Thesis

On

STUDIES ON LANGMUIR - BLODGETT THIN FILMS

Submitted by:

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I owe my sincerest gratitude to my parents for their love, blessings and encouragement in every walk of life.

Gitanjali Dhir

CERTIFICATE

This is to certify that the **thesis entitled "STUDIES ON LANGMUIR AND BLODGETT THIN FILMS"** submitted by MS. Gitanjali Dhir in the partial fulfillment for the award of degree of M.Sc in Physics from the school of Physics and Material Sciences, Thapar University, Patiala, is a record of candidates own work carried out by her under our supervision and guidance. The experimental matter embodied in this report has not been submitted in part or full for credit towards any other degree at Thapar University, Patiala or any other university.

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Dedicated

to

My Parents

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LC	Liquid Crystal
NLC	Nematic Liquid Crystal
I	Isotropic
N	Nematic
SmA	Smectic A
SmC	Smectic C
LB	Langmuir-Blodgett
SA	Stearic Acid

CHAPTER-1

INTRODUCTION

ABSTRACT

The homeotropic alignment of the nematic liquid crystal M15 on Langmuir-Blodgett monolayers of stearic acid ($COOHC_{17}H_{35}$) was studied. The Langmuir monolayers were characterized by the most basic graph known as surface pressure-area isotherm. The Langmuir monolayer of stearic acid shows a hysteresis curve. Also the Langmuir monolayers of stearic and nematic liquid crystal with different concentrations (75:25, 50:50) were formed. The surface pressure-area isotherm shows that there is an effective lift-off in the area as a function of the amount of nematic liquid crystal added to the system. The monolayer deposited on the substrate was characterized by Fourier transform of infra-red radiation (FTIR) and Scanning Electron Microscope (SEM). The monolayers of stearic acid were deposited onto glass plates coated with indium tin oxide, which were used to assemble sandwich cells of thickness that were filled with the nematic liquid crystal by the capillary action and thickness (4 micron) is controlled by using Myler spacer. The homeotropic alignment of nematic liquid crystal and film morphology was investigated as function of temperature and voltage by using optical microscopy. The result shows that the desired homeotropic alignment by the stearic acid monolayer has been provided to the nematic liquid crystal which is confirmed by the appearance of the black portion in the texture. This shows that the molecules are aligned vertically to the surface of the substrate.

1.1 LANGMUIR BLODGETT TECHNIQUE

1.1.1 Introduction

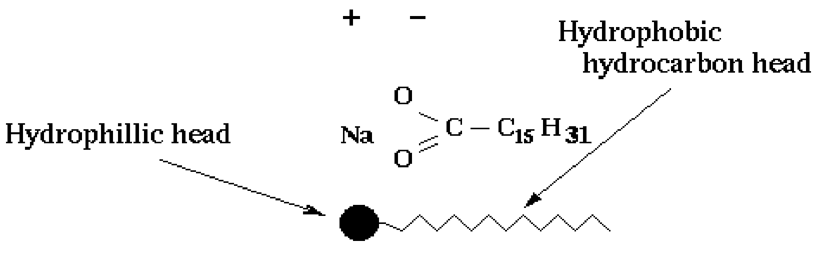
Langmuir- Blodgett (LB) is a technique to deposit thin films on the solid substrate in thickness ranging in nanometer. Thin Film deposition can be done by various techniques such as thermal evaporation, sputtering, electro-deposition, molecular beam epitaxy, absorption from solution, self-assembly, etc. The LB technique is one of the most promising techniques for preparing thin films as it enables: (i) The precise control of the monolayer thickness (ii) homogeneous deposition of the monolayer over large areas and (iii) the possibility to make multilayer structures with varying layer composition. An additional advantage of the LB technique is that monolayers can be deposited on almost any kind of solid substrate

In order to understand the thin film deposition by Langmuir and Blodgett technique we first need to understand about the concept of the monolayers.

1.1.2 Monolayers: two dimensional phases

A monolayer is a single, closely packed layer of atoms, molecules, or cells. A Langmuir monolayer is a one-molecule thick layer of water insoluble material spread onto an aqueous subphase. Langmuir monolayers are amphiphilic materials that possess a special molecular structure - contain both a water loving polar part (hydrophilic) and water hating non-polar part (hydrophobic) as shown in fig 1.1. This property turns out to be very important in determining the special structures formed by amphiphilic molecules. The formation of these special structures is responsible for the use of amphiphilic in a large number of applications ranging from oil recovery to efficient delivery of drugs at a desired site in the body to their use in soaps and detergents.

They are called surface active because they have the unique properties of getting adsorbed at various interfaces (e.g. air-water, oil-water etc.) and altering the properties of the interface. The hydrophilic part of an amphiphilic molecule (usually called the head) is a polar molecule whereas the hydrophobic part (called the tail) is a hydrocarbon chain 8-16 Carbon atoms in length.



A typical amphiphillic molecule.

Fig: 1.1 A Sodium Salt palmatic acid with COO^- group is hydrophilic and C_{15} long carbon chain is hydrophobic.

A vast range of the molecular material are well suited for the formation of these insoluble monolayers at the air water interface. These include lipids, proteins, nanoparticles, polymers and many other biomolecules. Modern chemical engineering has made possible to synthesize almost any type of functional molecule in such a way that it has the necessary hydrophobic appendages to be insoluble in water and suitable for creating the monolayers. Recent research have shown that novel compound such that carbon nanotube, nanowires, graphines are also suitable to form Langmuir film.

1.1.3 History of Langmuir and Langmuir Blodgett films

Advances to the discovery Langmuir-Blodgett Films began with Benjamin Franklin in 1773 when he dropped about a teaspoon of oil onto a pond. Franklin noticed that the waves were calmed almost instantly and that the calming of the waves spread for about half an acre. What Franklin did not realize was that the oil had formed a monolayer on top of the pond surface. Over a century later, Lord Rayleigh quantified what Benjamin Franklin had seen at a pond. Knowing that the oil, oleic acid, had spread evenly through water, then Lord Rayleigh calculated that the thickness of the film was 1.6nm by knowing the volume of oil dropped and the area of coverage. In addition, he used these calculations to prove Avogadro number. With the help of her kitchen sink, Agnes Pockels showed that area of films can be controlled with barriers. She added that surface tension varies with contamination of water. She used different oils to deduce that surface pressure would not change until area was confined to about 0.2 nm^2. This work was originally written as a letter to Lord Rayleigh who then helped Agnes Pockels become published in the journal, Nature, in 1891. Agnes Pockels' work set the stage for Irving Langmuir who continued to work and confirmed Pockels' results. Using Pockels' idea, he developed the Langmuir trough. His observations indicated that chain length did not impact the affected area since the organic molecules were arranged vertically. Langmuir's breakthrough did not occur until he hired Katherine Blodgett as his assistant [2].

The monolayer's formation can now be realized at the interface between the two phases. By simply observing that some of the molecules will orient themselves at the interface say liquid and gas to reduce the surface energy.

The common concept of Surface chemistry related to LB is given as follows

1.1.4 Surface tension

The molecules in the liquid have a certain degree of attraction to each other. The degree of this attraction is dependent on the properties of the substance .The interactions of a molecule in a bulk of the liquid are balanced by an equally attractive force in all directions. The molecules surface of a liquid experience an imbalance of forces i.e. a molecule at the air/water interface has a larger attraction towards the liquid phase than towards the air or gas phase as shown in fig:1.2.The line of force acting on the surface molecule is the surface tension [4].

Therefore there will be a net attractive force towards the bulk and the air/water interface will spontaneously minimize the area and contract.

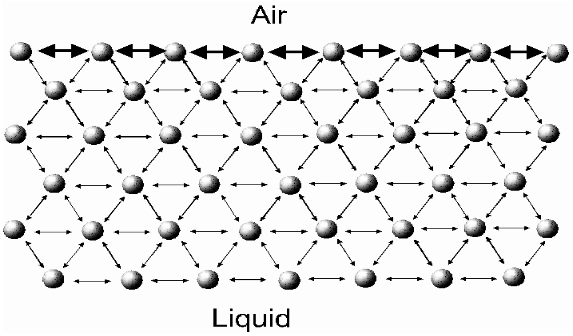


Fig: 1.2 Schematic illustration of the interaction of molecules at an interface and bulk.

The net effect of the situation is the presence of free energy at the surface. The excess energy is called surface free energy and can be quantified as a measurement of the energy/area. It is also possible to describe this situation as having a line tension or surface tension which is quantified as force/length measurement. The common units for the surface tension are dynes/cm or mN/m. Surface tension depends on the following:

(a) Nature of the liquid: Polar liquids such as water have strong intermolecular interactions because of the presence of electronegative element and hence charge distribution so more is the interaction between the positive and negative charged dipoles, and thus high surface tensions.

(b) Dependence on temperature. An increase in the temperature of the system will lower the surface tension. Because of the reason that with an increase in the temperature the interaction of polar molecules decreases due to the change of molecular dipoles, So lesser interaction and less surface tension.

(c) Surfactants: these are the molecules which are amphiphilic in nature. The presence of surfactants will also lower the surface tension because of the reason that amphiphilic nature of surfactant make them to interact with water surface. So forces lying on surface of water are changed and surface tension is decreased.

The cause of formation of monolayer can be understood as follows:

The monolayer formed at the interface has the properties different from that of the either of the bulk phases [5]. The monolayer formed at the interface is a consequence of the molecules being electrical neutral; then the forces between them will be short range and hence the corresponding surface layer will be no more than one or two molecule thick. In contrast, the columbic forces associated with charged species can extend to considerable region. So till now the situation the situation can be visualized as shown in fig 1.3.

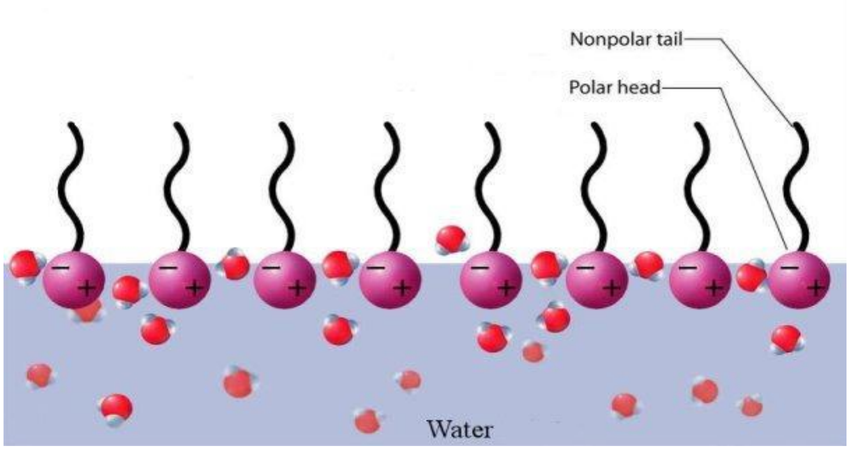


Fig: 1.3 A schematic illustration showing the components of an amphiphilic (left), and the orientation of an amphiphilic adopted at an interface (right).

1.1.5 Preparation of the monolayer

There exists a wide range of surfactants with an amphiphilic nature which drastically lower the surface tension of water. Many of these amphiphilic substances insoluble in water can with the help of a volatile and water insoluble solvent easily be spread on a water surface to form an insoluble monolayer at the air/water interface. By simply dissolving them in the suitable solvent (e.g., chloroform) .When the solvent has evaporated, the organic molecules may be compressed to form a '2-dimensional' solid with the help of various techniques which will be discussed later in the Langmuir Blodgett technique setup. Now in order to understand the spreading of the monolayer we will first introduce the concept of Surface pressure.

As earlier was mentioned the air/water interface possesses an excess free energy originating from the difference in environment between the surface molecules and those in the bulk. This interfacial free energy is accessible by measurements of the surface tension, Π.

The surface pressure of the system may be defined as the surface tension of the pure subphase minus the surface tension of the subphase with the amphiphilic floating on the surface which varies with the molecular area.

$$\Pi = \gamma_0 - \gamma \qquad (1.1)$$

Where γ is the surface tension in absence of a monolayer and γ_0 the surface tension with the monolayer present. The surface tension of water is around 73mN/m at 20^{o}C, which is an exceptionally high value compared to other liquids and consequently makes water a very good subphase for monolayer studies. So when the material is first applied to the surface of water, spreading will continue until the surface pressure has risen to an equilibrium value.

Now we need to know about the equilibrium value of the spreading pressure. This equilibrium spreading pressure is defined as that spontaneously generated when the bulk solid is placed in contact with a water surface [3]. If this pressure is exceeded then the monolayer is expected to form crystals if its surface pressure is greater than the equilibrium pressure. The formation of small droplets or lenses is often observed when excess monolayer material is spread. The measurement of the surface pressure can be done by the two most commonly used methods:

1. Langmuir balance
2. Wilhelmy plate.

Both have the same sensitivities (approximately 10^{-3}mNm^{-1}). But the use of wilhelmy plate is more popular. An absolute measurement of ∏ can be made by suspending a plate from a sensitive balance in the monolayer.

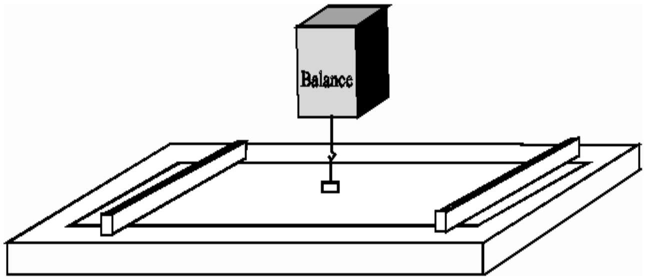


Fig: 1.4 Schematic illustration of a Langmuir film balance with a Wilhelmy plate electrobalance measuring the surface pressure, and barriers for reducing the available surface area.

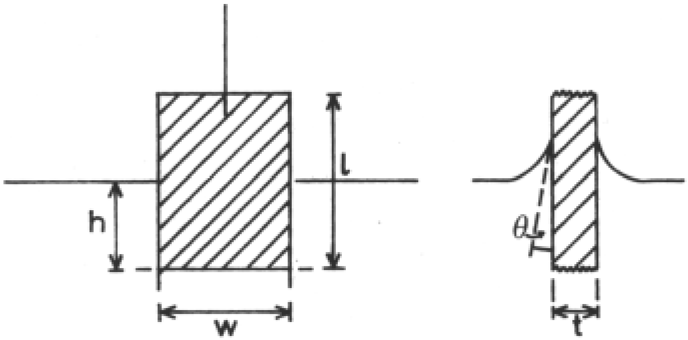


Fig: 1.5 A Wilhelmy plate partially immersed in a water surface.

The plate is very thin and made of platinum, but even plates made of glass, quartz, mica and filter paper can be used. The forces acting on the plate consist of the gravity and surface tension downward, and buoyancy due to displaced water upward. For a rectangular plate of dimensions l_p, w_p and t_p, of material density ρ_p, immersed to a depth h_l in a liquid of density ρ_l, the net downward force is given by the following equation**:**

$$F = \rho_p g l_p w_p t_p + 2 \gamma (t_p w_p) (\cos) - \rho_l g t_l w_l h_l, \qquad (1.2)$$

Where γ is the liquid surface tension, **θ**is the contact angle of the liquid on the solid plate and g is the gravitational constant. The surface pressure is then determined by measuring the change in F for a stationary plate between a clean surface and the same surface with a monolayer present. If the plate is completely wetted by the liquid (i.e. cos**θ** = 1) the surface pressure is then obtained from the following equation:

$$\prod = -\Delta\gamma = -[\Delta F / 2(t_p+w_p)] = -\Delta F / 2w_p, \text{ if } w_p >> t_p \qquad (1.3)$$

The sensitivity can thus be increased by using a very thin plate. The force is in this way determined by measuring the changes in the mass of the plate, which is directly coupled to a sensitive electrobalance. The monolayer can also be held at a constant surface pressure, which is enabled by a computer controlled feedback system between the electrobalance and the motor responsible for the movements of the compressing barrier.

1.1.6 Surface-Pressure isotherms:

In order to have a more realistic view of what is said above before discussing the wilhelmy plate We need to plot the graph of surface pressure versus area per molecule at a constant temperature and this is also commonly known as the π-A-isotherm .This is the most important indicator of the monolayer properties of the amphiphilic materials as shown in fig: 1.6.

Usually an isotherm is recorded by compressing the film (reducing the area with the barriers) at a constant rate while continuously monitoring the surface pressure. Depending on the material being studied, repeated compressions and expansions may be necessary to achieve a reproducible trace. A schematic π-A-isotherm is shown in Figure below. This diagram is not for any particular substance but shows most of the features observed for long chain compounds [6].

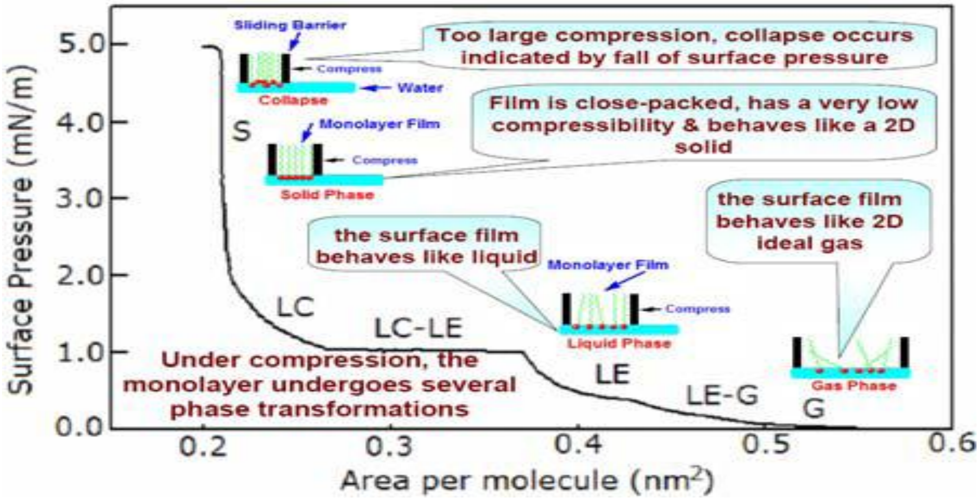


Fig: 1.6 Schematic of surface pressure–area per molecule (π -A) isotherm showing different phases of monolayer at air-water interface.

A number of distinct regions are immediately apparent on examining the isotherm. These regions are called phases. As one can see when the monolayer is compressed it can pass through several different phases which are identified as discontinuities in the isotherm. The phase behaviour of the monolayer is mainly determined by:

1. The physical and chemical properties of the amphiphilic.
2. The subphase temperature and the subphase composition.

For example, various monolayer states exist depending on the length of the hydrocarbon chain length and the magnitude of other cohesive and repulsive forces existing between head groups. An increase in the chain length increases the attraction between molecules, condensing the π-A-isotherm. On the other hand, if an ionizable amphiphilic is used the ionisation of the head groups induces repulsive forces tending to oppose phase transitions**.**

Now we will one by one discuss the different phases appearing on a general level:

GASEOUS STATE

The region marked as G on the figure is known as the gaseous phase. In the gaseous state, the molecules are far apart on the water surface that they exert little force on each other. If the behaviour of the gaseous monolayers can be modeled using a 2-dimensional variation of the conventional kinetic theory, then the molecules in the film may be assumed to move about with an average translational kinetic energy of KT/2 for each degree of freedom [1]. This leads to the following ideal gaseous monolayer equation

$$\Pi a = KT \qquad (1.4)$$

As a gaseous monolayer is compressed on the subphase surface, the expanded (liquid-like) state will normally appear. This phase change is normally thought of as a first order thermodynamic transition.

LE-G PHASE

If we decrease the surface pressure from the gaseous phase we come to the LE-G phase. This phase is commonly referred to as the expanded (liquid-like) state .Usually this is accompanied by the constant pressure region in the isotherm, in which the floating film consists of a mixture of two phases. This phase change is also thought to be of the first-order thermodynamic transition. The molecules are less randomly oriented than the gaseous phase.

LE-PHASE: EXPANDED MONOLAYER PHASE

As the surface pressure is more compressed the liquid state will be formed called the expanded monolayer phase LE .The area per molecule in the expanded monolayer is much less than that expected for the gaseous monolayers .In this phase, the area per molecule varies considerably with the surface pressure and the observed molecular area.

LE-LC PHASE

On further increasing the surface pressure the appearance of the condensed phase will occur in this phase.

LC-PHASE

In this phase the floating film appears as a mixture of two phases: liquid and condensed phases on the application of the further pressure

CONDENSED PHASE

On further increasing the pressure the monolayer gets completely converted into solid state. In the condensed monolayer states the molecules are always closely packed and are oriented with the hydrocarbon chain pointing away from the water surface. The emergence of each condensed phase can be accompanied by constant pressure regions of the isotherm. The constant pressure region is a characteristic of a first order thermodynamic transition. There has been however been some debate on this point .For example, many isotherms like the simple long chain organic compounds do not show(completely) horizontal sections for the expanded to condensed transition. This has led to some speculations that higher order transitions may be involved. However, it is probably more likely that constant ∏ regions are not observed because of the effect of impurities. The finite number of molecules involved in monolayer phase transition (compared to 3-dimensional phase transitions) can also considerably shorten the constant pressure plateau [1].

As the length of the hydrocarbon chain in a simple fatty acid is increased, the expanded state disappears and a direct transition from the gas to a condensed phase takes place.

Monolayers can be compressed to pressures considerably higher than the equilibrium spreading pressure. The surface pressure continues to increase with decreasing surface area until a point is reached where it is not possible to increase the pressure any further and the area of the film decreases if the pressure is kept constant, or the pressure falls if the film is held at a constant area. This is referred to as Collapse. The forces acting at this point are quite high. For e.g.: a surface pressure of 100 mNm^{-1} acting on a layer of molecules 2.5 nm high corresponds to a 3-dimensional pressure of about 400 atmospheres.

The onset of collapse depends on many factors, including the rate at which the monolayer is being compressed and the history of the film. Therefore to be meaningful the pressure value should specify the exact conditions for the collapse. When collapse occurs the molecules are forced out of the monolayers. Some of the aspects of the phase diagram:

The expanded to condensed phase changes in simple long chain compounds are affected by the length of the hydrocarbon chain and the temperature. For example, typical isotherms of a fatty acid with a single hydrocarbon chain (left) and a phospholipid with two hydrocarbon chains (right) are illustrated in fig: 1.7. Fatty acid has three distinct regions gas (G), liquid (L1) and solid (S), while the phospholipid has an additional almost horizontal transition phase (L2-L1) between the two different liquid phases. This is very common for phospholipids and the position of this horizontal transition phase is very temperature dependent. As the temperature is increased the surface pressure value at which the horizontal transition phase occurs will increase and vice versa**.**

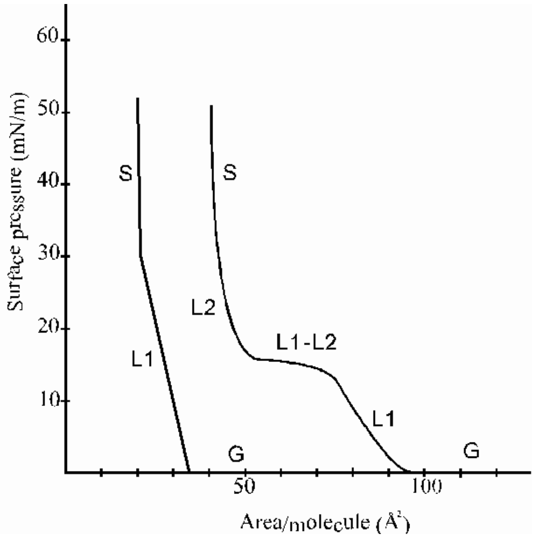


Fig: 1.7 Typical isotherm of a fatty acid and a phospholipid.

Other structures are also possible for the amphiphilic molecules. For example, if the molecules possess a strong polar head group relative to the non-polar part of the molecule, "micelles" are formed if the concentration of the amphiphilic material is above a certain value (critical micelle concentration) [7]. In this arrangement the molecules are arranged in spheres, with the polar head groups on the outside and the hydrocarbon chains towards the centre as shown below in fig 1.8.

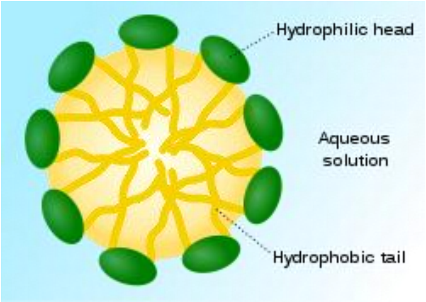


Fig: 1.8 Scheme of a micelle formed by phospholipids in an aqueous solution.

If the head group of the amphiphilic molecules is not strong compared with the hydrophobic part, the molecules can form spherical “vesciles” in which the double layers form the shell with water both outside and inside e.g. in phospholipids. They can be visualised as a bubble of liquid within another liquid as shown in the figure shown 1.9.

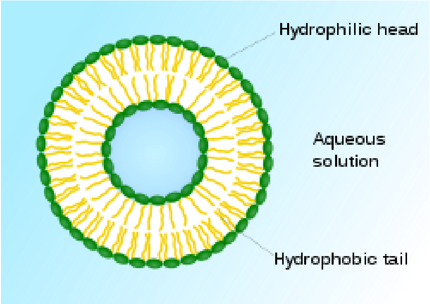


Fig: 1.9 A schematic diagram of the vesciles.

1.2 LANGMUIR BLODGETT FILM DEPOSITION TECHNIQUE

The experimental setup of the LB technique along with the detailed discussion of each part of the setup is discussed here in this section.

The LB technique can be divided into two parts: The first one includes the building of the pressure till the condensed monolayer is formed and the second one includes the dipping of the substrate in the condensed monolayer phase for its deposition.

1.2.1 Various parts of the set up

A) Trough

The LB trough's general objective is to create, modify and study the properties of monolayers at gas-liquid or liquid-liquid interface of amphiphilic molecules. An amphiphilic molecule is one that contains both a hydrophobic and hydrophilic domain (e.g. soaps and detergents). The LB trough helps to prepare a monolayer of amphiphilic molecules on the surface of a liquid, and then compress or expand these molecules on the surface, thereby modifying the molecular density, or area per molecule. This is accomplished by placing a subphase (usually water) in a trough, spreading a given amphiphile over the surface, and then compressing the surface with barriers .As shown in the figure below:

Fig: 1.10 A schematic diagram of LB Trough.

B) Materials appropriate for the trough

In early experiments, the trough was first constructed from metals such as brass. However difficulties arose with contamination of the sub-phase by metal ions. To combat this, glass troughs were used for a time, with a wax coating to prevent contamination from glass pores. This was eventually abandoned in favour of plastics that were insoluble in ordinary solvents, such as Teflon (polytetrafluoroethylene). Teflon is hydrophobic and chemically inert, making it a highly suitable material and the most commonly used for troughs today. Occasionally metal or glass troughs coated with a thin layer of Teflon are used [8].

The trough is glued onto an aluminium base plate, in which there are water channels for the thermostation on the subphase. The temperature is adjusted with a water bath circulator, which is connected to the trough with special connectors. These connectors include valves in both parts, so the connection can be opened without any leakage.

C) Substrate

It’s a substance that on which the condensed monolayer transfer takes place. The substrate can be of two types: - hydrophilic (e.g.: glass) or hydrophobic (e.g.: mica).Now there are many parameters associated with the substrate surface that can influence the deposition :

1. Its exact chemical composition may affect ion exchange in the substrate surface (whether it contains gaps or voids) is also important in determining the quality of the deposited layer.

2. The adhesion of the first layer to the underlying substrate is particularly critical and will determine the quality of the subsequent layers.

D) Barriers

Systems are made of movable Teflon barrier blocks that slide parallel to the walls of the trough and are in contact with the top of the fluid. Another version with a variable perimeter working zone is the circular trough in which the monolayer is located between two radial barriers. A constant perimeter trough was developed later in which the barrier is a flexible Teflon tape wrapped around three pairs of rollers. One of the pairs is fixed and the other two are movable on trolleys, so that the length of the tape remains constant as the area of the working zone is changed. Some troughs allow for preparation and deposition of alternating monolayers by having two separate working zones that can be compressed independently or synchronously by the barriers [8].

The barriers are made out of hydrophilic material, which ensures that the film does not escape the barrier. The barrier material is polyacetal (Derlin) and it should be noted that Derlin is not resistant to acids or chloroform, so these should not be used as cleaning agents. Chlorinated solvents such as these can still be used as spreading solvents. The barrier is equipped with a round rod, which fits into the barrier holder.

E) Barrier driving system

The barrier position is controlled by a micro step driven stepping motor. The motor moves the barrier holder using a tooth belt. The holder itself is attached to a linear motion system, which is equipped with ball bearings. The barrier driving system is equipped with adjustable safety switches which stop the barrier immediately when the barrier holder hits the switches. The position is relative and so a zero point at a known position must be set manually [9].

F) Surface balance

The surface pressure is measured by using the Wilhelmy plate method (round rod optional) [1]. The Wilhelmy plate is a carefully sandblasted platinum plate or a clean paper plate, which is put partly under the surface of the subphase. Normal practice is to position the plate so that one third of it is under the subphase. The force acting on the plate depends on surface pressure. This force is measured using the electro-balance [9].

1.2.2 Cleaning

Before an experiment the trough and barriers must be cleaned. Use rubber gloves to minimise oils from the skin contaminating the apparatus. The importance of cleanliness cannot be overstated. A recommended cleaning procedure is to first brush with a soft brush covered in ethanol or another organic solvent (mechanical and chemical cleaning) and then rinse with ion exchanged water. Scratches on the surface should be taken care.

1.2.3 Deposition principle

The surface pressure and temperature of the monolayer are first controlled so that so that the film is in the stable state. For e.g. for fatty acid type materials, deposition generally proceeds from either the Liquid Solid or Solid phase The molecular organization in the resulting LB film will depend on these initial conditions.

The monolayer is applied to the subphase via a micro syringe. Following compression through the barriers provided at the sides of the trough, Langmuir-Blodgett troughs are used to transfer Langmuir films to solid substrates in a controlled environment. In the case of Langmuir-Blodgett (LB) deposition the sample is moved vertically through the monolayer while with the Langmuir-Schaefer (LS) method the sample is brought to the interface horizontally.

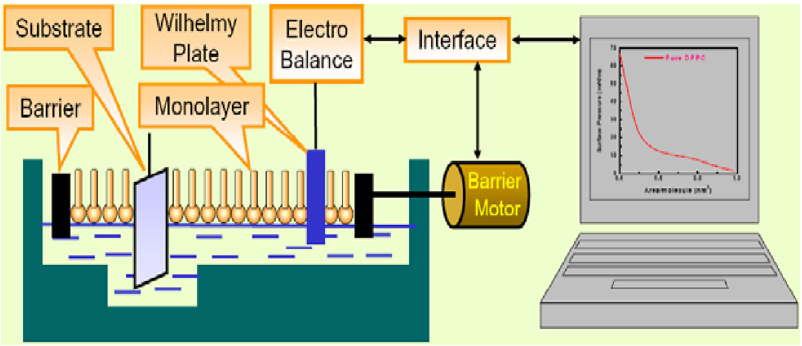
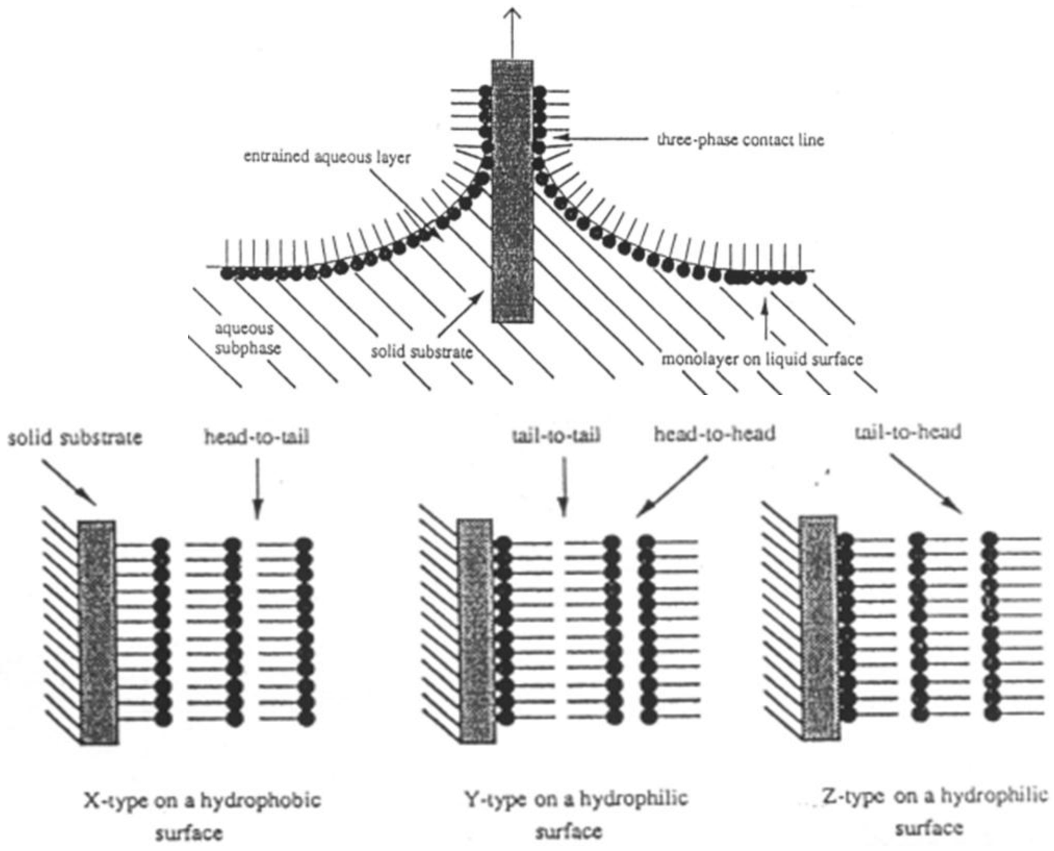


Fig: 1.11 Schematic of LB trough. The Wilhelmy plate monitors the surface through a microbalance interfaced with computer. Barrier movement is also controlled by computer. And on the left is: a typical LB film deposition instrument installed in our laboratory.

By dipping a solid substrate up and down through the monolayer while simultaneously keeping the surface pressure constant by a computer controlled feedback system between the electrobalance measuring the surface pressure and the barrier moving mechanism. Consequently the floating monolayer is adsorbed to the solid substrate. Multilayer structures of hundreds of layers can be produced [1]. These multilayer structures are commonly called Langmuir-Blodgett or simply LB films. The deposition process is schematically shown in fig: 1.12.



(i) **(ii)** **(iii)**

Fig: 1.12 Deposition of a floating monolayer on a solid substrate and in the lower part of the diagram is Different types of deposited LB films.

If the substrate is hydrophilic then the monolayer is deposited on each transversal of the monolayer /air interface. As shown in figure part (ii) these stack in ahead-to-head and tail-to tail pattern: this deposition mode is known as Y-type. Although this is the most frequently encountered situation, there are instances in which the floating monolayer is only transferred to the substrate as its being inserted into subphase, or only transferred to the substrate as its being removed. These deposition modes are called X-type (monolayer transfer on the down stroke only). It is favoured by high pH values and also the appropriate choice of dipping conditions. The Z-type transfers on the upstroke only. These are favoured by low pH values. The physical insight may be gained through the following diagram:

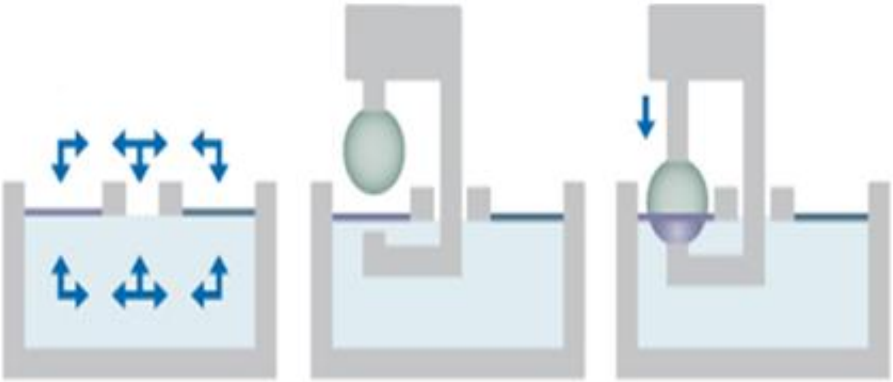


Fig: 1.13 A schematic showing the Deposition mechanism.

Density, thickness and homogeneity properties are preserved when transferring the Langmuir film onto the sample, giving the possibility to make organized multilayer structures with varying layer composition. There are several parameters that effect on what type of LB film is produced. These are:

1. The nature of the spread film,
2. The subphase composition and temperature
3. The surface pressure during the deposition and the deposition speed
4. The type and nature of the solid substrate
5. The time the solid substrate is stored in air or in the subphase between the deposition cycles.

1.2.4 Transfer ratio

The quantity and the quality of the deposited monolayer on a solid support is measured by the “Transfer Ratio” (Tr). This is defined as the ratio between the decrease in monolayer area during a deposition stroke i.e. A_L, and the area of the substrate, A_s .Therefore we can write that:

$$\Gamma = A_L/A_s \qquad (1.5)$$

For ideal transfer the Tr is equal to 1.The transfer ratio outside the range of 0.95 to 1.05 suggest poor film homogeneity. Depending on the behaviour of the molecule the solid substrate can be dipped through the film until the desired thickness of the film is achieved. Different kind of LB multilayers can be obtained by successive deposition of monolayers on the same substrate.

1.2.5 Deposition speed

As the substrate is lowered into the subphase, it can be moved quite rapidly without affecting the monolayer transfer. However, on withdraw through the floating monolayer it is important not to raise the substrate faster than the rate at which the water drains from the solid. This drainage is not due to the gravity but is a result of the adhesion between the monolayer being transferred and the material on the substrate which acts along the line of contact and so drives out the water film. The rate at which the film can be build up is limited by the rate at which ascending substrate sheds water. It is normal to transfer the initial monolayer onto a solid substrate relatively slowly: speeds of 10 $\mu m\ s^{-1}$ to few $mms^{-1}$are typical. However, much faster speeds, up to several cm s^{-1}, are possible once the initial layer has been transferred. To improve the film deposition, it is often appropriate to temporarily halt the dipping process after an upstroke and wait until the monolayer is completely dry before continuing the deposition cycle [1].

1.2.6 Water quality

The water subphase should be of highest purity .Both distilled and deionized water can be used. Cleanliness is the keyword to surface chemistry for depositing thin films.

1.2.7 Deposition onto the rough and porous surfaces

The surfaces of actual substrate that are used for LB deposition are likely to be rough on a molecular scale; they may even contain large pits or holes. The monolayer may be deposited conformally, preserving the surface variations of the underlying substrate, or it may span the voids and other defects in the substrate .Under water; a bilayer formed. Experiments show that LB multilayer films can be used to reduce the permeation of gases through porous membranes. However, if the substrate is very irregular, then it is possible that the LB film can follow the undulation. For surface roughness on the nanometre scale, at the moment of deposition, the monolayer will bridge over voids, supported by a layer of water. When this layer has drained off or dried, the film will collapse [1].

1.2.8 Post deposition treatments

Following LB deposition it is possible to treat monolayer and multilayer films in several ways. These from simple processes, such as storage in a desiccator to remove the water ,to more complex procedures for cross linking the monomer molecules in an LB array .Other common procedure are outlined below:

(i) Skeletonization

This process can be understood by taking some example say of long chain fatty acid materials. They are often deposited as a mixture of a fatty acid and a salt. The exact composition of the deposited layer depends upon the type of ion in the subphase and the pH of the latter. The free acid may be removed from the film by soaking the LB layers in a suitable solvent. One to five minutes in alcohol or acetone is usually sufficient to remove the free acid from a LB film. This skelotonization process reduces the refractive index of the multilayer structure making it suitable for use as an antireflection coating for glass [1].

(ii) Removal of outer layers

In air, LB layers of long chain materials are usually hydrophobic (with the alkyl chain on outside), while the structures are hydrophobic under water. It might be thought that it is relatively easy to produce a polar surface in air by changing the dipping sequence for example, finishing the LB deposition under water, removing the floating monolayer and withdrawing the multilayer structure through the clean water surface. This usually leads to the hydrophobic film, as the outer layer falls off when the substrate is raised through the water surface. Two other approaches have also been suggested by:

1. The multilayer is polymerized under the water surface (e.g., using ultraviolet light).The floating monomer monolayer is then removed before the substrate with the stabilized polar surface is withdrawn.
2. The transfer of the monomer material takes place normally and the deposition is stopped with the substrate submerged. The floating monomer monolayer is then removed, replaced by a simple long chain say fatty acid layer, and the monomer multilayer structure will be hydrophobic in air. However, after polymerization the required polar surface may be exposed by removing the outer fatty acid layer in a solvent [1].

(iii) Elimination of the alkyl chain

All LB material possesses long alkyl chains. These confer the monolayer forming ability to the compounds. However, the presence of such chains in the deposited multilayer can reduce the thermal stability of the functional groups. A long alkyl chain is used for the monolayer formation and, after LB deposition; this group is eliminated, usually thermally. For example this technique has been applied to prepare polyamide and polyphenylenevinylene LB films [10].

1.3. MONOLAYER MATERIALS

Different materials are favourable for this technique. A wide range of materials are suitable for the LB technique for example: fatty acids, substituted aromatic compounds, porphyrins and phthalocyanines, conducting polymers, liquid crystals etc. The thumb rule for the material to make it appropriate for the LB technique is that it should be amphiphilic in nature i.e. it should be having both water loving and water hating part. Some details of the materials used in our work are given below:

1.3.1 Fatty acids

1.3.1.1 Introduction to fatty acids

Fatty acids are merely carboxylic acids with long hydrocarbon chains. The hydrocarbon chain length may vary from 10-30 carbons (most usual is 12-18). Most naturally occurring fatty acids have a chain of an even number of carbon atoms, from 4 to 28[11]. The non-polar hydrocarbon alkane chain is an important counter balance to the polar acid functional group. In acids with only a few carbons, the acid functional group dominates and gives the whole molecule a polar character. However, in fatty acids, the non-polar hydrocarbon chain gives the molecule a non- polar character.

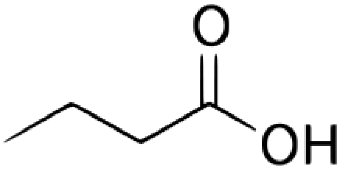


Fig: 1.14 A diagram of butyric acid, a short chain fatty acid.

1.3.1.2 Types of fatty acid

a) Unsaturated fatty acids

Unsaturated fatty acids have one or more double bonds between carbon atoms. (Pairs of carbon atoms connected by double bonds can be saturated by adding hydrogen atoms to them, converting the double bonds to single bonds. Therefore, the double bonds are called unsaturated.)

The two carbon atoms in the chain that are bound next to either side of the double bond can occur in a cis or trans configuration.

Cis:

A cis configuration means that adjacent hydrogen atoms are on the same side of the double bond. The rigidity of the double bond freezes its conformation and, in the case of the cis isomer, causes the chain to bend and restricts the conformational freedom of the fatty acid. The more double bonds the chain has in the cis configuration, the less flexibility it has.

Trans:

A trans configuration, by contrast, means that the next two hydrogen atoms are bound to opposite sides of the double bond. As a result, they do not cause the chain to bend much, and their shape is similar to straight saturated fatty acids.

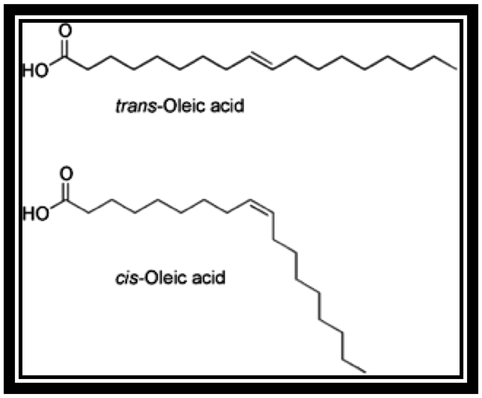


Fig: 1.15 A schematic of the difference between cis and trans fatty acids.

b) Saturated fatty acids

Saturated fatty acids are long-chain carboxylic acids that usually have between 12 and 24 carbon atoms and have no double bonds. Thus, saturated fatty acids are saturated with hydrogen (since double bonds reduce the number of hydrogens on each carbon). Because saturated fatty acids have only single bonds, each carbon atom within the chain has 2 hydrogen atoms (except for the omega carbon at the end that has 3 hydrogens).

They differ in length as well.

Length of free fatty acid chains

Fatty acid chains differ by length, often categorized as short, medium, or long.

- Short-Chain Fatty Acids (SCFA) are fatty acids with aliphatic tails of fewer than six carbons (i.e. butyric acid).
- Medium-Chain Fatty Acids (MCFA) are fatty acids with aliphatic tails of 6–12 carbons [12].
- Long-chain fatty acids (LCFA) are fatty acids with aliphatic tails longer than 12 carbons [13].
- Very-Long-Chain Fatty Acids (VLCFA) are fatty acids with aliphatic tails longer than 22 carbons.

1.3.2 Reason for their applicability to the LB technique

A simple long-chain fatty acid consists of –an alkyl chain-terminating in a carboxylic acid group (COOH).The polar acid head confers water solubility while the hydrocarbon chain prevents it. It is the balance between these two opposing forces that results in the formation of the insoluble monolayer at the air/water interface. Any change in the nature of either the alkyl chain or the polar end group will affect the monolayer properties.

The solubility of the fatty acid in water decreases as the length of the alkyl chain is increased. To obtain the insoluble monolayer of a non-ionized fatty acid (i.e. the situation at sufficiently low pH values), the molecule must contain 12 carbon atoms. For e.g.: $C_{11}H_{23}COOH$: n-dodecanoic acid forms a slightly soluble gaseous monolayer at the low temperatures. The addition of two or more carbon atoms causes the gas phase to condense at lower surface pressures and an expanded monolayer phase to be formed. The further addition of the carbon atom results in the appearance of condensed monolayer phases. Above we discussed about the long chain acid and now instead of acid we will discuss some other “head group”:

Long chain compounds terminating in some other than acid group will form the insoluble monolayer at the air/water interface. The polarity of the head group will determine the stability of the layer. The absence of the head group (i.e. a simple long chain hydrocarbon) or a weakly polar head group (e.g.: CH_2I or CH_2Cl) will simply result in the formation of the lenses or drops on the water surface. On the other hand if the dipole moment associated with the headgroup is large (e.g.: SO_3^-), then the compound becomes too soluble in the aqueous subphase. The high surface pressure condensed LS, S and CS monolayer states as explained earlier in the isotherms are found to occur with long chain amphiphilic compounds possessing a variety of polar ends. Thus is evident that these phases are associated with different arrangements of the hydrocarbon chains [1].

A simple modification to the alkyl group in a long-chain fatty acid is to replace some or all, of the hytdrogen atoms with fluorine. Since a fluorocarbon chain is more hydrophobic than the hydrocarbon chain, it is expected that shorter chains will be needed to confer monolayer forming properties on a particular polar head group. This is found to be the case. Monolayers of many amphiphiles containing fluorocarbon chains are more stable than those formed from their hydrocarbon counterpart [1].

The following LB Films have been made using fatty acids:

1. LB Films of mixed protein–fatty acid onto Si/SiO2 substrates [11].
2. Conducting LB films of BEDO-TTF (BO) and stearic acid [12].
3. Langmuir–Blodgett films of fatty acids and their salts [13].
4. Different fatty acid salt (cadmium arachidate, lead arachidate, zinc arachidate etc.) Langmuir–Blodgett (LB) films were deposited onto piezoelectric quartz crystal microbalance (QCM) electrode surfaces [14].
5. A composite film of dimyristoyl-phosphatidylcoline (DMPC) and bacteriorhodopsin (BR) fabricated by multilayer molecular thin film method using fatty acid and lipid on a quartz substrate or a hydrogenated amorphous silicon thin film [15].
6. Recent progress in the metallic conducting Langmuir–Blodgett (LB) films built from TTF derivative and fatty acid is reported [16].
7. Langmuir–Blodgett films of long-chain hydroxyl fatty acids e.g. of 2-hydroxy stearic acid (2 HSA) and 16-hydroxy stearic acid (16-HSA) [17].
8. Mixed Langmuir–Blodgett (LB) films based on crown derivatized platinum nanoparticles (NPs) and fatty acid [18].
9. Langmuir-Blodgett (LB) films of fatty acid salts of bivalent metals [19].

1.3.3 Liquid crystals

Everyone is familiar with solids, liquids, and gases as the three common phases of matter, fewer people recognize that certain substances exist in a fourth phase of matter between the solid and liquid phases. This phase of matter is called the liquid crystal phase and is as distinct from the three common phases as they are from each other. They were first discovered in 1888 by F. Reinitzer. He is known as the grandfather of the Liquid crystal science [23-27]. In the solid phase, the molecules have a large amount of both positional and orientational order, in that the molecules maintain specific positions and orientations. In the liquid phase, there is no positional and orientational order i.e. totally disorder state of molecules, since the molecules diffuse about quite randomly, constantly changing both their positions and orientations [23]. In the liquid crystal phase, the molecules can diffuse about, much as they do in liquids i.e. an intermediate state between solid and liquids, but as they diffuse they maintain a small amount of orientational order and sometimes a small amount of positional order also. This is illustrated in fig. 1.16, where it is clear that the snapshot of the molecules in the liquid crystal phase reveals that there is a slight tendency for the molecules to point up and down.

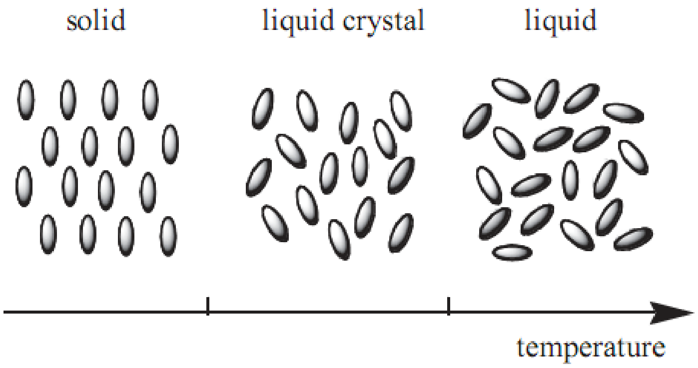


Fig: 1.16 A schematic showing difference in the molecular structure of solids, liquids and gas.

This preferred direction of orientation is called the director, and a liquid crystal with only orientational order as shown in fig. 1.16 is called a nematic liquid crystal. The amount of order is measured by the order parameter of the liquid crystal, which can be found by averaging the function:

$$S = \langle P_2(\cos\theta) \rangle = \left\langle \frac{3\cos^2\theta - 1}{2} \right\rangle \qquad (1.6)$$

where θ is the angle that a long axis make with a particular direction.

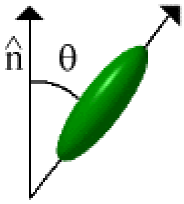


Fig: 1.17 A schematic showing the director.

Averaging this function of θ instead of just θ alone gives a value between 0 and 1 for the amount of orientational order. The order parameter is highly dependent on temperature is illustrated in figure 1.17.

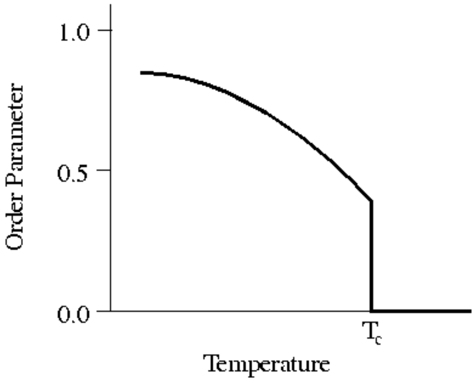


Fig: 1.18 Schematic diagram showing the variation of the order parameter with the temperature.

The molecules of a LC phase diffuse much like the molecules of a liquid, but as they do so they maintain some degree of orientational order and sometimes positional order also [23]. The amount of order is quite small relative to a crystal. This is due to the fact that most of the order of the crystal is lost when it transforms to a LC is revealed by the amount of the latent heat. The value is around 250 J/g which is very typical of a crystal to liquid transition. And when a LC transform to a liquid the latent heat is as small as 5 J/g. The small amount of order in a LC reveals itself by mechanical and electromagnetic properties typical of crystals [28].

1.3.3.1 Types of liquid crystals:

A number of different types of molecules form liquid crystal phases. The common property among them is anisotropy.

The LCs based on the molecular structure:

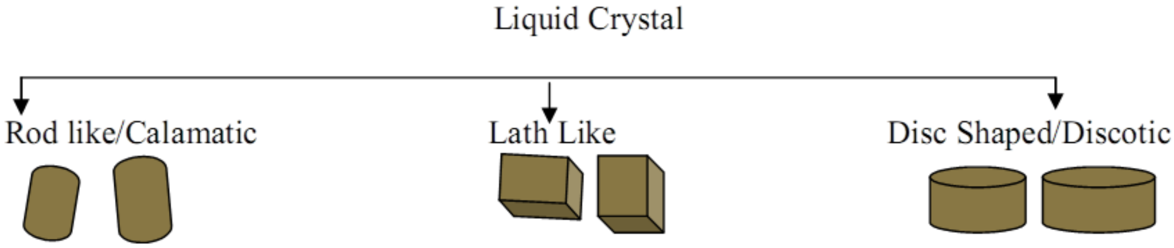


Fig: 1.19 The figure shows the molecular structure of the various Liquid Crystals.

The other type of categorization is based on the molecular order. They are:

1. Thermotropic Liquid Crystal: Both calamatic and discotic liquid crystal are called thermotropic liquid crystals. The liquid crystal phase is stable for a certain range of temperature interval. Pure compounds or mixtures fall in this category.
2. Lyotropic Liquid Crystal: There are some types of molecules which forms LCs only when mixed with a solvent of some kind. For these compounds the concentration of these compounds is just as important, than the temperature in determining whether a LC is stable or not. These compounds are given the name Lyotropic LC.

1.3.3.2 Liquid crystal phases

The various LC phases (called mesophases) can be characterized by the type of ordering. One can distinguish positional order (whether molecules are arranged in any sort of ordered lattice) and orientational order (whether molecules are mostly pointing in the same direction), and moreover order can be either short-range (only between molecules close to each other) or long-range (extending to larger, sometimes macroscopic, dimensions). . It was in 1922 that a French scientist named George Friedel [29-30] proposed a classification scheme based on the molecular arrangement where he named different liquid crystal systems: nematic, smectic and cholesterols.

The various LC phases are discussed below:

a) Nematic phase: The name comes from the Greek word for thread, since in a polarizing microscope; there are often many dark lines visible which are like thread [1]. These lines are defects in the orientational order and are called disclinations. The direction preferred by the molecules is undefined at these disclinations. In this phase the molecules maintain a preferred orientational direction. There is no positional order in this phase as shown in the fig: 1.20.

Fig: 1.20 Molecular arrangements in a nematic phase.

The following figure shows the texture of a LC in a nematic phase:-

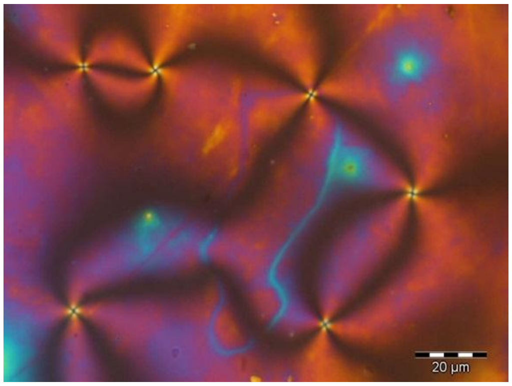


Fig: 1.21 Texture of a liquid crystal in a nematic phase.

b) Cholestric phase: The cholesteric phase is like the nematic phase in having long-range orientation order and no long-range order in positions of the centers of mass of molecules. It differs from the nematic phase in that the director varies in direction throughout the medium in a regular way. The configuration is precisely what one would obtain by twisting about the x axis a nematic initially aligned along the y axis. In any plane perpendicular to the twist axis the long axes of the molecules tend to align along a single preferred direction in this plane, but in a series of equidistant parallel planes, the preferred direction rotates through a fixed angle. The secondary structure of the cholesteric is characterized by the distance measured along the twist axis over which the director rotates through a full circle. This distance is called the pitch of the cholesteric. The periodicity length of the cholesteric is actually only half this distance since n and −n are indistinguishable. A nematic liquid crystal is just a cholesteric of infinite pitch, and is not really an independent case. In particular, there is no phase transition between nematic and cholesteric phases in a given material.

c) Smectic Phase: The important feature of the smectic phase, which distinguishes it from the nematic, is its stratification. The molecules are arranged in layers and exhibit some correlations in their positions in addition to the orientational ordering.

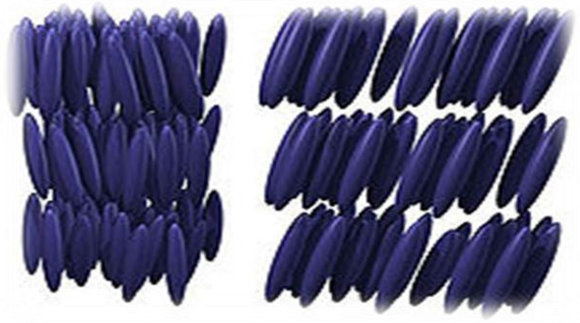


Figure: 1.22 Smectic A phase (left) has molecules organized into layers. In the smectic C phase (right) the molecules are tilted inside the layers.

A number of different classes of smectics have been recognized.

i. Smectic A: In addition to the orientational order of nematics, there is positional order since the centers of mass are arranged in layers. If the director is perpendicular to the layers in which the molecules are most likely to be, then it is called a Smectic A phase.
ii. Smectic C: If the director makes an angle other than the 90^0 to those layers, it is a Smectic C phase. In these two phases, there is no positional order within the layers. The name smectic comes from the Greek word for soap, since the mechanical properties of these phases were of the soap like.

Many phases with the layering order of the smectic A and C phases are discovered. Some involve hexagonal or rectangular positional order in the plane of the layers but not from one layer to the next for the directions of axes of the rectangular or hexagonal lattice. This type of order has come to be known as bond orientational order and the phase that possess it is known as smectic hexatic phase. And many more like them exist. The best way to keep track of all these smectic and crystal phases is to use a chart listing the various phases and their important properties.

Table (1.1) The table showing the various phases and their properties.

Non Tilted Phases	Tilted Phases	In Plane Order	Molecular Rotation
Smectic A	Smectic C	None	unhindered
Hexatic B	Hexatic F, I	Bond order	unhindered
Crystal B	Crystal G, J	Positional	unhindered
Crystal E	Crystal H, K	Positional	hindered

1.3.5 Reason for their applicability to the LB technique

MOST practical applications of liquid crystals require control of molecular alignment at macroscopic scales this is achieved most simply by confining the liquid-crystalline phase between mechanically rubbed surfaces. Recent developments have shown that liquid-crystal alignment can also be controlled by optical means by dispersion with UV-curable polymers, dyes and sometimes by making the liquid crystal mixtures at optimized ratios. These light sensitive dispersions can be oriented either homotropically or homogenously by illumination with polarized light in a desired direction. The thin films of LC are used for information storage and display devices of the liquid crystals. Liquid crystals have characteristics of fast electro-optic switching and optical bistability.

The following LB films of LCs have been synthesized:

1. Sensitive methods for estimating the anchoring strength of nematic liquid crystals on Langmuir-Blodgett monolayers of fatty acids [31].
2. Langmuir Blodgett films of arachidic acid and a nematic liquid crystal: Characterization and use in homeotropic alignment [32].

3. Studies on the aggregation behaviour of a side-chain liquid crystalline polymer in Langmuir-Blodgett films [33].
4. Study of Langmuir and Langmuir-Blodgett Films of Ferroelectric Liquid Crystals by Fourier Transform of Infrared and Polarization Modulated Infrared Reflection Absorption Spectroscopies [34].
5. Liquid Crystal Side Chain Copolymers as Langmuir-Blodgett and Magnetically Aligned Thin Films [35].
6. Ultrathin Films of Smectic Liquid Crystals on Solid Substrates [36].
7. "Command Surfaces" of Langmuir-Blodgett Films. Photoregulations of Liquid Crystal Alignment by Molecularly Tailored Surface Azobenzene Layers [37].
8. Molecular orientation in liquid crystals on a photochromic polyion complex LB film by FTIR spectroscopy [38].
9. Monolayers and Langmuir-Blodgett Films of a Liquid-Crystalline Polysiloxane with a Schiff Base Mesogenic Unit in the Side Chain [39].
10. Surface Pressure-Induced Layer Growth of a Monolayer at the Air-Water Interface [40].

REFERENCES

1. Michael C. Petty, Handbook of Langmuir-Blodgett Films, Cambridge University Press, (1996).
2. http://www.ksvinc.com/LB.htm#Deposition - LB films.
3. M. Iwahashi, N. Maehara,Y. Kaneko, T.Seimiya, S.R.Middleton, N.R.Pallas, B.A.Pathica, Spreading pressures for fatty acid crystals at the air/ water interface, J Chem . Soc. Faraday Trans., **81**, 973-981(1985).
4. A. J. Walton, Three phases of matter, McGraw-Hill, Maidenhead, (1976).
5. A.W. Adamson, Physical Chemistry of surfaces, 4th edition, John Wiley, New York, (1982).
6. G.L. Gaines, Insoluble Monolayers at liquid gas interfaces, Wiley-Interscience, New York (1966).
7. W.D. Harkins, Physical Chemistry of surface Films, Reinhold, New York (1952).
8. O. V. Chechel, & E. N. Nikolaev, Devices for production of Langmuir-Blodgett films – Review (1991).
9. K.S.V., Lab manual, Operational manual LB device, 6-8, 11-14.
10. Y. Nishikata, M.Kakimoto, A. Morikawa, Y. Imai, Preparation and characterization of poly(amide-imide) multilayer films, Thin Solid Films, **160**,15, (1988).
11. J. M. Chovelon, M. Provence, N. Jaffrezic-Renault, S. Alexandre, J. M. Valleton, Materials Science and Engineering: C, Volume 22, Issue 1, pp 79-85, (2002).
12. Y. Ishizaki, M. Suzuki, H. Ohnuki, T. Imakubo, M. Izumi, Synthetic Metals, Vol. **133-134**, 669-670 (2003).
13. J. B. Peng, G. T. Barnes, I. R. Gentle, Advances in Colloid and Interface Science, Vol. **91**, Issue 2, pp 163-219 (2001).
14. Hanming Ding, Victor Erokhin, Manoj Kumar Ram, Sergio Paddeu, Claudio Nicolini, Materials Science and Engineering: C, Vol. **11**, Issue 2, pp. 121-128 (2000).
15. Yutaka Tsujiuchi, Keigo Furuya, Jun Matsumoto, Yukinobu Makino, Manabu Ito, Hiroshi Masumoto, Takashi Goto, Thin Solid Films, Vol. **518**, Issue 2, pp. 600-605 (2009).

16. H. Ohnuki, Y. Ishizaki, M. Suzuki, B. Desbat, P. Delhaes, M. Giffard, T. Imakubo, G. Mabon, M. Izumi, Materials Science and Engineering: C, Vol. **22**, Issue 2, pp. 227-232 (2002).
17. A. Dhathathreyan, Colloids and Surfaces A: Physicochemical and Engineering Aspects, Vol. **318**, Issues 1-3, pp.307-314 (2008).
18. Sara Cavaliere-Jaricot, Julien Haccoun, Arnaud Etcheberry, Michel Herlem, Henri Perez, Electrochimica Acta, Vol. **53**, Issue 20, pages 5992-5999 (2008).
19. V. Erokhin, P. Facci, S. Carrara, C. Nicolini, Thin Solid Films, Vol. **284-285**, pp. 891-893 (1996).
20. IUPAC Compendium of Chemical Terminology, 2nd Ed., International Union of Pure and Applied Chemistry (1997).
21. P.J.Collings, Liquid Crystals: Nature's Delicate Phase of Matter, Princeton University Press, Princeton, (1990).
22. P.G. De gennes and J. Prost, The Physics of Liquid Crystals, 2nd Ed., Oxford University Press, Oxford, (1995).
23. S. Chandrasekhar, Liquid Crystals 2nd Ed., Cambridge University Press, Cambridge, (1992).
24. F. Reinitzer, Monatsch Chem., **9**, 421, (1888).
25. O. Lehmann, Z. Physikal. Chem., **4**, 462, (1889).
26. P.J. Collings and M.Hird, Introduction to LC: Chemistry and Physics, Taylor and francis Ltd, (1997).
27. R.B. Meyer, L. Liebert, L. Strzelecki and P. Keller, J.Phys. Lett. 36, L69, (1975).
28. D.Demus and L.Richter, Textures of Liquid Crystals (Verlag Chemie, New York), (1978).
29. Valentina S. U. Fazio, Francesca Nannelli, and Lachezar Komitov, Physical Review E, **63**, 061712.
30. John Collins, Denis Funfschilling, Michael Dennin, Thin Solid Films, **496**, 601, (2006).
31. Xiao Chen, Qing-Bin Xue, Kong-Zhang Yang, Qi-Zhen Zhang, Thin Solid Films 286, 232, (1996).
32. S. Payan, B. Desbat, Langmuir, **12**, 6627, (1996).

33. Z. Ali-Adib et al., Langmuir, **7**, 363, (1991).

34. M. Woolley, R. H. Tredgold, P. Hodge, Langmuir, **11**, 683, (1995).

35. Takahiro Seki et al., Langmuir,**9**, 211-218, (1993)

36. Takeshi Kawai, Thin Solid Films, **301,** 225, (1997).

37. Xiao Chen, Qing-Bin Xue, Kong-Zhang Yang, Langmuir, **11**, 4082, (1995).

38. J. Y. Fang, R. A. Uphaus, Langmuir, **10**, 1005, (1994).

CHAPTER-2

LITERATURE REVIEW

The first experimental studies of the interaction of LB films with nematic liquid crystals (NLCS) were initiated in 1978 [5-7]. Still earlier, the mode of anchoring of the nematic director on self-assembled amphiphilic monolayers, obtained by dipping the substrates in surfactant solutions, was studied [1-4], both experimentally and theoretically (using a thermodynamic approach in terms of interfacial surface tension). A shortcoming of the self-assembled films is that their surface density is usually not known and could hardly be controlled, although a dependence on the volume concentration is to be expected. The elegant work of Proust and Ter-Minassian-Saraga [l], providing a direct measure of this density by measuring the surface radioactivity of a labelled surfactant, cetyltrimethylammonium bromide (CTAB), is still the only one of this type. Nevertheless, qualitative observations of the variation of anchoring on self-assembled films of variable surface density are possible in a concentration gradient of the surfactant, e.g. Lecithin181. Since then, a number of papers [9-19] have been published, emphasizing, in particular, the mode of nematic anchoring on multilayer LB films and its dependence on the number of layers [9.10,11,13], the temperature driven anchoring transitions [14,17,18] and the theory [9,13,14,19]. Till date the work is being done on this.

Takahiro Seki et al. in 1992 [19] investigated reversible homeotropic p: planar photochemical alignment controls of a nematic liquid -crystal (LC) using photochromic command layers comprised of Langmuir-Blodgett (LB) film of side chain type azobenzene (Az) amphiphilic polymers. Photo response of the LC alignment are examined by changing such details as the molecular structure of the LB films, number of deposited layers, two dimensional density of Az units, the deposition method, and the method of light irradiation. It was confirmed by this LB study that single Az monolayers are sufficient to induce LC alignment changes, provided that the Az unit is separated from the poly (viny1 alcohol) backbone by a methylene spacer of adequate length. The effect of the spacer length on the commanding ability could be correlated to UV-Vis spectral changes of Az monolayers upon contact with LC molecules. As for the packing density of the Az unit on the substrate, photoregulation requires an area of less than 1.0 nm^2 per Az unit. Both vertical dipping and horizontal lifting methods were applicable to obtain photo responsive LC cells; however, preparation by the vertical dipping was more beneficial in that homogeneously aligning LB films are obtained on which LC molecules are oriented parallel to the dipping direction. Irradiation of linearly polarized UV light induced subsequent reorientation of LC molecules directing orthogonal to the polarization plane. This reorientation behaviour strongly depended on the spacer length of the Az LB films and deposition numbers.

M. Woolley, R. H. Tredgold and P. Hodge in 1994 [20] deposited on a wide variety of substrates by evaporation in vacuo and, where possible, by the Langmuir-Blodgett technique to form multilayer films of two cyanobiphenyl materials and a variety of alkyl 4'-alkenoxybiphenyl-4-carboxylates with different chain lengths. These films were characterized by optical microscopy, low-angle X-ray diffraction and, where appropriate, FTIR. The materials were studied by DSC and under the polarizing microscope using thicker layers pressed between two glass plates. All the materials studied exhibited at least one smectic phase. Two materials could also be deposited by the Langmuir-Blodgett technique, in one case forming a bilayer structure and in the other case forming a monolayer structure.

J.Y. Fang and R.A. Uphaus in 1994 [21] synthesized monolayers containing a nematic liquid crystal and stearic acid were characterized at various mole fractions by determination of surface pressure-area isotherms at the air-water interface. The surface- composition phase diagrams indicated that compression induces a new phase transition in the films, which changes from a mixed monolayer to a supermonomolecular system. X-ray diffraction and optical absorption spectra demonstrated that the supermolecular array consists of an island liquid crystal monolayer and a uniform stearic acid monolayer.

Xiao Chen in 1995 [22] investigated Langmuir and Langmuir-Blodgett (LB) films of a newly synthesized side-chain liquid crystalline polymer (PSLC) and its blend with arachidic acid (AA) by means of surface pressure-area isotherms, hysteresis curves, X-ray diffraction and polarized IR and UV-Vis spectroscopies. The results showed that AA matrices can enhance monolayer stability and improve the packing of side chains in the film. At high surface pressure, the mixed monolayer undergoes a phase transition from an ordered liquid condensed to a solid like phase, corresponding to the formation of aggregates or crystallites. Two types LB films (Y and X) can be obtained on the hydrophobic substrates under the condition of different deposition pressures and AA's proportion. A detailed analysis of the IR dichroism was done. The hypsoshift of UV-Vis absorption in the film compared with the spectrum in solution indicated that H aggregates form between the chromophore.

Xiao Chen in 1996 [23] investigated the aggregation behaviour of a newly synthesized ferroelectric side-chain liquid-crystalline polysiloxane (denoted as PSLC) in Langmuir-Blodgett (LB) films. The surface pressure-area isotherm and hysteresis experiments for arachidic acid (AA) / LC mixed monolayer confirmed existence of aggregation or phase-separation during compression. From the UV-Vis spectra, H-aggregate formation could be seen. To study the aggregate structure and molecular packing of PSLC, cyclic voltammetry combined with transmission electron microscopy and scanning electron microscopy morphology observations was used.

S. Payan et al. in 1996 [24] Investigated Monolayer and multilayers of ferroelectric liquid crystals (FLC) obtained by the Langmuir-Blodgett (L-B) technique on the water subphase and were characterized by surface pressure measurements and by polarization modulated infrared reflection absorption spectroscopy (PM-IRRAS). Moreover, five layers of FLC were successfully transferred onto CaF_2 and gold solid substrates and were studied by conventional Fourier transform infrared spectroscopy and by the PM-IRRAS method. Finally, the influence of the temperature on the structural arrangement of L-B films has been discussed.

Takeshi Kawai in 1997 [25] examined the molecular orientation of liquid crystals mixed with stearic acid in Langmuir–Blodgett LB films on the polyion complex 35 with azobenzene-containing fatty acid and polycation using Fourier transform infrared FTIR reflection-absorption RA and UV–Vis spectra. It was found from UV–Vis measurements that the polyion complex in these LB films shows reversible photoisomerization when irradiated by UV or visible light.

Valentina S. U. Fazio, Francesca Nannelli and Lachezar Komitov in 2001 [26] studied the anchoring of the nematic liquid crystal N-(p-methoxybenzylidene!-p-butylaniline ~MBBA on Langmuir-Blodgett monolayers of fatty acids ($COOHC_nH_{2n+1}$) as a function of the length of the fatty acid alkyl chain n (n 5, 15, 17, 19, 21). The monolayers were deposited onto glass plates coated with indium tin oxide, which were used to assemble sandwich cells of various thicknesses that were filled with MBBA in the nematic phase. The mechanism of relaxation from the flow-induced quasiplanar to the surface-induced homeotropic alignment was studied for the four aligning monolayers. It was found that the speed of the relaxation decreases linearly with increasing length of the alkyl chain n, which suggests that the Langmuir-Blodgett film plays a role in the phenomenon. This fact was confirmed by a sensitive estimation of the anchoring strength of MBBA on the fatty acid monolayers after anchoring breaking, which takes place at the transition between two electric-field-induced turbulent states, denoted as DSM1 and DSM2 ~where DSM indicates dynamic scattering mode. It was found that the threshold electric field for the anchoring breaking, which can be considered as a measure of the anchoring strength, also decreases linearly as n increases. Both methods thus possess a high sensitivity in resolving small differences in anchoring strength.

B. N. Klimov and E. G. Glukhovskoy in 2002 [27] described the use of liquid-crystal (LC) cells for the visualization of the Langmuir–Blodgett (LB) film structure and presented images appearing in LC cells upon LB film application. The images were analyzed in relation to the LB film structure (application conditions) and to the relief formed by indium tin oxide (ITO) electrodes.

John Collins in 2005 [28] studied the behaviour of a mixed Langmuir monolayer consisting of a fatty acid and a nematic liquid crystal and demonstrated that the mixed monolayer successfully transfers as a Langmuir–Blodgett film which were characterize by using UV spectroscopy. An important application of Langmuir Blodgett films is in the alignment of liquid crystals for electro-optical applications, such as displays. They showed that including the liquid crystal in the Langmuir Blodgett film produces homeotropic alignment for a system which fails to align by other standard techniques.

REFERENCES

1. Proust J E, Ter-Minassian-Saraga L, C R. Acd, Sci. Paris, **274,** 1105, (1972).

2. Proust J E, Ter-Minassian-Saraga L and Guyon E, Solid Slate Commrrn, **11**, 1227, (1972).

3. Proust J E, Ter-Minassian-Saraga L, C R. Ad, Sci. Paris C, **276,** 1731

4. Porte G, J. Physique, **37,** 1245, (1976).

5. Hiltrop K and Stegemyer H, MOL Crysr. Liq. Crysf. Lex , **49**, 61, (1978).

6. Hiltrop K and Slegemyer H, Ber. Bunrenges. Phys. Chem,, **85,** 582, (1981).

7. Hiltrop K and Slegemyer H, Liquid Crystals and Ordered Fluids **4**, ed J Johnson and R Porter, 515, (1988).

8. Blinov L M, Davydova N N, Sonin A A and Yudin S G, Sov. Phys.-Crysmllogr. **29**, 320, (1984).

9. Blinov L M, Sonin A A , Langmuir **3**, 660, (1987).

10. Saunders F C, et al., Mol. Crysr. Llq. Cryst, **122**, 297,(1985).

11. Nishikata Y, Morikawa A. Takigucbi Y, Kanemoto A, Kakimoto M and Imai Y, J, AppL Phys. **27,** L1163, (1988).

12. Grosperrin C, Rapport de SInge, Laboraroiw de Physique des Solides, Orsay, (1989).

13. Flatischler K, Komitov L, Lagerwall S T, Stebler B and Strigazzi A, Mol. Cryst. Liq. Cryst, **198,** 119, (1991).

14. Fang J Y, Wei Y, Sun Zh and Stroeve P, Phys. Lett., **157 A,** 396, (1991).

15. Fang J. Wei Y and Sun Zh, MOL Cryst. Liq. Cryst., **222**, 71, (1992).

16. Komitov L. Stebler B. Gabrielli G, Puggelli M, Sparavigma A and Strigazzi A Mol. Cryst, Liq. Crysl, at press.

17. Shonova N, Petkova J I and Petrov A G C R. Acad. Bulg. Sci. at press.

18. Alexe-Ionescu A L, Barbero G, Ignatvo A and Miraldi E, Eur. Conf. on Liquid Crystals (Films, 1992); 1993 Appl. Phys. A, **56,** 453, (1992).

19. Takahiro Seki et al., Langmuir, **9**, 211-218, (1993)

20. M. Woolley, R. H. Tredgold, P. Hodge, Langmuir, **11**, 683, (1995).

21. J. Y. Fang, R. A. Uphaus, Langmuir, **10**, 1005, (1994).

22. Xiao Chen, Qing-Bin Xue, Kong-Zhang Yang, Qi-Zhen Zhang, Thin Solid Films 286, 232, (1996).

23. Xiao Chen, Qing-Bin Xue, Kong-Zhang Yang, Langmuir, **11**, 4082, (1995).

24. S. Payan, B. Desbat, Langmuir, **12**, 6627, (1996).

25. Takeshi Kawai, Thin Solid Films, **301,** 225, (1997).

26. Valentina S. U. Fazio, Francesca Nannelli, and Lachezar Komitov, Physical Review E, **63**, 061712.

27. B. N. Klimov, E. G. Glukhovskoy, Technical Physics, **47**, 1576 (2002).

28. John Collins, Denis Funfschilling, Michael Dennin, Thin Solid Films, **496**, 601, (2006).

CHAPTER-3

EXPERIMENTAL AND CHARACTERIZATION TECHNIQUES

This chapter provides information about the various steps involved in the experimental part. Like section 3.1 gives details about the materials used, 3.2 gives the information about the preparation of the LB monolayer, 3.3 provides the details of the various steps involved in the fabrication of its cell and in section 3.4 the various characterization techniques used for the LB monolayer and morphological studies are described.

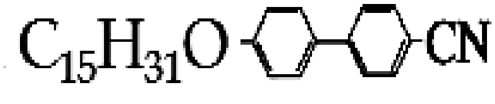
3.1 Materials

The materials studied in this present work are commercially available, Liquid crystal (M15) were purchased from BDH Chemicals Ltd. England and used without further purification. The observed phase sequence is:-

$$\mathrm{K} \xrightarrow{48^{\circ}\mathrm{C}} \mathrm{N} \xrightarrow{68^{\circ}\mathrm{C}} \text{Isotropic}$$

Where K stands for the crystalline phase and N for the nematic phase.

The molecular formula of M15 is 4-cyano-4-n-alkoxybiphenyls and the molecular structure of the M15 Liquid crystal is shown in the figure below:-



The fatty acid used is stearic acid and was obtained from Loba Chemie Pvt. Ltd. The molecular formula of stearic acid is: $C_{17}H_{35}COOH$.The chloroform used was purchased from SDFCL and was of 99.0 % purity. The deinoised water used was obtained from milli pore.

3.2 Film preparation using LB Technique

1 mg/ml solution of stearic acid or stearic/nematic mixtures in chloroform were spread with the help of micro-syringe onto the surface of ultrapure milli pore water in an LB trough held in a clean room environment to limit contamination of the trough by dust. Then it was left for 15-20 minutes. We used ITO coated glass as substrates. They were first cleaned in the ultrasonic bath filled with a solution of ultrapure water and ammonia and then plates were cleaned with acetone. These were immersed in the subphase before the spreading of the monolayer. The monolayers were compressed at the rate of 5mm/min until the pressure of 35mN/m was reached. The transfer onto the substrate was done at 35mN/m at the speed of 2mm/min during the extraction of the ITO coated glass plate. The film thus formed was kept safely in a dessicator for 4-5 hours.

3.3 Fabrication of the cell

Inorder to study the opto electrical properties of the LB monolayer and the NLC we need to fabricate the cell.

It involves three steps: Assembling, Sealing and Filling of the cell.

1. i. Assembling: For the assembling of the cell the ITO sides of the two plates were kept inside (i.e. they are facing each other) and the separation was provided by a Mylar spacer of known thickness (6 micron).
2. ii. Sealing: The two opposite sides of the assembled cell were sealed by optical adhesive epoxy. The electrodes were connected at the ITO coated surface using indium ingot to obtain the better contacts.
3. iii. Filling the cell: The cell thus formed is placed on a hot plate and the desired liquid crystal is placed at one of the opening of the cell. The LC thus gets filled inside by the capillary action. The cell is left undisturbed till it reaches the room temperature. Now the left two openings of the cell were sealed with the epoxy.

The schematic diagram of the experimental is shown below:

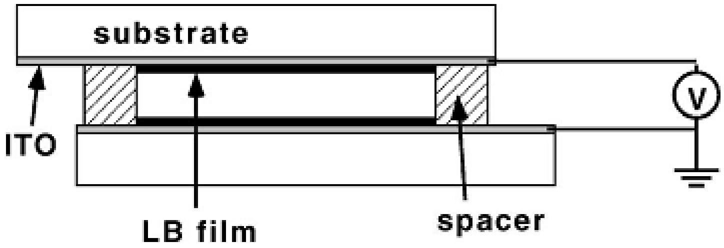
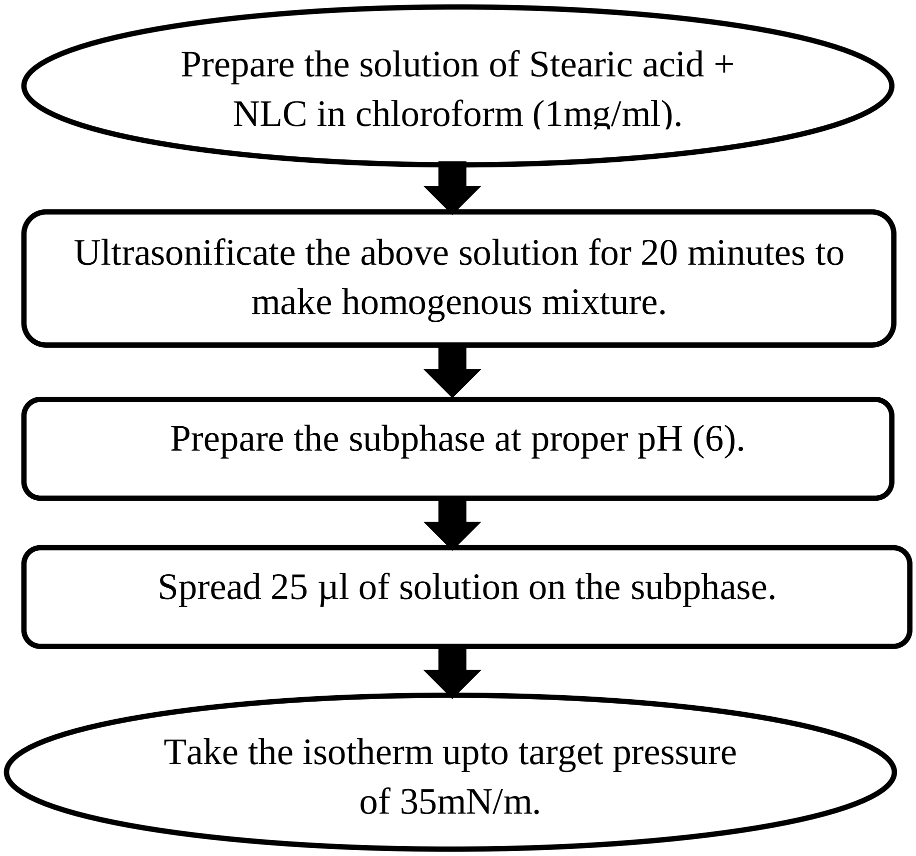


Fig: 3.1 A schematic of the final outlook of the cell prepared.

3.4 METHODOLOGY

LB monolayer preparation



Prepare the solution of Stearic acid + NLC in chloroform (1mg/ml).

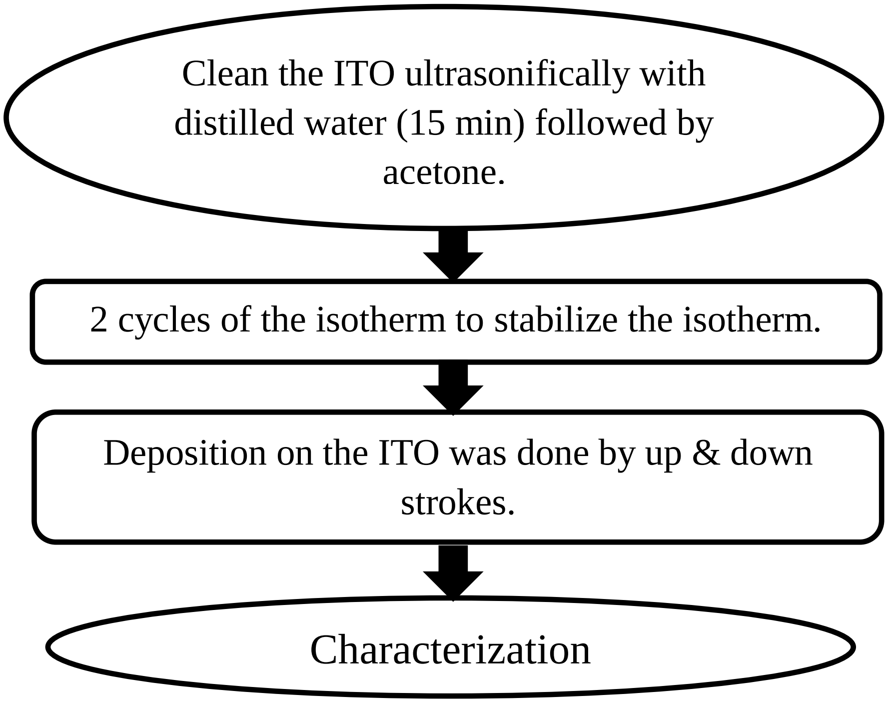
Ultrasonificate the above solution for 20 minutes to make homogenous mixture.

Prepare the subphase at proper pH (6).

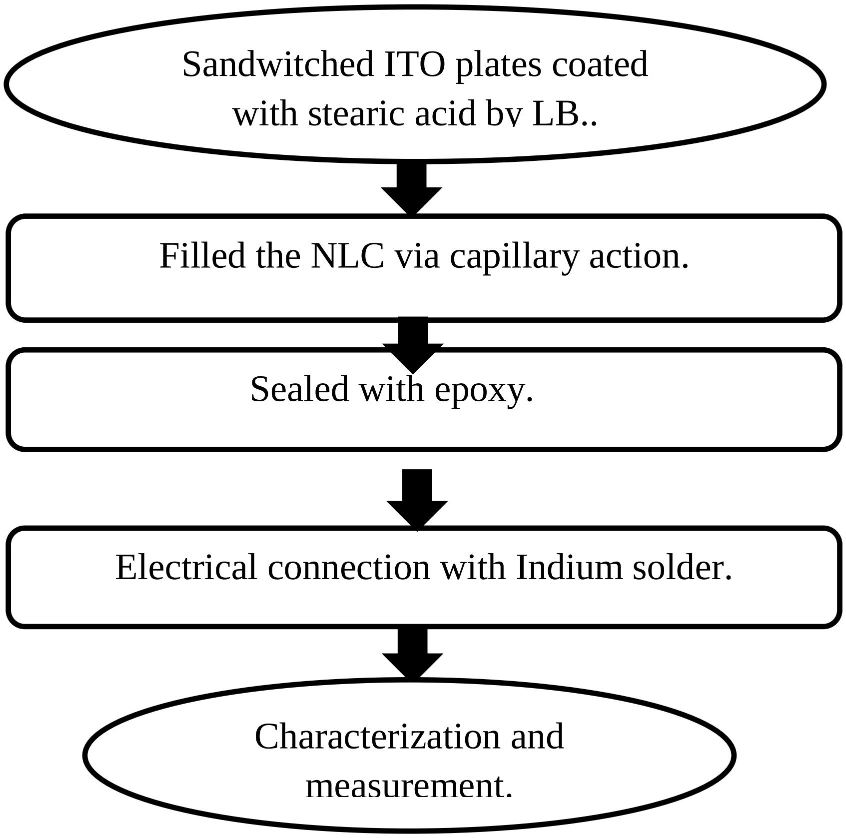
Spread 25 µl of solution on the subphase.

Take the isotherm upto target pressure of 35mN/m.

LB Film preparation



LC Cell fabrication



3.5 Characterization Techniques used in the work

The characterization of the LB film was done with the isotherm of Surface pressure (π) - mean molecular area (A) and FTIR (Fourier Transform of Infra-red Radiations). The LC cell was characterized with optical microscope. The details are given below:

3.5.1 LB MONOLAYER CHARACTERIZATION

- **Surface-pressure (π) – Area (A) isotherm**

The Surface-Pressure (π) – Area (A) isotherms were taken on Mini Trough KSV-NIMA 5000. The most basic characterization of Langmuir monolayer is the measurement of the surface pressure versus area isotherms. The various phase transitions occurring in the monolayer can be visualized through this isotherm. As discussed earlier surface pressure (π) is defined as the surface pressure of the pure water (γ_0) minus the surface pressure of the water-monolayer system (γ), i.e., $\pi = \gamma_0 - \gamma$.

3.6 LB FILM CHARACTERIZATION

3.6.1 Fourier Transform Infrared Spectroscopy (FTIR)

This is a very important characterization technique for determining the functional group and molecular structure. FTIR is most useful for identifying chemicals that are either organic or inorganic. It can be utilized to quantitate some components of an unknown mixture. It can be applied to the analysis of solids, liquids and gasses [1].

FTIR is perhaps the most powerful tool for identifying types of chemical bonds (functional groups). The wavelength of light absorbed is characteristic of the chemical bond. By interpreting the infrared absorption spectrum, the chemical bonds in a molecule can be determined. FTIR spectra of pure compounds are generally so unique that they are like a molecular "fingerprint". While organic compounds have very rich, detailed spectra, inorganic compounds are usually much simpler [1].

3.6.1.1 Quantitative Analysis

Because the strength of the absorption is proportional to the concentration, FTIR can be used for some quantitative analyses.

Molecular bonds vibrate at various frequencies depending on the elements and the type of bonds. For any given bond, there are several specific frequencies at which it can vibrate. According to quantum mechanics, these frequencies correspond to the ground state (lowest frequency) and several excited states (higher frequencies). One way to cause the frequency of a molecular vibration to increase is to excite the bond by having it absorb light energy. For any given transition between two states the light energy (determined by the wavelength) must exactly equal the difference in the energy between the two states [usually ground state (E0) and the first excited state (E1)].

The energy corresponding to these transitions between molecular vibrational states is generally 1-10 kilocalories/mole which corresponds to the infrared portion of the electromagnetic spectrum.

Difference in Energy States=Energy of Light Absorbed

$$E1 - E0 = h\,c / \lambda \qquad (3.1)$$

Where h =Planks constant, C = speed of light and λ = the wavelength of light.

Fig: 3.2 The outer view of the FTIR present in the lab.

3.6.2 Scanning Electron Microscope

The Scanning Electron Microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface morphology, composition and other properties such as electrical conductivity.

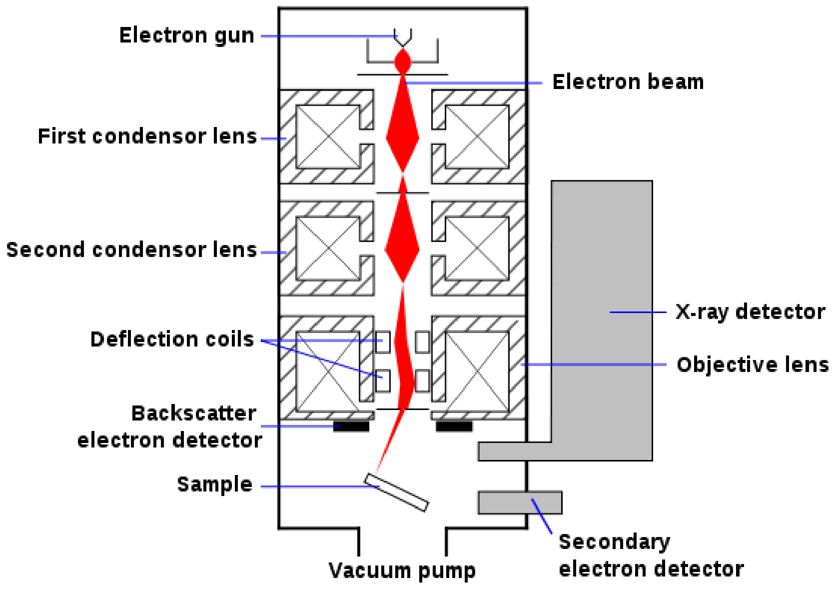


Fig: 3.3 A schematic diagram showing the various parts of the SEM.

3.6.2.1 Scanning process and image formation

In a typical SEM, an electron beam is thermionically emitted from an electron gun fitted with a tungsten filament cathode. The electron beam, which typically has an energy ranging from 0.5 keV to 40 keV, is focused by one or two condenser lenses to a spot about 0.4 nm to 5 nm in diameter. The beam passes through pairs of scanning coils or pairs of deflector plates in the electron column, typically in the final lens, which deflect the beam in the x and y axes so that it scans in a raster fashion over a rectangular area of the sample surface. When the primary electron beam interacts with the sample, the electrons lose energy by repeated random scattering and absorption within a teardrop-shaped volume of the specimen known as the interaction volume, which extends from less than 100 nm to around 5 µm into the surface. The energy exchange between the electron beam and the sample results in the reflection of high-energy electrons by elastic scattering, emission of secondary electrons by inelastic scattering and the emission of electromagnetic radiation, each of which can be detected by specialized detectors.

1.6.3 Optical Polarizing Microscope

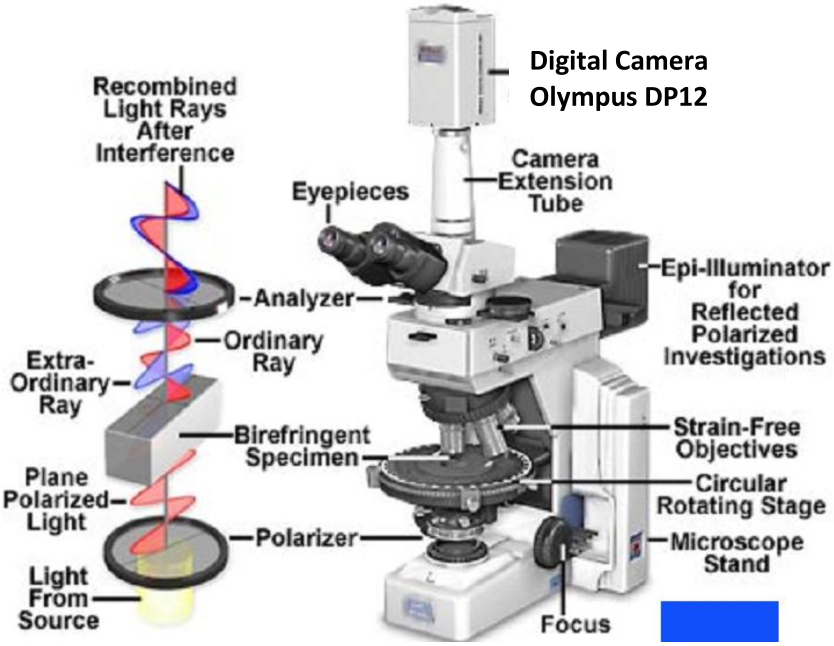


Fig: 3.4 A schematic diagram showing the various parts of the optical microscope and the phenomenon taking place.

Light from an incandescent source is passed through a polarizer, so that all of the light getting through must vibrate in a single plane. The beam is then passed through a prism that separates it into components that are separated by a very small distance - equal to the resolution of the objective lens. The beams pass through the condenser, then the specimen. In any part of the specimen in which adjacent regions differ in refractive index the two beams are delayed or refracted differently. When they are recombined by a second prism in the objective lens there are differences in brightness corresponding to differences in refractive index or thickness in the specimen. If the sample is colorless, transparent, and isotropic, and embedded in a matrix with similar properties, it will be difficult to image. This is due to the fact that our eyes are sensitive to amplitude and wavelength differences, but not to phase differences.

CHAPTER-4

RESULTS AND DISCUSSION

Overview

This chapter provides insight into the various results that were obtained in the present work. The results regarding the characterization of LB monolayer with π- A isotherms, FTIR and SEM. And also of the cell made of LB monolayer of stearic acid filled with NLC with Optical Polarizing Microscope.

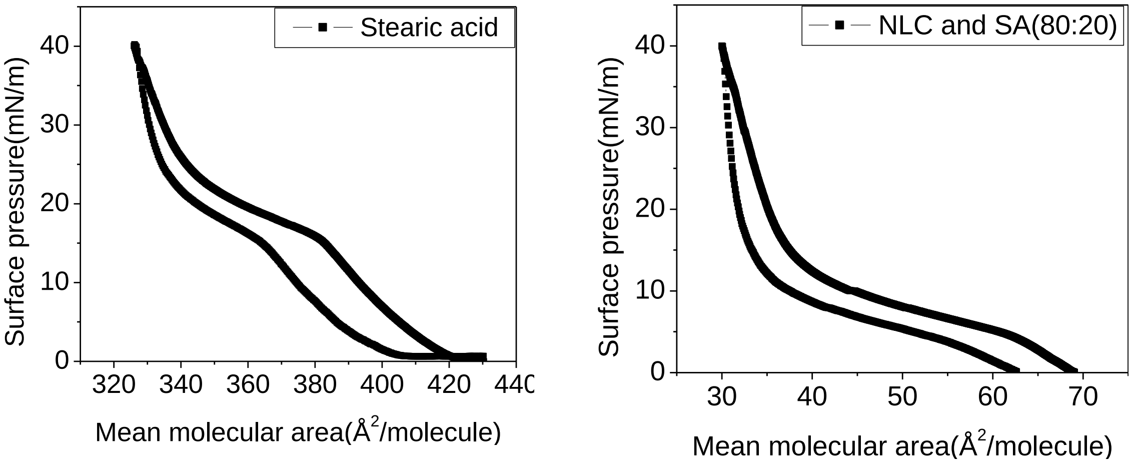
4.1 SURFACE-PRESSURE (π) – AREA (A) ISOTHERM

a) Stearic acid

The pure stearic acid isotherm is consistent with the behaviour expected from the literature. The measured isotherms are reproducible as we remain below the collapse pressure. The hysteresis curves of the stearic acid and for stearic acid and NLC system is shown in the figure 4.1a and 4.1b. The pure stearic acid isotherm shows three phases at room temperature as shown in fig: 4.1a. Up to an area of 400 $Å^2$ / molecule the molecules are in gaseous phase. At this point (the lift off point) we observed the first rise in the isotherm that corresponds to the Expanded- Liquid phase. The next rise corresponds to the Liquid-Condensed phase.

b) Nematic Liquid Crystal (NLC) and Stearic acid (SA)

When the NLC is added to the stearic acid then the changes appear in the lift off point. The lift off point occurs at a higher area per molecule. This is due to the space occupied by the NLC molecules. The isotherm for the mixture suggests that during the compression and expansion cycle most of the NLC is recovered as the expansion cycle is following the compression cycle. But it is not fully recovering which means that there is a loss of the material in the system.



(a) (b)

Fig 4.1(a) Plot of isotherm for Stearic acid (b) Plot of isotherm for NLC and SA in (80:20)

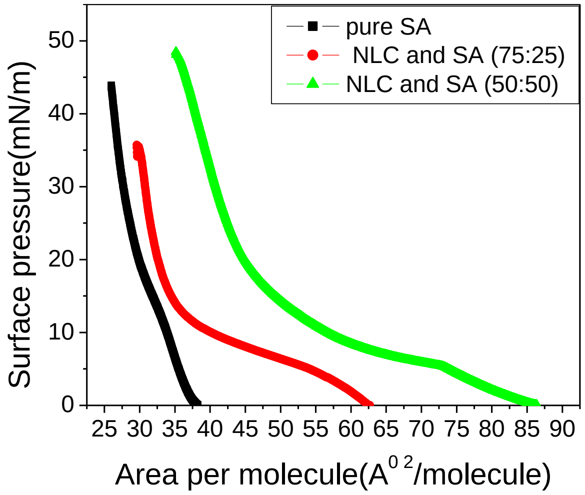


Fig: 4.2 Plot of isotherm for pure Stearic acid (square), NLC and SA in 75:25 (circle) and NLC and SA in 50:50 (triangle).

The isotherm for the pure stearic acid and for stearic acid and NLC composite in the ratios (75:25, 50:50) were observed (fig: 4.2) .The spreading amount of 25µl of the concentration 1mg/ml solution was placed on the trough. As the amount of NLC is increased the area per molecule is increasing with it, which suggests the NLC molecules are occupying more area at air-water interface. There is increase in the liftoff point with every addition of NLC in the stearic acid. In the fig: 4.2 black line is indicating the isotherm of pure stearic acid, circle is for NLC and SA in ratio 75:25 and the triangle is for the NLC and SA in ratio 50:50.

4.2 Fourier Transform of Infrared Radiation Spectroscopy:

The FTIR plot of 5 monolayers reveals the bonding of molecules in stearic acid (fig: 4.3). The strong bands at 2270 and 1786 cm^{-1} are due to O-H vibration bands and C=O stretching mode. The C-H vibration modes are at 3089 cm^{-1}. The C-O stretching band is at 1275 cm^{-1}.

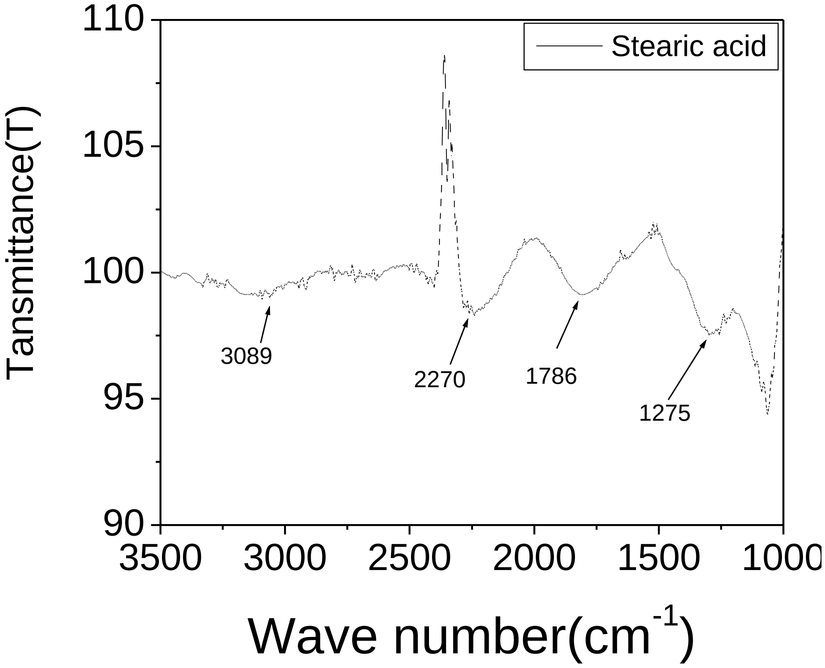


Fig: 4.3 FTIR spectra of LB film of stearic acid having 5 monolayers.

The FTIR plot for the film of SA and NLC in 75:25 (5 monolayers) is shown in the fig: 4.4. The stretching corresponding to C-H at 3055 cm^{-1} is weak. The C≡N stretching at 2218 cm^{-1} is medium. The 1806 cm^{-1} is for C=O stretching mode while the aromatic C=C stretching is at 1568 cm^{-1} is strong. The C-O and O-H vibration mode are at 1227 cm^{-1} and 2629 cm^{-1} respectively.

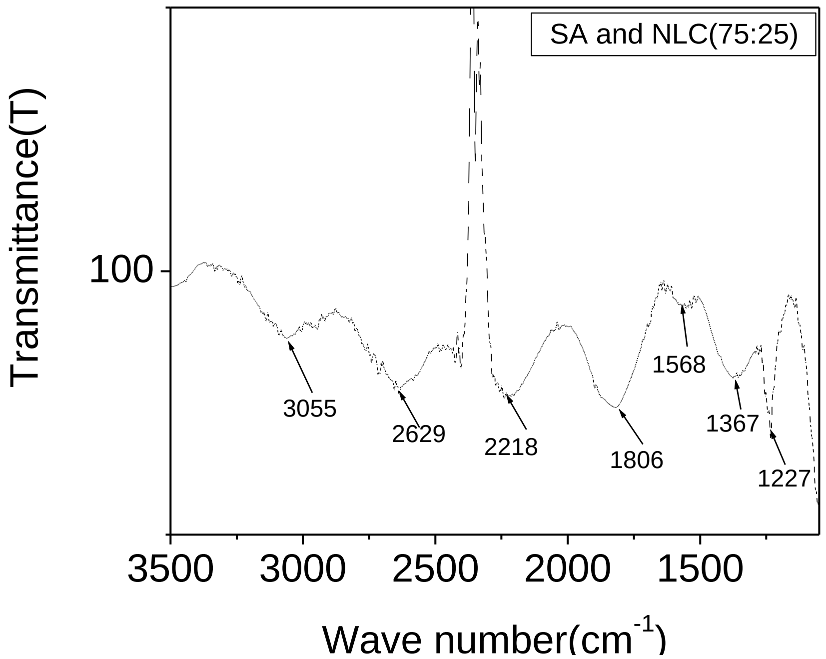


Fig: 4.4 FTIR spectra of the LB film of stearic and NLC (75:25) having 2 monolayers on ITO.

4.3 SCANNING ELECTRON MICROSCOPE:

Figure 4.5 shows SEM micrograph of the LB films of stearic acid at two different magnifications 10,000 and 100,000 were taken. These revealed that the deposition is homogeneous.

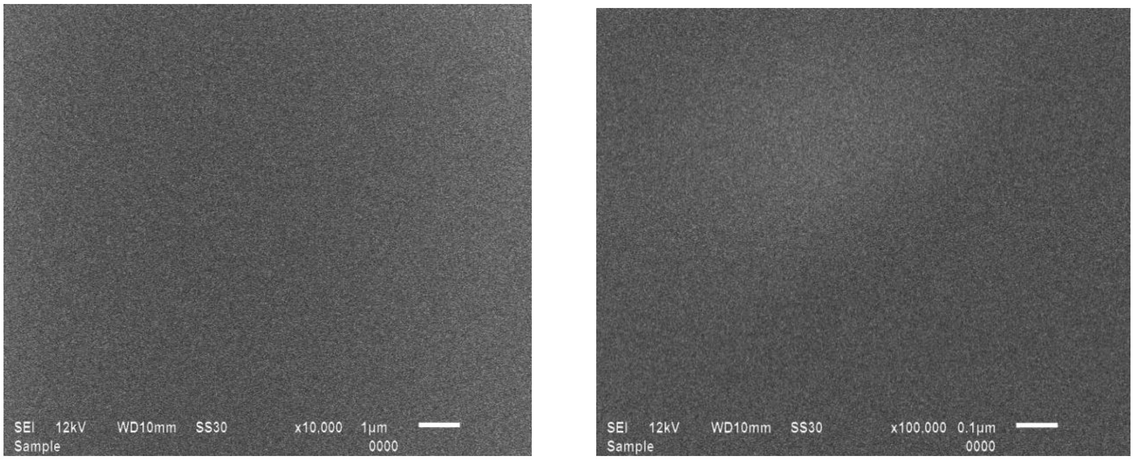


Fig: 4.5 SEM micrographs of LB film of stearic acid on cover slip having 10 monolayers.

The SEM micrograph of the LB film having 10 monolayers of stearic acid and 50 monolayers of NLC reveals the deposition (fig: 4.6).

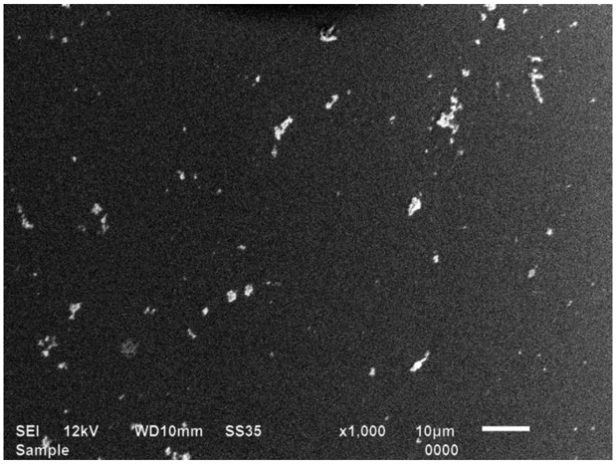


Fig: 4.6 SEM micrographs of LB film of SA with 10 monolayers on which 50 monolayers of NLC have been depositedon cover slip.

4.4 POLARIZING OPTICAL MICROSCOPY

The LC cell thus formed was observed under crossed polarizer microscopically as a function of temperature and applied voltage under polarized light. The textures were captured with the Olympus digital camera on heating (fig: 4.7), cooling (fig: 4.8) and with the applied voltage (fig: 4.9). The changes in the textures indicate the phase transition as well as alignment of NLC molecules in a unique direction. When the NLC is filled into the cell all the molecules are arranged in a random fashion. The LB film of stearic acid tries to help the NLC molecules to arrange in the perpendicular direction. This arrangement of the molecules is known as homeotropic alignment. The schematic of the arrangement of the NLC molecules is shown in fig: 4.7.

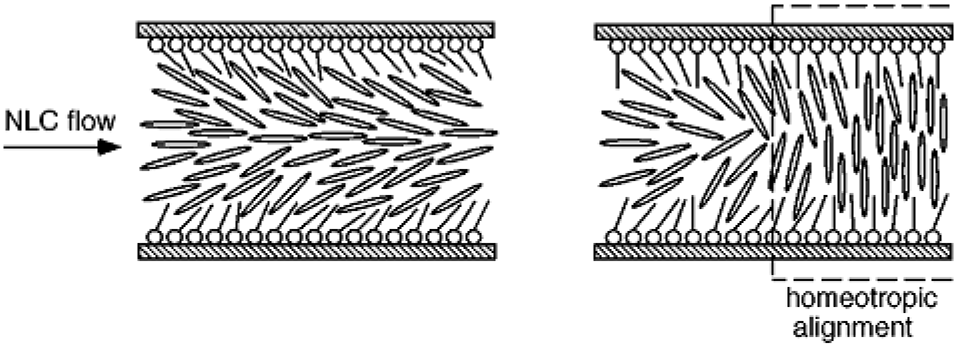


Fig: 4.7 Left part of the figure shows the schematic diagram showing that during the filling of the LC, the LB monolayer seems to be strongly influenced by the flow with the chains distorted in the filling direction. A splay-bend deformation is induced in the NLC by the flow. The Right side of the figure shows that when the flow stops the LB film and the splay bend deformed LC both contributes to the relaxation towards the homeotropic state.

4.4.1 Micrographs on heating:

LB films of stearic acid (5 layers) were deposited on ITO plates, which help for aligning NLC molecules (M15). As we increase the temperature upto 48^{o}C, nematic phase is shown by the NLC molecules (Fig: 4.7c). Due to thermal fluctuations of the NLC molecules with temperature, rod like molecules get penetrate and homeotropic alignment (the black portion) appears in the optical texture (Fig: 4.7g), where all the molecules are aligned in the perpendicular direction by the LB film of stearic acid. This alignment is getting disturbed near the isotropic temperature due to penetration of NLC molecules with rise in the temperature. So here the schilieren texture (thread like structure) is observed (Fig: 4.7g). This schilieren texture is due to the behaviour of NLC molecules during the relaxation process.

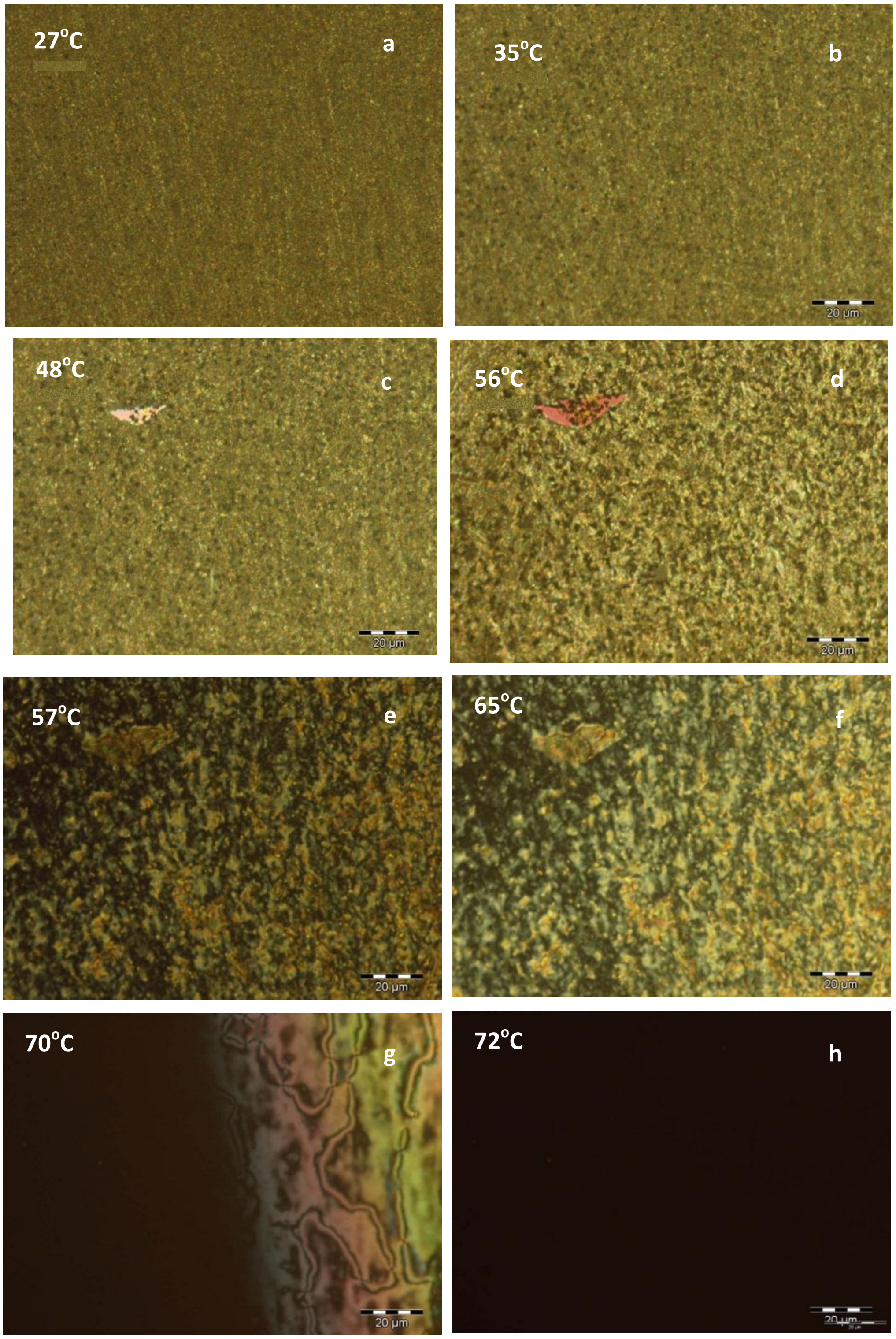
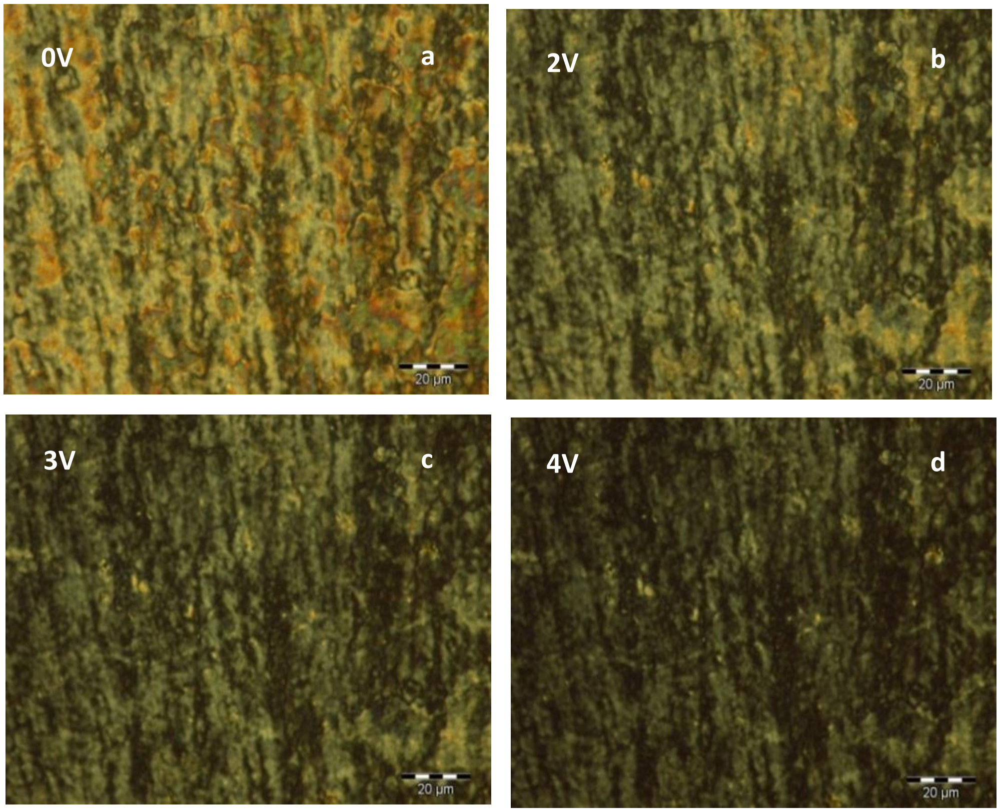


Fig: 4.8 Micrographs at 10X showing the variations during heating from room temperature to isotropic state.

4.4.3 Micrographs with voltage:

Film morphology with the application of electric field as a function of voltage (in nematic phase at 48^{o}C) is investigated under crossed polarizer. When electric field is applied to NLC molecules under strong anchoring force provided by stearic acid, then molecules try to align in the preferred direction of electric field (i.e. perpendicular to the substrate). With the application of the electric field, NLC molecules start penetrating under strong anchoring for relaxation. When they get sufficient field (9 Volt), all LC molecules are aligned in the upward direction and we get homeotropic alignment (fig: 4.8h). These optical textures provide information about the homeotropic alignment of NLC molecules under the application of electric field. With the application of the strong field there is no change in texture and we get saturation above 9 volt.



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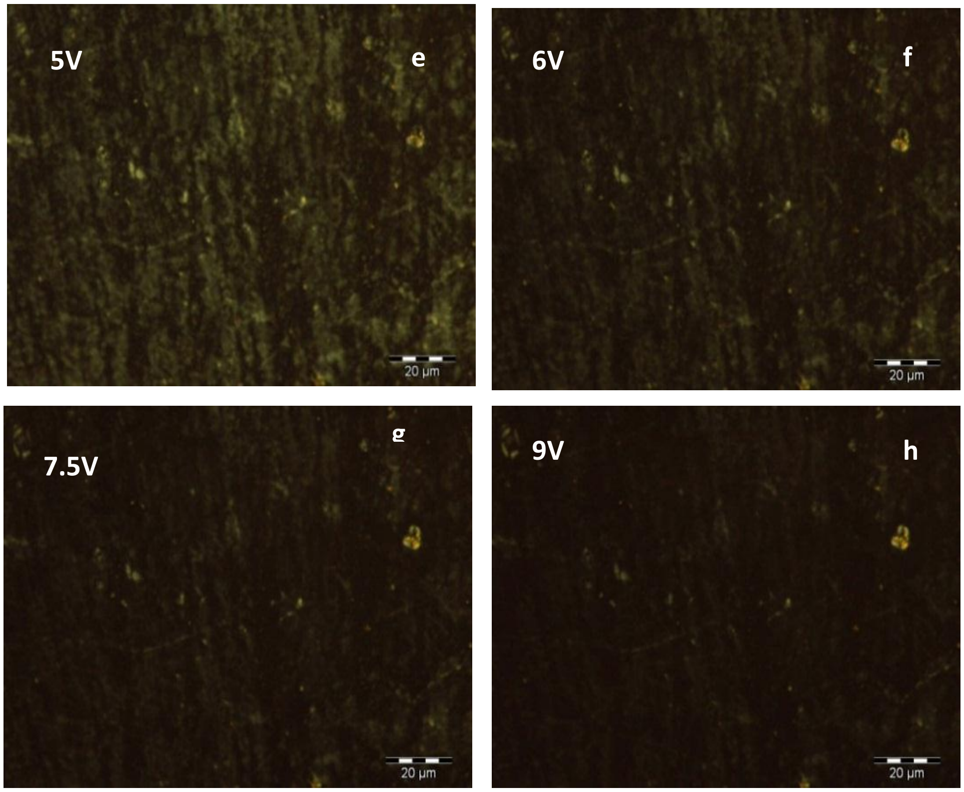

Fig: 4.9 Micrographs at 10X showing the variations with the applied voltage from 0V to 9V.

CHAPTER-5

CONCLUSION AND FUTURE SCOPE

We have successfully achieved vertical alignment of stearic acid on ITO substrate via Langmuir-Blodgett technique in our research work. The role of this alignment by LB technique is very important in technology. This rubbing free alignment provides a very good anchoring to rod like liquid crystal (NLC) molecules in relaxation process in electro-optic study. Scanning Electron Microscopy (SEM) and Optical microscopy provides information about uniformity in film morphology. Temperature dependent film morphology of NLC cell provides information about the schieleren texture near the isotropic temperature. This thread like structure is stable upto few degree of temperature near the clearing point. Here the system does not relax to homeotropic state. The most interesting result of homeotropic alignment is achieved with the application of voltage or electric field to the NLC cell, where the LC molecules get relaxed under the strong anchoring provided by the LB film of stearic acid.

Hence the present knowledge about the alignment of LC with the help of LB film of stearic acid may be considered for developing new kind of rubbing free aligned NLC display technology based on the Langmuir-Blodgett technique. LB film of stearic acid give rise to the well aligned rod like molecules of the Liquid crystal (NLC). Hence the present research work provides general information about the anchoring parameter that will enable us for designing appropriate alignment material, possessing advanced performance of LC display based on various alignment technologies in future.