Among the many classes of materials that have been used for LB film formation, the conducting polymers deserve special attention. Perhaps the most exciting development in the area in recent years has been the demonstration of the use of a conducting polymer based LB film as the active element of an electronic device. FETs have been fabricated by Stubb's group in Finland, and also by Rubner's group in the USA, in which mixed LB films of different conducting polymers have been used [15].

5.1. Molecular Electronics

The research on the possible fabrication of Molecular Electronic Devices (MED) has raised hopes for the development (perhaps in the not very distant future) of the so-called nanotechnology, whereby devices will have nanometric dimensions. Such an achievement would certainly provoke a revolution in electronic devices, information technology and in science and technology as a whole These systems will be fabricated in such a way as to make use of specific interactions between molecules, interactions that will lead to functions being performed similar to those now realized by semiconductor and magnetic materials. The realization of such systems will only be possible if suitable techniques are developed for assembling molecular structures. Of the many possible approaches, the Langmuir-Blodgett (LB) technology is certainly one of the most important, for it provides not only a method of assembling molecular systems in a controlled manner but can also take advantage of the self-assembling nature of certain molecular species.

The first requirement for building an MED is the development of a molecular switch capable of shifting information, reversibly, from one stage to the other. This achievement would be equivalent to the discovery of the transistor in conventional microelectronics[19]. The information must be accessible at the molecular level, so that the "state" of the switch can be determined. The information must be transported over distances by molecular wires and/or molecular networks. Finally, the switches and networks need to be assembled in three dimensional structures or arrays that will ultimately lead to the MED. Work on LB films has encompassed all the different stages mentioned. Both optical and electrically reversible switching, for example, have been observed in LB films in which the switching function originated from a number of different processes such as electrochromism, photodimerization and electron transfer. Figure 9 illustrates a porphyrin-phthalocyanine arrangement in which electron transfer can occur upon excitation by visible laser light[20]. Three- dimensional molecular memories have been suggested based on electron motion perpendicular to LB multilayers of macrocyclic compounds.

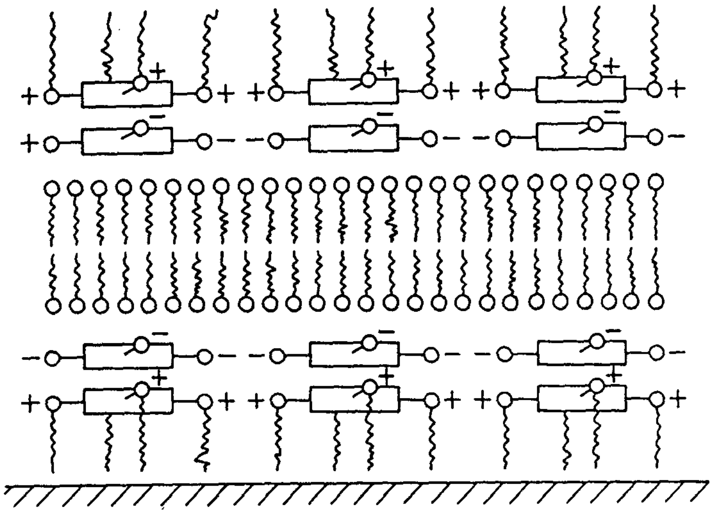

Figure 9: Electron transfer. LB film of porphyrin-phthalocyanine heterodimers in which electron transfer can occur parallel to the substrate by exposing the film to visible laser light. From ref. [20].

The need to access individual molecules in order to store and retrieve data is a problem which appeared to be almost unsurpassable until very recently. Now that instruments such as the scanning tunneling microscope (STM) and atomic force microscope (AFM) are available it is possible to probe surface properties of LB films down to atomic dimensions. Accordingly, these techniques have been used for molecular resolution images of LB films which paves the way for investigations on the access of individual molecules.

Despite the worldwide effort of interdisciplinary teams working on the different aspects of M.E., real applications remain something for the future. Several issues are yet to be addressed including the need to detect and repair failures in components that do not perform correctly. Additionally, the interpretation of some of the most important recent results is still open to discussion. For instance, organic molecular rectifiers based on LB films have been built but there has been some debate as to whether the observed rectifying function is molecular in origin[18]. Also, it cannot be claimed at the moment that the STM and AFM data are completely free from experimental artefacts.

VI. The State of the Art

Conducting polymers are now at the forefront of research in LB films because of their improved mechanical and thermal properties, and also because some of them are electroactive and therefore suitable for fabricating electronic devices. For the characterization of Langmuir monolayers on the water surface and LB deposited films there is a trend towards the use of experimental methods that are capable of providing information at the molecular level. The tilt of molecules and structuring of the monolayer have been observed by synchrotron X-ray and Neutron diffraction and reflection measurements, while the advent of the STM and AFM technologies has made it possible to probe LB deposited films with molecular resolution. Another important development is the use of sophisticated theoretical methods, e.g. Monte Carlo and molecular dynamics, to simulate Langmuir monolayers and LB films, and the computer aided design of special molecules to suit a particular application. Nevertheless, theoretical analyses of LB and Langmuir films are still at an embryonic stage.

Almost two decades of extensive research on LB films and on their possible applications have elapsed, and these films continue to be referred to only as "promising" for technological applications. It appears that, so far, the only commercial application of an LB-based device is a low-level radiation source to act as standard for calibrating tritium detectors, which was developed by Martin Taylor's group at Bangor University in the United Kingdom. The source consists of LB films from palmitic acid mixed with small amounts of tritiated palmitic acid deposited on an aluminum plate.

In fact, if one inspects the special issues of scientific journals dedicated to LB films one may say that some possible applications have been mentioned over the last 15 years, without any major breakthrough towards making them a reality. One may wonder, then, whether LB films will ever be used in commercially available devices. In this respect, an important point must be borne in mind: technology is about concentrating research and development efforts into specific final products, e.g. a device made from a specific material that performs a specific function. Research on LB film, however, has been more akin to fundamental science, in particular because the background knowledge of property-structure correlations is yet to be established for these films. Fundamental science is about opening up new possibilities and extending horizons, and this is precisely what has been done in the LB field as demonstrated by the large number of different types of molecule and molecular assembly investigated for LB film formation and also by the immense number of different applications. Before the feasibility of a specific commercial device is demonstrated so that the research efforts may be directed towards it, the potential of LB films are likely to remain unfulfilled.

Many problems must be solved before LB films can be used in real applications, the most important of which are the lack of thermal stability and the poor molecular alignment in many films[18]. The LB technology will also have to be adapted for the cost-effective mass production of LB-based devices. Langmuir troughs, albeit in some cases fully automated and highly sophisticated, are designed with the specific purpose of being used in research and development. They usually allow for the incorporation of experimental techniques for monolayer characterization, dipping facilities for alternate layers and for a variety of substrates, etc. For device mass production, trough design will have to change drastically; troughs may need to be miniaturized, and a number of them placed in an assembly line harmoniously linked to other industrial processing unities.

As far as molecular electronics is concerned, the capability for storing optical and electrical data has been clearly demonstrated, and there is now the hope that data can be accessed at the molecular level with the use of STM and AFM techniques. While it is almost certain that some of the devices are to be built using the LB technique, chemisorption methods such as the one developed by Sagiv[21] may also be employed. Like the LB technology, chemisorption can also allow the deposition of monomolecular films on solid substrates and take advantage of the self-assembling nature of some of the molecules. Incorporation of biological molecules capable of self-assembling into electronic devices may lead to the fabrication of so-called biochips and ultimately to the development of the biological computer. Again, the study of fundamental properties of the deposited films is essential for further progress to be made.

Any major achievement in the field is likely to depend on the cooperative work of multidisciplinary teams composed of Chemists, Biochemists, Biologists, Electronic Engineers and Physicists.

Acknowledgments

I thank FAPESP and CNPq which are sponsoring the LB work in São Carlos.

References

1. G. G. Roberts, Langmuir-Blodgett Films (Plenum Press, N.Y. 1990).
2. O. N. Oliveira Jr. and D. M. Taylor, Ciência-Hoje **67**, 18 (1990).
3. A. Ulman, J.Mater.Educ., **11**, 205 (1989).
4. I.R. Peterson, J.Phys.D: Appl.Phys., **23**, 379 (1990).
5. A. Barraud, Thin Solid Films, **175**, 73 (1989).
6. R. H. Tredgold, Rep.Prog.Phys., **50**, 1609 (1987).
7. V. K. Agarwal, Physics Today, **41**, 40 (1988).
8. M. B. Biddle and S. E. Rickert, Ferroelectrics, **76**, 133 (1987).
9. T. Moriizumi, Thin Solid Films, **160**, 413 (1988).
10. M. Vandevyver, Thin Solid Films, **159**, 243 (1988).
11. R. H. Tredgold, Advances in Physics, **26**, 79 (1977).
12. M. Sugi, J.Mol. Electronics, **1**, 3 (1985).
13. R. A. Hann, Phil. Trans. R.Soc. Lond. A **330**, 141 (1990).
14. P. Hodge, F. Davis and R. H. Tredgold, Phil. Trans. R.Soc. Lond. A**330**, 153 (1990).

15. M. F. Rubner and T. A. Skotheim, in Conjugated Polyners, J. L. Brédas and R. Silbey (eds.), Kluwer Academic Publishers, p.363 (1991).
16. D. M. Taylor, O. N. Oliveira, Jr. and H. Morgan, J. Coll. and Interface Sci., 139, 508 (1990).
17. 0 . N. Oliveira Jr., "Electrical Properties of Langmuir Monolayers and LB-Deposited Filrns", PhD. Thesis, University of Wales, Bangor, U.K., 1990.
18. M. C. Petty, "Possible Applications for Langmuir-Blodgett Films", Thin Solid Films, in press.
19. J. de Rosnay, "Molecular Information Processing and Molecular Electronic Devices", Proc. 5th International Conference on Langmuir-Blodgett Films, (Paris, August 1991) p. AI.
20. J. F. Lipskier, T. H. Tran-thi, S. Palacin, S. Gaspard, D. Houde and C. Pepin, Proc. 5th International Conference on Langmuir- Blodgett Filrns (Paris, August 1991) p. C02.
21. J. Sagiv, J.Am.Chem.Soc. **102,** 92 (1980).