Chapter 1

Introduction
Abstract

This chapter gives a brief outline of the relevant basic things to understand the results and discussions throughout the thesis.
1.1 Introductory remarks:

The study of thin organic films have received more and more attention in many fields due to their diversity in many practical and commercial devices such as sensors, detectors, displays, electronic circuits and FET [1-3]. The growth of organic thin films on solid surfaces is attracting significant interest due to their technological applications in micro and opto-electronic devices[4-8]. The potential application of organic thin films has expanded enormously because of unlimited ability to synthesize organic molecules with desired structure and functionality in conjunction with sophisticated thin film deposition technique enables the production of electrically, optically and biologically active components on a nanometer scale. Various techniques have been reported to prepare organic thin films in a well-ordered way, using various deposition techniques including thermal evaporation, micro-imprinting lithography, direct deposition, laser stereolithography, sputtering, Layer–by-Layer self assembly (LbL), Langmuir-Blodgett (LB) technique, solvent casting, spin coating, dip coating, plasma polymerisation, molecular beam epitaxi, and soft lithography. However among all these techniques, in my thesis I have chosen are Langmuir – Blodgett (LB) technique [9-10] and Layer by layer self assembled (LbL) technique [11-12]. The Langmuir–Blodgett (LB) and Layer by layer self assembled (LbL) techniques are best known methods because they afford control of the organization at the molecular level[13]. Among the various thin film preparation techniques Langmuir-Blodgett technique is one of the most versatile and promising method for the fabrication of organized molecular assemblies with a well-defined surface and an ideal system for the mimicking of the biological membranes [14]. The Langmuir–Blodgett (LB) techniques allows (1) an accurate control of the monolayer thickness and of the molecular organization, (2) homogeneous deposition of the monolayer over large areas compared to the dimension of the molecules, (3) it provides the possibility to fabricate multilayer with varying layer structures, crystal parameter and packing of the film can be controlled by changing various LB parameters [15-17], (4) an additional advantage with the ability to prepare molecules with hydrophobic or hydrophilic functional groups and also possibility to transfer monolayers on almost any
kind of solid substrate and (5) to elaborate bilayer structures with varying layer compositions.

Traditionally molecules used in LB research are amphiphilic in nature, meaning that the molecule has both hydrophobic (water-hating) and hydrophilic (water-loving) part and numerous polyaromatic hydrocarbon derivatives, because they form a excellent monolayer at the air-water interface [18]. Several studies indicate that non-amphiphilic (i.e. molecules without long alkyl chain) and some water soluble organic material cannot itself form a stable Langmuir monolayer (LM) at the air-water interface, because non-amphiphilic molecules tend to form microcrystals at the air-water interface and water soluble molecules move partially to the inside of subphase during the evaporation of the volatile solvent [19]. But this problem can overcome when doping non-amphiphilic and water soluble molecules with amphiphilic such as long chain fatty acids (e.g. Stearic acid, behenic acid, arachidic acid etc.) or some optically inert polymer (e.g. Poly methyl methacrylate) and phospholipids which form excellent high quality LB films [20-25] that can be easily transferred onto solid substrates [26]. Using non-amphiphilic molecules in place of their amphiphilic counterparts is a definite advantage, since they may be readily put to large scale industrial application and are cost effective. Moreover, the spectroscopic and aggregating properties of these molecules are very similar to the amphiphilic counter parts. However, water soluble charge transfer types of materials can form water insoluble complex monolayer when interact with the amphiphilic molecules. After completion of reaction kinetics, this complex Langmuir monolayer can be transferred on solid substrate at desired surface pressure to form mono- and multilayered complex LB films.

Some recent work has focused on liquid crystals (LC) as active or host material in organic LEDs, and it requires control of molecular alignment at macroscopic scales. The thin film of LC are used for information storage and display devices of the liquid crystals. The recently discovered liquid crystal molecules have been eagerly researched because these molecules adopt a compact packing arrangement and the ability to produce liquid crystal devices with macroscopically uniform alignment [27].

Decher and his group extended the pioneering work of Iler et al to a new preparative method of organized thin films by Layer by Layer (LbL) assembly an offering easy and
inexpensive process for multilayer formation. This technique has several advantages: (1) the preparative procedure is relatively simple and an elaborate apparatus is not required and can be applied to larger substrate dimensions, (2) a wide variety of different materials such as water soluble polyions or microions and bio-active molecules can be used to create the multilayer thin films, (3) any charged surface is employable and the individual layers can have distinct molecular thicknesses and ordering. Many inorganic macromolecules such as clay [28] and polymeric materials from biopolymer such as proteins [29-31], DNA have been assembling with this technique. The ultra thin films prepared by these methods have their potential application in the bio-sensor [32], optoelectronic devices [33], Photonic devices [34-36], models mimicking biological membrane [37], drug delivery [38], gene delivery [39-40] and drug formulation [41-42]. Many processing parameters such as solution concentration, ionic strength, temperature, humidity, adsorption time, solvent composition, pH allow a degree of control of the assembly process and therefore of the nanocomposite functionality and characteristics. For spectroscopic characterization, the traditional and conventional spectroscopic techniques such as UV-Vis absorption and steady state fluorescence spectroscopy are used. In some cases to get an idea about the surface morphology and aggregating species of the domain structure of organic thin films in the nanometer to micrometer order, a traditional imaging technique namely Atomic Force Microscopy (AFM) has been employed.

1.2 : Langmuir and Langmuir-Blodgett Films:

1.2.1: Introduction to Langmuir-Blodgett films:

Langmuir Blodgett (LB) is a well-established and sophisticated method during the last decades because of their suitability as models to study molecular organization [43-53] and a wide range of monolayers and multilayers of different molecules have been studied with this technique. To create mono and multilayer organic thin films on solid support, a liquid subphase (water) is used to form a monolayer at air/water interface. In this regard, the material is dissolved in an organic solvent (chloroform) and dispensed on to aqueous subphase. By the evaporation of this solvent, molecules move up to the air-water interface and produce a monolayer of molecules. It is possible to control the
formation of this layer with barriers. While compressing the barriers, a condensed monolayer of the molecules can be obtained on water surface. This monolayer is transferred to the substrate as a thin film. The transfer method is based on the lowering or rising of the substrate, which shows strong dependence on the hydrophobicity/hydrophilicity of the substrate. The structure of the LB films depends on parameters such as molecular structure, hydrophobicity/hydrophilicity, pH and temperature. LB technique is a very suitable method to create biologically friendly structures since for their production harsh-conditions and additional chemicals are not required.

1.2.2: History and Development of Langmuir and Langmuir – Blodgett film:
Mankind was already familiar with the effect of oil on the water surface in ancient times. A form of divinity was observed in Babylonia recorded on clay tablets around the 18th century B.C. The effect of oils spread on the water surface and ancient Greek writings already tell of the calming effect of oil on a rough sea. A paper marbling technique, which is Japanese printing art "suminagashi" literally means "ink-floating" or "ink-streaming", became popular in Japan 1200 years ago. A suspension of carbon particles in a protein solution was first spread onto a water surface. The application of gelatin to the uniform layer converts the film into a patch-work of colorless and dark domains [54]. This distinctive pattern can be picked up by paper on the water surface using a horizontal lifting technique. In 1774, Benjamin Franklin carried out his famous experiments on the clapham ponds, where Franklin dropped about a teaspoon of oil onto pond and discovered the advances of Langmuir–Blodgett films. In his report he showed that how a teaspoonful of oil had a calming influence on the surface of the pond. Franklin did not realize that the oil had formed a monolayer on top of the pond surface. Over a century later, Lord Rayleigh was first, who calculated the thickness of the oil layer in Franklin experiment to be arround 2nm by knowing the volume of oil dropped and the area of coverage. Lord Raleigh suspected that the maximum extension of an oil film on the water surface represents a layer of single molecule thick [55]. Additionally; he used this calculation to confirmed Avogadro number. With the help of kitchen sink, German women Agnes Pockles showed that the area of films can be controlled with
barriers. She used to determine the surface contamination as a function of area of the surface for different oils. Lord Rayleigh who then helped Agnes Pockels became published in the journal, “Nature” in 1891. Raleigh reported [56] in 1899 the precise thickness of a monomolecular layer of castrol oil on water to be one nanometer. Pockels continued her work and in 1892 published a paper in which she carried out significant studies of several materials (mostly household oils) required to form a monolayer. In addition she comments on the purity and cleanliness required to accurately perform measurements of surface tension. Also in this paper she reports values of the thickness of films of various amphiphilic substance, stearic acid on the surface of water [57] and results predict that the monolayer will be 2.3 nm thick. After the discovery of monolayer, scientist started investigation in order to compress the monolayer in the mobile barrier which was a simple trough made up of hydrophobic material. Using pockels idea, Irving Langmuir developed a special equipment surface film balance which now carries his name, Langmuir film balance. Irving Langmuir [58] studied the surface pressure versus area relationship of monolayers of amphiphilic compounds at the air–water interface. He was awarded the noble prize for his detailed studies on surface properties. Neil Kensington Adam summarized and expanded on the work of Langmuir in a series of several papers published in proceeding of the Royal society of Landon from 1921 to 1926 [59]. In collaboration with Katherine Blodgett [60], Langmuir demonstrate a process to deposit multiple monomolecular layers successively onto the same solid substrate. These built up mono or multilayers assemblies with controlled thickness [61] are now known as Langmuir-Blodgett (LB) films. The floating monolayer on the air-water interface is usually referred to as Langmuir (L) film. In the late 1960’s Khun and Mobius [62-63] showed how monolayers could be used to construct precise supramolecular structures. They used the Langmuir-Blodgett technique to demonstrate the fluorescence and quenching of dye molecules attached to fully saturated fatty acids under ultraviolet light. This work and the publication of Gaines “Insoluble Monolayers at Liquid-Gas Interfaces” in 1966 [64] initiated a revival of interest in the field.

The first international conference on Langmuir-Blodgett films was held in 1979. Research groups throughout the world are now working in this field to find the various applications. There are various technical applications of Langmuir – Blodgett films in
molecular electronics [65], optical signal processing [66], digital optical switching devices [67], light emitting diodes [68], biosensing devices [32]. In recent years nanocrystalline films obtained by Langmuir-Blodgett technique have been envisaged as a great potential towards the formation of nanoscale devices [69], drug delivery [38], gene delivery [39], molecular rectifier devices [70], optical switching devices [71] etc.

1.2.3: Formation of Langmuir Monolayers at the Air-Water interface:

Insoluble monolayers are formed on the clean surface of the subphase (water) by the spreading of insoluble or non-volatile substances over the surface. By simply dissolving in the suitable solvent (e.g chloroform), amphiphilic substances which is insoluble in water can be easily spread on the water surface to form an insoluble monolayer at the air-water interface. At the air-water interface, amphiphiles/surfactants can orient themselves in such ways that their polar heads are pulled into the aqueous surface whereas their hydrophobic tail is pointed away from the water surface. Monolayer formation on water surface is described schematically in fig. 1.1 and fig. 1.2.

![Diagram of a monolayer at the air-water interface.]

**Figure 1.1: A schematic illustration showing the components of an amphiphilic and the orientation of an amphiphilic adopted at an interface.**
Dipole-dipole interactions between the water molecules and the head group of the surfactants are responsible for keeping the hydrophilic head immersed in water. However because of the strong hydrogen bonding between the water molecules and the strong hydrophobic interactions between the hydrocarbon chains, the hydrocarbon tail is forced away from the water. To form a monolayer, a known amount of solution in a suitable solvent is deposited drop-wise on the surface of the water (the sub-phase) by using micro syringe system. Under suitable conditions, surfactant molecules are forced to come closer together and also align themselves at the air-water interface forming a layer that is one molecule thick. This layer is often called a monomolecular layer or a monolayer [72].

![Diagram of monolayer formation](image)

**Figure 1.2:** Formation of monomolecular or monolayer.
1.2.4: LB Forming Materials:

A wide range of materials are suitable for the LB technique for example: fatty acids, porphyrins, phthalocyanines, substituted aromatic compounds, conducting polymers, and liquid crystals. The main class of compounds which form stable Langmuir monolayers on the water subphase are those referred to as “amphipathic” or “amphiphilic”. Most monolayer-forming materials i.e amphiphilic molecule that contain two chemically distinct region, a hydrophilic head part i.e highly polar group (-COOH, -OH, -CN, -NH\textsubscript{3}\textsuperscript{+}, -PO\textsubscript{4}\textsuperscript{3-}, -(CH\textsubscript{2})\textsubscript{2}NH\textsubscript{3}\textsuperscript{+} etc) confers water solubility and a hydrophobic tail part i.e a sufficient large non polar moiety which prevents water solubility. Upon spreading these materials on a water subphase, the hydrophilic heads will immerse into the subphase and induce a uniform distribution across the available surface area, while the hydrophobic tails prevent the molecules from dissolving in the subphase. The monolayer forming abilities of the amphiphiles is depending on the ‘amphipathic balance’ that is the balance between hydrophobic and hydrophilic constituents within the same molecules. A vast range of material is well studied for the formation of Langmuir monolayer at the air water interface. This includes lipid, protein, bio active molecules, nanoparticle and many other bio materials. Recent research has shown that novel compound such as nanowires, carbon nanotube, graphines are also form suitable Langmuir monolayer. Amphiphilic molecules are also known as surfactants or surface-active molecules having unique properties of getting adsorbed at various interfaces (e.g oil-water, air-water etc) and altering the properties of interface. As they have one part of the molecule immersed in to the subphase and the other part pulling away from the subphase. These properties make the molecules float at the air-water interface [73] which have significant technological and biological applications. Depending on the nature of the hydrophilic head group on the surfactants they are classified as ionic and non-ionic surfactants. The ionic surfactants are further classified as cationic and anionic surfactants.
Table 1. The effect on the nature of the molecules when different head groups, R are attached to a $C_{16}H_{33}$ chain (Only amphiphilic and weakly amphiphilic molecule can form Langmuir film).

<table>
<thead>
<tr>
<th>No Film</th>
<th>Unstable Films</th>
<th>Stable Films with C-16 Chains</th>
<th>C-16 Chain Compound dissolve</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrocarbon</td>
<td>-C$_6$H$_4$OCH</td>
<td>-CH$_2$OH</td>
<td>-SO$_3^-$</td>
</tr>
<tr>
<td>-CH$_2$I</td>
<td>-COOCH$_3$</td>
<td>-COOH</td>
<td>-OSO$_3^-$</td>
</tr>
<tr>
<td>-CH$_2$Br</td>
<td></td>
<td>-CN</td>
<td>-C$_6$H$_4$SO$_4^-$</td>
</tr>
<tr>
<td>-CH$_2$Cl</td>
<td>-CONH$_2$</td>
<td></td>
<td>-NR$_3^+$</td>
</tr>
<tr>
<td>-NO$_3$</td>
<td>-CH=NOH</td>
<td>-C$_6$H$_4$OH</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>-NH$_3$CONH$_2$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>-NH$_2$COCH$_3$</td>
<td></td>
</tr>
</tbody>
</table>

The non-ionic surfactants are further classified as Zwitter ionic, semi-polar and single-bond surfactants. Depending on length to diameter ratio amphiphiles/surfactants prefer to form micelles, membranes, bilayers, vesicles etc and also responsible for their accumulation at interfaces (air-water or oil-water) in rather dilute regime.

A Micelle is an aggregate of amphiphilic molecules dispersed in a liquid colloid. A typical micelle in polar solvent forms an aggregate, an organised in spherical structure in such a way, that the polar (“head region”) groups face outwards and non-polar (tail region) groups are branched together at the center of the aggregates (fig. 1.3). For many systems, there is a critical concentration at which such structures start to form and this is known as the Critical Micelle Concentration (CMC). In a non-polar solvent such structures can also exist but with the polar groups facing inwards and the non-polar groups facing outwards.
Vesicles or liposomes are spherical lipid bilayers consist of close structure and approximately spherical in shape like micelles, whose walls are made from bilayers of amphiphilic molecules (fig 1.4). In this case, the hydrophobic part of all the molecules interacts with the similar part of the other molecules. That is the formation of vesicles at the air-water interface is due to the hydrophobic-hydrophobic interactions.

Figure. 1.3: Schematic representation of a micelles.

Figure. 1.4: Schematic representation of a vesicle.
Ideal LB compatible materials are the long chain alkanoic acids, e.g. stearic acid (SA) and arachidic acid (AA) as well as also zinc-arachidate. Their structures are shown in the fig 1.5 and fig.1.6.

![Figure 1.5: The components of an ideal amphiphilic molecule.](image)

![Figure 1.6: Ideal LB compatible molecule and its orientation adopted on the subphase.](image)

Generally an organic molecule having interesting physical characteristics (namely conducting, semiconducting, gas sensing) are attached to long hydrophobic chain (alkyl chain) are widely investigated compounds to make them LB compatible. Another method to make a molecule LB compatible is to attach a molecule into a polymeric backbone. However both these processes require expertization in synthesis and also time consuming and quite costly. Purification of these synthesized materials is also quite laborious and need a lot of expertization. However, novel material may not readily form a monolayer on the surface of the subphase and it must be modified in some way to render it suitable for use with the LB technique. The simplest method of achieving this is to mix the material with a conventional fatty acid in order to form a mixed Langmuir film or alternatively to cause the material to be adsorbed onto a fatty acid film [74].

1.2.5: Surface pressure:

The surface of a liquid has excess free energy due to the difference in environment between the interior molecules and those in the exterior. In the liquid, the molecules
have a certain degree of attraction to each other. The degree of this attraction, also called **cohesion**. It is an intrinsic property of a substance that is caused by the shape and structure of its molecules. In other words, cohesion allows for surface tension, creating a "solid-like" state upon which light (in weight) or low-density materials can be placed. A molecule in the bulk of a liquid is attracted equally in all possible directions by the neighboring liquid molecules, resulting in a zero net force. Thus the bulk/interior molecule of liquid balanced in all direction and practically in a uniform field of force. However a molecule on the surface of the liquid is attracted only sideways and towards the interior. The exterior molecule experienced an imbalanced force due to unbalanced molecular attraction and the molecule at the air-water is pulled down/interior phase than towards the air or gas phase. Hence, there will be a net attractive force tends to pull molecules into the interior of the phase to minimize its surface energy, hence to minimize its area and contract. It is schematically shown in the fig. 1.7

![Figure 1.7: Schematic illustration of the interaction of molecules at an interface and bulk.](image)

Under this condition, the air-liquid interface consequently produces excess free energy or interfacial free energy originating from the difference in environment between the surface molecules and those in the bulk. This interfacial free energy can be determined by the measurement of surface tension which is quantified as a force/length measurement. A contractive tendency on the part of the surface of a liquid to go into bulk of the liquid that allows it to resist an external force is defined as surface tension. In monolayer studies, surface tension is one of the main measurable parameters that can
provide insight into the structure and the composition of the film. Surface tension has the dimension of force per unit length or of energy per unit area representative of the cohesive energy present at an interface. Polar liquids such as water, has strong intermolecular interactions due to hydrogen bonding and thus have high surface tension. Any factor which decreases the strength of this interaction will lower the surface tension. It should be noticed that the surface tension remains constant at a constant temperature but an increase in the temperature of the system will lower the surface tension. Any contamination, especially by surfactants, lowers surface tension. When some impurity is added to the water surface then the surface tension is reduced. Also when a monolayer is compressed on the water surface, the instantaneous surface tension of that surface is reduced due to increase in impurity concentration on the surface. The surface tension of pure water is around 72.8 mN/m at 20°C and atmospheric pressure. If the surface tension of pure water is taken as a zero level reference then the decrease in surface tension can be measured with respect to this reference level and gives negative value. In LB techniques, the surface pressure – molecular area isotherm is one of the important parameter of monolayer properties. If the available surface area to the monolayer is reduced by a barrier system, the intermolecular distance decrease and the surface tension is lowered. The surfactant molecules start to interact and exert a repulsive effect on each other. The force exerted by the film per unit length, corresponds to a two-dimensional analogue of a pressure is called surface pressure π. Additionally, it is important to maintain constant surface pressure during deposition in order to obtain uniform LB films. Measurement of surface pressure can be done by means of a Wilhelmy plate or Langmuir balance [75]. Surface tension and the surface pressure has same unit and magnitude, but surface pressure increases when surface tension decreases. When a dilute solution of an amphiphilic molecule is spread on the water surface by a micro syringe (as shown in fig.1.8) the solution spreads rapidly to cover the available area. As the solvent is evaporated, a monolayer is formed. When the area of the monolayer is large, the distance between the adjacent molecules is also large and their interaction is weak. The monolayer is then regarded as two dimensional gas phase. Under this condition the monolayer has little effect on the surface tension of water.
1.2.6: Monolayer characteristics at the air-water interface: Surface pressure versus area per molecule (\(\pi-A\)) isotherm:

The plot of surface pressure as a function of the area of water surface at constant temperature is known as a surface isotherm which is the most important indicator of the monolayer properties of the surfactant molecules [76]. This are mostly known as a surface pressure/area isotherm and often abbreviated to “isotherm”. This plot can be measured on a point-to-point basis [77].
A schematic representation of surface pressure versus area per molecule isotherm is shown in fig.1.9. This diagram is not for any particular substance but shows most of features observed for long chain compounds [64]. They give rich information on the stability of the monolayer at the air-liquid interface, the existence of phase transition as well as conformational transformation and reorientation of the molecules in the two dimensional systems [76]. A number of distinct regions are apparent on examining the isotherm and it passes through several different phases during compression which are marked by discontinuities in the isotherm. The phase behavior of the isotherm depends on the physical and chemical properties of the monolayer materials, the subphase temperature at which the experiment is carried out and the subphase composition [73]. Various thermodynamic states observed in isotherm depending on the length of the hydrocarbon chain length, magnitude of the cohesive and repulsive forces.

**Gaseous phase (G):** The region marked as G on the fig.1.9 is gaseous phase. In the gaseous phase, the intermolecular distance should be very large as well as very weak interaction between the adjacent molecules and also they exert little force on each other.
The molecules in gaseous phase obey a thermodynamic equation of state in two-dimensions (2D) [73,76]. By assuming that the molecules have an average translational kinetic energy of \( \frac{1}{2} kT \) for each degree of freedom, the 2D total kinetic energy will be \( kT \), where \( k \) is Boltzmann constant and \( T \) is temperature. This yields the following equation:

\[
\Pi A = KT
\]

**LE-G phase:** As a gaseous monolayer is compressed on the water surface, the pressure increases and the two-dimensional monolayer goes expanded (liquid like) state. Therefore, LE-G state usually in this stage that the floating film consists of a mixture of two phases. The molecules are less randomly oriented than the gaseous phase.

**LE - phase or Expanded monolayer phase:** As the surface area of the monolayer is further reduced, the interactions between molecules increases with increasing surface pressure formed the expanded monolayer phases called “Liquid-Expanded” (LE). In the LE phase, the monolayer is coherent, but the molecules still possesses degrees of freedom. The hydrocarbon chains in such a film are less randomly oriented and are pointing away from the water sub-phase.

**LE-LC Phase:** Further compression, the transition from the liquid to the condensed states can occur in the monolayer. The co-existence of both the Liquid Expanded - Liquid Condensed (LE-LC) transition may be directly observed in the floating monolayer by Brewster angle microscopy [78].

**LC phase:** Upon further compression causes the pressure begins to rise more steeply as the liquid expanded phase gives way to a Liquid Condensed (LC) phase.

**Condensed phase:** On further increase of pressure by moving barrier the floating monolayer get completely condensed and form solid region. In the condensed phases, the monolayers exhibit a strong lateral cohesion. The molecules are closely packed because of the strong hydrophobic interactions between the chains and uniformly
oriented pointing away from the interface. If the monolayer is further compressed after reaching the condensed state the monolayer will eventually collapses into three-dimensional structures due to mechanical instability and molecules are forced out of the interfacial film. The collapse is generally seen as a rapid decrease in the surface pressure followed by smaller surface areas, either sliding over upon it, or folding under into the subphase.

![Schematic representation of molecules at different phases during monolayer compression.](image)

Following the definitions above, one can see that fatty acids have 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 common for phospholipids and the position of this horizontal transition phase is temperature-dependent.
Figure 1.11. Schematic $\pi$-A isotherms of long-chain fatty acid(a) or phospholipid(b). The overall shape of the isotherms mainly depends on the subphase temperature, the hydrocarbon chain length and the presence of unsaturated acyl chains.

1.2.7: Types of monolayer

(i) Mixed monolayer:

The current research work contains the fabrication of ultrathin Langmuir-Blodgett film of non-amphiphilic organic molecules mixed with a building matrix such as long chain fatty acid (stearic acid, Arachidic acid) or an inert polymer (viz. polymethyl methacrylate). In such studies, the dilute solutions of the sample and matrix molecules are prepared in a highly volatile and water insoluble solvent such as chloroform. These two solutions are mixed in a predetermined ratio and gently spread on the water surface by a microsyringe. After sufficient time is allowed to evaporate the solvent, the barrier is compressed slowly and the molecules are arranged in an organized way and formed a highly stable monolayer at the air-water interface which can be easily transferred onto a solid substrate to get mono and multilayered Langmuir-Blodgett (LB) film. Non-amphiphilic molecules are not ideal for the formation of stable Langmuir monolayer. However, when they are incorporated into a building matrix, the sample molecules may
be sandwiched among the matrix molecules and form stable Langmuir monolayer at the air-water interface. The monolayer thus formed is known as Langmuir mixed monolayer. A schematic representation of the organization of molecules in the mixed monolayer is shown in fig. 1.12

![Schematic representation of a mixed Langmuir film at the air-water interface.](image)

The miscibility study of the Langmuir monolayer is very important to explore the information not only on the orientation of the molecules but also on the interaction involved within the sample and matrix molecules which are very much responsible for the stability of the monolayer at the air-water interface. To analyze the degree of miscibility and thermodynamic nature of mixing of the binary components in mixed Langmuir monolayer can examined the average area per molecule as a function of the film composition at different surface pressures.

It should be mentioned in this context that for the ideal case of either complete miscibility or complete immiscibility, the law of additivity of area [79-81] is given by

\[ A_{\text{ideal}} = A_1 N_1 + A_2 N_2 \]  

(1)

Where, \( A_{\text{ideal}} \) is the ideal area per molecule, \( N_1 \) and \( N_2 \) are the mole fractions of the constituents molecules of the mixed monolayer, \( A_1 \) and \( A_2 \) are the area per molecules (monomer) of single component at a fixed surface pressure.

The deviation from the ideal behavior can be found by computing the excess area of mixing \( A_\varepsilon \), which is given by \( A_\varepsilon = A_{12} - A_{\text{ideal}} \)  

(2)

Where, \( A_{12} \) is the experimentally observed area per molecule of the mixed monolayer.
The excess or deficit of area $A_E$ delivers detailed information about the nature of interactions that occurs among the constituents molecules of the mixed monolayer. If the components are completely immiscible, then $A_E$ will be zero and therefore a plot between $A_E$ versus $N_i$ will be a straight line which indicates the ideality curve. However, any deviation from the straight line from the additivity rule either positive or negative will indicates the presence of different interactions between the two components i.e. films are either ideally mixed or completely immiscible [82]. To confirm whether the components of the monolayer are completely immiscible or ideally mixed further measurements should be performed such as Brewster angle microscopy or atomic force microscopy. For a mixed monolayer, $A_E$ will be positive for repulsive interactions between the constituent components, the cohesive interactions can be repulsive i.e. an expansion in the monolayer and a larger mean molecular area, resulting in fewer interactions. Whereas $A_E$ will be negative if attractive intermolecular forces exist i.e., cohesive interactions are attractive such as more hydrophobic interactions between the different chains, and the molecules occupy smaller mean molecular area than expected.

Figure 1.13: schematic diagram for various cases of miscibility study.
However, complete immiscibility means strong attractive interaction among like molecules and almost no interactions between unlike molecules.

(ii) Complex monolayer:
This type of monolayer can be formed by the water soluble charge transfer (cationic/ anionic) types of materials [84-85]. In our work, we use one types of ionic material which is water soluble and other types of oppositely charged materials which is water insoluble. This water insoluble oppositely charged material can form a stable Langmuir (L) monolayer at the air-water interface. For the formation of stable and floating layers on the water subphase, first of all a dilute solution of oppositely charged water insoluble Arachidic Acid (AA) having concentration (0.5mg/ml was used for all experiments and kept constant) in chloroform was spread at the air-water interface of the LB trough to prepare a Langmuir monolayer. Allowing sufficient time to evaporate the solvent the barrier was compressed slowly to reach the nominal initial surface pressure and then the barrier was kept fixed. After delay for few minutes to stable the monolayer, dilute aqueous solution of water soluble substance methylene Blue (MB) were slowly injected to the back side of the LB trough by a micro syringe so as not to disturb the preformed AA monolayer. After that the corresponding increase in surface pressure versus time was recorded.

![Figure 1.14: Reaction kinetics of water soluble material.](image)
When water soluble molecules started crossing the barrier through the sub phase, reaction kinetics is started and it is observed that the surface pressure increases with the passage of time. As soon as the water soluble molecules came into contact with the AA monolayer, interaction occurred between AA and MB molecules and to form AA-MB complex at the air-water interface. With the passage of time the rise in surface pressure clearly indicates that the number of AA-MB complex at the air water interface increases. After a certain time gap, the surface pressure becomes stable. The flat plateau like region observed in the surface pressure-time curve, indicates the completion of adsorption process. Moreover, the area per molecule of this complex monolayer is greater than the area per molecule of AA monolayer. However, the barrier is kept fixed at a particular position, hence the tendency to increase the surface pressure gradually. This increase in surface pressure with time is actually a direct evidence of reaction kinetics between AA-MB complex molecules. Reaction kinetics is given below.

\[
\begin{align*}
\text{C}_{19}\text{H}_{31}\text{COOH} \quad &\quad \text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S} \\
\downarrow \quad &\quad \downarrow \\
\text{C}_{19}\text{H}_{31}\text{COO}^- \quad &\quad \text{C}_{16}\text{H}_{18}\text{N}_3\text{S} \quad \rightarrow \text{COMPLEX}
\end{align*}
\]

1.2.8: Two-dimensional phase rule:
Surface pressure – area isotherms can reveal the miscibility in mixed monolayers and directly represent phase diagrams. Other phase diagrams can be generated from the surface pressure-area isotherm measurements when performed at different temperatures. By plotting the surface pressure at which the transition between phases occurs as a function of temperature, a 2D phase diagram can be constructed. This type of phase diagram reveals the miscibility of the components in the case of mixed films.

To better understand the phase diagrams, we have used the Gibb’s surface phase rule described by Gaines and Petty [64, 73]. In monolayer experiment, there are four degrees of freedom: temperature, external pressure, monolayer surface pressure and the composition of the mixed film. When the temperature and external pressure are kept
fixed, the number of degrees of freedom for a monolayer system is expressed by the equation:

\[ F = C^b + C^s - P^b - (q-1) \]  \hspace{1cm} (3)

Where \( F \) is the number of degrees of freedom, \( C^b \) and \( C^s \) are the number of components in the bulk and on the surface, respectively, \( P^b \) is the number of phases in the bulk. Here, \( q \) is the number of monolayer phases present in equilibrium with one another. For a two components monolayer system at the air-water interface, \( C^b = 2 \), \( C^s = 2 \) and \( P^b = 2 \). So, the eq3 simplifies to

\[ F = 3 - q \]  \hspace{1cm} (4)

For a monolayer of two components that are miscible, two homogeneous phases will be present at equilibrium with each other and so \( q = 2 \) and hence the system will have one degree of freedom. Therefore, collapse pressures will show variation as a function of film composition i.e the collapse pressure changes as a function of the molar fraction. On the other hand, in a two component, mixed monolayer system in which the film components are immiscible, there are three equilibrium surface phases and so \( q = 3 \) and thus the system will have zero degree of freedom. This means that collapse pressure will be independent of composition.

The phase rule and the equilibrium spreading pressure provide a useful tool to detect the miscibility of the monolayer in terms of number of phases on the surface. It gives insight into the conditions at which the experiment should be performed to obtain desirable and reproducible monolayers. The phase rule determines the miscibility of the components at the equilibrium spreading pressure. However, some of the components of the monolayer might be miscible at low surface pressure and become immiscible upon compression [64].
1.2.9. Forces responsible for the formation and stability of Langmuir monolayer:

The monolayer stability and hence, the monolayer homogeneity is one of a prerequisite to elaborate organized Langmuir-Blodgett films with a high structural quality. Monolayers of organic molecules are molecular assemblies formed spontaneously on surfaces by adsorption and are organized into more or less ordered domains [86-87]. Hydrophilic head groups are consist of polar groups such as carboxylic acid, sulphates, amines, alcohols etc. These are all attracted to the polar media such as water and the forces acting on them are predominantly ionic and columbic type \(1/r^2\), \(r\) being the intermolecular separation). On the other hand, hydrophobic groups such as a hydrocarbon chain, fats, lipids etc. are almost water insoluble and the forces acting on them are predominantly Van der waal’s type \(1/r^{12}\) or \(1/r^6\). The monolayer packs tightly due to the van der Waals interactions [88], thereby reducing its own free energy [86]. The sum of these attractive or repulsive forces as well as the changes in entropy during monolayer compression plays important role in determining the phase behavior of the monolayer at the air-water interface. The origin of these forces has been discussed in detail by Israelachvill [89]. However the magnitude of the individual contribution of the above mentioned forces is governed by the temperature at which the experiment is carried out and also the molecular structure of the surfactant. The \(p^H\) and composition of the subphase also influence the phase behavior of the spread monolayer. Generally, an increase in temperature causes an expansion of monolayer due to the increase in thermal movement of the constituent molecules.

(i) Van der waals’ force:

The condensed states in the monolayer are mainly due to the the weak Van der Waals’ attractive forces between the hydrophobic part. These forces are mainly short-range and inversely proportional to the sixth power of the intermolecular separation. According to quantum mechanical calculations for long, linear hydrocarbon chains, a fifth order dependence has been suggested [90]. Again for saturated hydrocarbon, the extent of the force is directly proportional to the number of carbon atoms present in the carbon chain.
(ii) Electrostatic Interactions:

Interaction between the polar head groups in a spread monolayer is known as dipole-dipole interaction. This occurs mainly in the monolayer. However, if the constituent molecules of the floating monolayer are partially ionized, ion-ion and ion-dipole interaction may take place [91]. The ion-dipole and ion-ion interactions are inversely proportional to the second and third power of the intermolecular separation respectively. Increase in ionization leads to an expansion of the monolayer due to the repulsion between the ions of the same kind.

1.2.10: Formation of Langmuir-Blodgett (LB) film:

The compressed monolayer (i.e condensed phase) can be transferred on to solid substrate to form Langmuir-Blodgett (LB) film. This process involves moving the substrate through the monolayer at the air-subphase interface. To obtain high quality and defect free films, the monolayer has to be in the solid state [92]. The properties of such films largely depend on fabrication procedure and also on various LB parameters such as surface pressure and temperature of the monolayer. Langmuir-Blodgett (LB) deposition has been successfully carried out, when the surface pressure is high enough to ensure that there is sufficient attractive force(lateral cohesion) in the interfacial film so that the monolayer does not fall apart during transfer to a solid plate. In general the Langmuir monolayer can be transferred like a “carpet” from the water subphase onto a solid plate can be made by successfully raise and lower a solid substrate through the monolayer while maintaining the surface pressure is kept fixed by computer controlled feedback system between the electro balance measuring the surface pressure and the barrier moving mechanism. Consequently the floating monolayer is adsorbed to the solid substrate and in this way multilayer structures of hundreds of layers can be produced. K. Blodgett and I. Langmuir first described this technique [39] and accordingly this is called Langmuir-Blodgett (LB) technique. The deposition process is schematically shown in figure 1.15.
The Langmuir-Blodgett (LB) deposition technique offers a great development of the thin film concept and control over the architecture of the films at the molecular level. However, depending on the behavior of the molecule the solid substrate can be dipped through the film until the desired thickness of the film is achieved. Different kinds of LB films can be produced by successive deposition of monolayers on the different substrate (hydrophilic/hydrophobic) shown in fig.1.16. Depending on the nature of the substrate the Langmuir film can transfer in three different modes, namely Y, X, Z are mentioned below:
(a) \textit{Y type deposition:}

This is the most common method for the deposition of a Langmuir monolayer onto a solid substrate. Y-type deposition refers to the situation in which a substrate picks up material from the subphase on both the downward and upward directions. Such a two way deposition leads to stack in head-to-head and tail-to-tail fashion resulting in a so called Y type film. In figure 1.16a a well organized monolayer at the air-water interface is shown. For a hydrophilic substrate, the substrate immersed into the subphase before the monolayer formation and then the hydrophilic part of the substrate can interact with the hydrophilic part of the molecules. After transfer of the first monolayer during upstroke, a hydrophilic substrate becomes hydrophobic. Therefore the second monolayer will be deposited at the downstroke.

On the other hand for a hydrophobic substrate becomes hydrophilic in nature after first monolayer transfer during downstroke because hydrophobic alkyl chains interact with the substrate surface. Therefore the second layer is transferred during upstroke and then it becomes hydrophobic again. This type of film deposition is known as Y-type deposition technique. Subsequently, multilayers of LB films will build up by successive depositions of single layers on a solid substrate as shown in figure 1.16d.

![Diagram](image.png)

\textbf{Figure: 1.16a: Monolayer after compression}
Chapter 1: Introduction

Figure 1.16b: Transfer of first layer.

Figure 1.16c: Transfer of second layer.

Figure 1.16d: Y-type film on a hydrophobic substrate.
(ii) X-type and Z-type depositions:

In X-type deposition the molecules are arranged in head to tail configuration and picks up on the substrate during the downstroke or immersion. In contrast, Z-type deposition is when the molecules arranged in tail-to-head configuration and transfer only upstroke or emersion. These two type of deposition are as shown in the fig 1.17 and 1.18. Here in both the cases the films are less stable compared to Y-type deposition because in that deposition the neighbouring molecules are interact via compatible parts i.e hydrophobic-hydrophobic or hydrophilic-hydrophilic in nature and also ensure the maximum stability of multilayer coverage.

Figure 1.17: X-type deposition scheme.
However, for an ideal X-type multilayered film the transfer ratio is always one for the immersion and zero for the emersion whereas for an ideal Z-type Langmuir-Blodgett multilayered film, the transfer ratio is always zero for immersion and one for the emersion. However both these X type and Z type deposition have great importance in nonlinear optical application due to their non-Centro symmetric structure [93].

1.3. Layer by Layer self-assembled films (LbL):

Polyelectrolytes multilayers self-assembled by the Layer by Layer exhibited unique layer sequence for fabrication of organized thin film and seen as the true alternative to the LB technique. This method is based on strong interaction between two oppositely ion-pairs to buildup multilayered structures. Therefore, Layer-by-layer (LbL) self assembly [94-99] also known as electrostatic self assembly is a recent approach toward nanoscale multimaterial films that allows versatility of surface modification of various substrates on a molecular level, owing to its simplicity and universality [100]. The fabrication of multicomposite films by the LbL procedure has the ability to control the molecular orientation and organizations in the nanometers scale with precisely tuning.
the macroscopic properties of organic and polymer thin films. Large varieties of charged materials, including almost all kinds of polyions, dyes [101], biopolymer such as proteins [29-31], DNA [102], Light emitting polymers [103-104], inorganic macromolecules such as clay [27-28] have been assemblies using this technique. This technique also has the benefit to being able to control the total thickness and composition of individual layers in the films. In addition, it avoids defect propagation from layer to layer and also it is a simpler technique involving simple equipment. It also supplies physically strong films and possibility to be deposited on supports of any shape and dimension.

There are many factors influencing the microstructure of the layer-by-layer self assembled multilayers, such as the molecular configuration of polyelectrolytes, stretching extent of polymer chains, average charge density, adsorption speed etc.

The potential for co-release of two or more drugs with different release profiles, or even time-dependent staged delivery becomes plausible through the use of top-down compartmentalized regions of LbL thin films [105-107]. Such translation relies on the ability to show the power of multilayer systems in meaningful biomedical applications, as well as the potential for commercial manufacturability of the LbL process. The field has been growing rapidly, and many researchers have contributed to the development of new LbL drug delivery systems [108-111]. A unique advantage to the use of LbL assembly is its ability to incorporate drugs in high concentrations within a multilayer thin film.

1.3.1: History of Layer by Layer adsorption process:

Engineering and development of Organic compounds having Multilayer assembly on surfaces has been explored over a decade ago [112]. Multilayer assembly such as “layer-by-layer (LbL) assembly,” or “molecular self-assembly,” was introduced a method to functionalize surfaces and to fabricate thin films. For fabrication of the thin films, Decher and collaborators was first introduced the polyelectrolyte multilayer architecture formation by the alternate LbL self-assembly to a solid support, which allows control over several critical factors such as control over the thickness of the thin film and
morphology of each bilayer. Eventually, in 1995, T. Mallouk [113] was first
demonstrated the multilayer films assembly on non-planar surfaces, namely on
microparticle and then brought to a sheer explosion by H. M€ohwald and his team a few
years later [114-115]. Polyelectrolyte multilayers were even deposited on nanoparticles
[116-117] a process that was further enhanced [118-119] and which led to very
interesting and very small multifunctional objects [120-121]. This self assembled
technology can be performed on various insoluble substrates and have applications in
chemosensing, biotechnology, and nanotechnology [111, 122]. The process started with
simple bola-shaped amphiphiles [94] and was quickly extended to simple
polyelectrolytes [96] and functional macromolecules including proteins [20-31] or DNA
[102]. Eventually, in 1994, biological nanoparticles [123] and inorganic nanoparticles
[124-125], including magnetic [126] and gold [127] nanoparticles, were added to the list
of possible multilayer film constituents. The LbL technique was first applied to assemble
oppositely charged polyelectrolytes depositing alternating layers of oppositely charged
materials with wash steps in between. Due to its simplicity and the unprecedented choice
of different components for polyelectrolyte multilayers and related systems, the method
is today well established in materials science and in making its way into the life science
as well. Specifically, in 2010, more than 1000 articles were published in this field.

The first implementation of this technique is attributed to R. K. Iler of DuPont, who
carried it out using microparticles (charged alumina and silica particles) in 1966 [93].
There has been a renewed interest over the past fifteen years due to the boom in
nanotechnology research [93]. The method was later revitalized by the discovery of its
applicability to a wide range of polyelectrolytes by Prof. Gero Decher initially appeared
in 1991 [94, 128]. In 1997, Science published a review authored by Gero Decher that
reinvigorated research in the layer-by-layer assembly field [100]. His Science article
reviewed those earlier efforts and has spurred a renaissance of interest in electrostatic
LbL assembly chemistry. Decher’s goal was to devise procedures that could be used to
construct future nanodevices, biomedical applications in drug delivery, cell technology
[129-130]. Decher’s approach to this problem was based on his belief that there must be
a fixed relationship between nanoscopic order and macroscopic orientation. To achieve
this goal, one must know the location or orientation of every molecule in respect to the entire nanostructure. Decher claimed that high-quality multilayer thin films cannot easily be used covalently bound layers. He claims that the steric demands are too great for proper layering to occur. This reasoning drove Decher to develop a simple approach to layer-by-layer assembly that would be independent of both the topography and size of the substrate. The simple solution to this problem was using a method that does not have steric constraints. Electrostatic interactions were chosen in place of covalent bonds. By taking a polyanion and polycation (fig.1.19), Decher was able to design a scheme for the deposition of polymer thin films on a surface. A simple representation can be made by defining two oppositely charged polyions as + and −, and defining the wash step as W. To make an LbL film with 5 bilayers one would deposit W+W−W+W−W+W−W+W−W+W−W+W−W+W−W+W−W+W−W, which would lead to a film with 5 bilayers, specifically + − + − + − + − + − + − + − + − + −.

Over the last decade there have been hundreds of articles published highlighting various electrostatic LbL assemblies [131]. These articles use inorganic/inorganic, inorganic/organic, organic/organic, biological/organic, and biological/biological bilayer assemblies. Caruso and Möhwald created protein/polyelectrolyte-based multilayer systems in 1999 using polystyrene particles as a substrate for colloidal LbL assembly [132]. Using fluorophore labeled proteins; they were able to successively manufacture spherical multilayer-assembled shells. This is an example of biological/organic multilayer assembly. Biological/biological multilayer assemblies have potential applications in gene therapy and especially thin film designs. For example, in 2006 Ji described an LbL assembly that could purportedly serve as a DNA delivery device [133].

LbL offers several advantages over other thin film deposition methods. LbL is simple and inexpensive. There are a wide variety of materials that can be deposited by LbL including polyions, metals, ceramics, nanoparticles, and biological molecules. Another important quality of LbL is the high degree of control over thickness, which arises due to the linear growth of the films with the number of bilayers. The fact is that each bilayer can be as thin as 1nm; this method offers easy control over the thickness with 1nm.
resolution. LbL has found applications in corrosion control, biomedical applications, [134] ultra strong materials, [135] and many more [136].

1.3.2: Basic principles of the layer-by-layer technique:
The fabrication of multicomposite films by the LbL procedure means assembly of hundreds of different materials in a single device using environmentally friendly, ultra-low-cost techniques. Layer-by-layer synthesised thin films have found applications, in a variety of scientific applications, and these include biosensors, controlled drug delivery, surface coatings, and environmental applications in the degradation of toxic pollutants [137-143]. To build up of mutlilayers structure, sequencial dippings are performed by the electrostatic attraction between the oppositely charged constituents [144]. However, hydrogen bonding [145-147], hydrophobic interactions [148] and vander Waals forces [149-150], coordination bonding, [151-152] Charge transfer, [153] biological recognition [154] etc. can also be used as the driving force for the LbL assembly systems or influence the stability, morphology and thickness of the films. Since the process is done by dipping a substrate in solutions, there are no size and shape limitations.

Figure: 1.19: A simple model of the Layer-byLayer sequential adsorption.
Generally, LbL self-assembly proceeds as follows: A charged substrate is immersed into the first polyelectrolyte solution for a long enough time to absorb the first monolayer. Then a washing cycle follows to remove unbound polymer material. After the first layer is adsorbed, the substrate is then dipped into a polyelectrolyte solution of opposite charge. This second polyelectrolyte adsorbs to the surface due to electrostatic attraction and actually overcompensates for the surface charge [155] resulting in a reversal of the surface charge. This procedure is then repeated until the required number of layers has been deposited. Some LbL processes require no washing cycles thus shortens the duration of the assembly process [156].

![Chemical structures of ionic sites of polyelectrolytes.](image)

**Figure 1.20:** Chemical structures of ionic sites of polyelectrolytes.

### 1.4: Characterisation of Ultra Thin Films:
Once stable films is formed onto a solid substrate it is important to study the structural photophysical, electrical, morphological and other properties of LB films in order to understand the nature of organization of the specific molecules in the ultra thin films as well as to understand the feasibility of this film to some specific technological applications.

A variety of techniques have been used to analyze such systems in order to study their structural and morphological properties. Atomic Force Microscope (AFM), Scanning Electron Microscope (SEM), Scanning Transmission Microscope (STM), Transmission Electron Microscope (TEM), Brewster Angle Microscope (BAM), Fluorescence Imaging Microscope (FIM) etc. are used to get a visual picture of the ultra structure and domain structure of the LB and LbL films. For photophysical characterizations, UV-Vis...
Absorption Spectroscopy, Fluorescence Spectroscopy, Time Resolved Spectroscopy, Fourier Transform Infrared Spectroscopy (FTIR), Raman Spectroscopy, Grazing Incidents X-ray Diffraction (XRD), Electron and Neutron diffraction and various other experimental techniques are used. Recent research interests also emphasize on the study of various other characteristics namely pyroelectricity, magnetism, second harmonic generation, lasing action, light emitting diode etc. of LB films of various organic, metallorganic and polymeric materials.

This work is concentrated on the spectroscopic studies of mono and multilayered Langmuir – Blodgett (LB) and Layer by layer (LbL) films of various molecules. For LB technique I have mixed inert fatty acid (Behenic acid, Arachidic acid) and inert polymer matrix (Poly methyl methacrylate) and some water soluble anionic, cationic materials are used for LB film preparation. And for Layer by layer process I have chosen cationic polymer (poly allylamine hydrochloride, PAH) and other anionic polyelectrolytes.

1.4.1 Spectroscopic Characterisation:

The conventional spectroscopic techniques such as UV-Vis absorption spectroscopy, fluorescence spectroscopy and FTIR spectroscopy are used for spectroscopic characterization of the ultra thin film prepared in this research work. These techniques are discussed in the experimental part of chapter 3

1.4.2 The Basic Concept of Photoluminescence:

Photoluminescence is characteristics of the absorbing system with energy ranging from a few electron volts to several electron volts. Infact the word photoluminescence is a special kind of luminescence (light emission) and is initiated by photo excitation. It covers any form of matter that will absorb light energy and then release that energy in the form of light. Atoms or molecules get excited and eventually moves in the next higher energy state, this is why the interaction of an atom or molecule of a substance with an electromagnetic field of suitable frequency leads the atom or molecule to the absorption of photons in the form of light. The atom or molecule excited in the higher state must return to the ground state unless it gets involved in a photochemical reaction.
so that it loses its own identity. The excited molecule may lose its excitational energy by following different photophysical path ways. These photophysical processes generally occur in a period less than the natural radiative lifetime of the molecule. Consider a molecule may get excited by absorption of energy hv. And it moves in to the higher energy level \( A^* \) The equation is given as follows

\[
A + hv = A^*
\]  

(5)

Here \( A^* \) is an electronically excited molecule with excess vibrational energy in \( S_1 \) state or the molecule may be excited to the higher singlet state such as \( S_2^* \), \( S_3^* \), etc. There are various pathways through the excited molecule \( A^* \) may returns to the ground state by losing the excitational energy. The different path ways are as follows:

1. Unimolecular process
2. Bimolecular process

**1.4.2.1 Unimolecular Process:**

The rate constants of photo physical processes in which the intrinsic properties of the molecule do not depends on the external perturbation, such as the presence of other molecule, is referred to as unimolecular process. In the absence of bimolecular quenching and other photophysical reaction, the excited molecule deactivates its excess energy and come back to the ground state. The various steps followed by the molecule inorder to come back to the ground state and their transition schemes are given in the following table. Here \( A \), \( A^* \) and \( A^3 \) are the molecule present in the ground state, first excited singlet state and molecule in the triplet state respectively. Various transition schemes occurring frequently in unimolecular processes are depicted in the modified Jablonski [157] diagram and are shown in the fig.1.21.
Chapter 1: Introduction

The emission of the excitational energy of an excited species provides considerable and most reliable information about the nature of the primary photophysical process. $S_0$, the detailed knowledge about the various processes through which this excitational energy is emitted, is of fundamental importance. This excess energy may be lost either by the direct emission or by following various intermediate pathways. The Unimolecular process subdivided in to two categories as follows:

1) Radiative transition.

2) Non-radiative transition

### 1.4.2.1 Radiative transition:

There are several possibilities of excited state returns to the ground state by emission of radiation. Generally, a radiative transition can be defined as a transition between different multiplicities of a molecular entity associated with the absorption or emission of photons. In such case the excited species emitted its excitational energy or radiation and deactivates to the ground state or the ground state molecules are absorbed energy and excited to the next higher energy state by absorption of radiation. These types of
transitions are normally denoted by straight arrows. For example, the radiative transition from $S_1$ to $S_0$ is denoted by the symbol $S_1 \rightarrow S_0$. There are several photophysical ways by which the excited molecules lose its excitational energy and deactivated to the ground states. There are two type of radiative transition viz.

1. Fluorescence

2. Phosphorescence

Through these two processes the excited molecules can come back to the ground state. The next section gives a brief idea about these two important types of radiative transition.

**Figure 1.21: Various transitions occurring in unimolecular processes depicted in Jablonski diagram.**

### 1.4.2.1 1.1. Fluorescence emission:

A molecule raised to an upper vibrational level of any excited state rapidly loses its energy either by emission of radiation or by collisional deactivation. The excess excitational energy in a vibration – coupled electronic transition is quickly lost to the surroundings. For an allowed transition the molecules come to stay at the vibrational
level of the first excited state for $10^{-8}$ s. The molecule present in the zero – vibration level of the first excited state emitting radiation and may returns to the ground state. This is known as fluorescence emission. It is in accordance with Franck – Condon principle is expected similar to that of absorption. In such case the frequency of the initial absorption is higher than the frequency of the emitted radiation. This is because when it is coming to the zeroth vibrational level of the first excited state it lost some part of the energy. Shortly, the radiative transition between two electronic states having the same multiplicity is referred to fluorescence emission. According to M. Kasha’s rule $[158]$ the fluorescence emission is defined as the electronic transition from $S_1$ to $S_0$. In some cases, molecules are found to exhibit dual fluorescence $[159-161]$. These are the exception of M. Kasha’s rule. This dual fluorescence may be due to simultaneous emission of radiation from $S_2$ to $S_1$ as well as $S_0$. This has been attributed to the thermalization and low population density of the state $[162-163]$. The twisted intermolecular charge transfer (TICT) is also an important reason for the occurrence of dual fluorescence $[164-166]$. In case of simplest fluorescence, the radiated emission is of the same frequency as that of the exciting radiation. It is observed only in the gas phase at low pressures and only with atoms or simple molecule. The rate constant for the fluorescence emission ($k_f$) is defined as, $k_f = 1/\tau_N$, where $\tau_N$ is the natural radiative lifetime of the molecule. In presence of external deactivating processes, the average lifetime is found to reduce appreciably. Hence the modified expression for the life time is $\tau_N = 1/(K_f+\Sigma K_i)$. Where, $+\Sigma K_i$ represents the rate constant for the $i^{th}$ unimolecular competitive process. Generally it is observed from the Franck – Condon principle that the fluorescence spectra is always have the higher wave length than that of the absorption spectra. Such a bathochromic shift indicates that the emitted quanta are of lower energy than that of the absorbed quanta i.e. $h\nu_f < h\nu_a$ and this type of shift is called Stoke’s shift. However, under certain conditions such as high temperatures, (i.e. when the higher vibrational levels of the ground state are thermally populated) reverse phenomenon known as Anti- Stoke’s shift ($h\nu_f > h\nu_a$) may also be observed.
The quantum efficiency of fluorescence $\varphi_f$ is defined as,

$$\varphi_f = \frac{\text{Rate of emission}}{\text{Rate of absorption}}$$

i.e. $\varphi_f = \frac{K_f[S_1]}{I_a}$

Here $[S_1]$ is the concentration of the lowest excited singlet molecule. Again, in photostationary equilibrium condition, the rate of the formation of $S_1$ is same as that of the deactivation of $S_1$.

i.e. $I_a = (K_{IC} + K_{ISC} + K_f) [S_1]$

$$\Rightarrow [S_1] = \frac{I_a}{K_{IC} + K_{ISC} + K_f}$$

So, the expression of quantum efficiency of fluorescence $\varphi_f$ becomes

$$\varphi_f = \frac{K_f}{K_{IC} + K_{ISC} + K_f} = \frac{K_f}{K_f + \sum K_i}$$

1.4.2.1 1. 2 Phosphorescence emissions:

Phosphorescence is a specific type of photoluminescence related to fluorescence. Unlike fluorescence, a phosphorescent material does not immediately re-emit the radiation it absorbs. The slower time scales of the re-emission are associated with "forbidden" energy state transitions in quantum mechanics. As these transitions occur very slowly in certain materials, absorbed radiation may be re-emitted at a lower intensity for up to several hours after the original excitation. In this process the transition occur between two electronic states having different multiplicity. This transition can occur when two excited states possess comparable energies. The spectroscopic transition between the singlet ($S = 0$) and triplet state ($T = 1$) is forbidden according to selection rule $\Delta S = 0$. 

Chapter 1: Introduction
Hence theoretically the phosphorescence transition is spin forbidden as $\Delta S \neq 0$ in such transition. However kinetically the transition between two excited states may take place that is through radiation less transition induced by the collisions known as inter – system crossing. This inter – system crossing makes a triplet state highly populated. Although population of triplet states by direct absorption from the ground state is insignificant, a more efficient process exists for population of triplet states from the lowest excited singlet state in many molecules. This process is referred to as intersystem crossing, and is a spin-dependent internal con-version process. Once the molecule from the excited singlet state comes to the excited triplet state through intersystem crossing, it cannot return to the excited singlet state again. Hence it ultimately reaches the zeroth vibrational level of the excited triplet state.

Although transition from excited triplet state to the ground state is spin forbidden however, transition may take place but very slowly compared to an allowed electronic transition. The phosphorescence emission consists of frequencies lower than that absorbed initially. This type of emission is spin forbidden and is not observed under ordinary conditions. However the transition probability $T_{1\leftarrow S_0}$ transition may be enhanced by spin – orbit coupling interactions achieved by a number of ways such as;

* External heavy atom perturbation.
* Presence of paramagnetic molecules.

Phosphorescence in rigid glass matrices deactivates the vibrational energy due to collision is minimal [167-169]. Because of the forbidden nature of $T_{1\leftarrow S_0}$ transition, $T_1$ is a long lived state. Generally phosphorescence is not observed at room temperature. But at room temperature phosphorescence is observed for some fluid or solid substances [170]. The simultaneous radiative transition from higher energy triplet states is known as dual phosphorescence [171]. This type of phosphorescence is also observed for some compounds. The Quantum yield of phosphorescence, $\phi_p$ is defined as number per second of quanta emitted as phosphorescence in $[T_1]$ is the concentration of the triplet molecules.
\[ \phi_p = \frac{\text{Rate of phosphorescence}}{\text{Rate of absorption}} \]

\[ \Rightarrow \phi_p = \frac{K_T[T_1]}{I_a} \]

Here \([T_1]\) is the concentration of the triplet molecules. Again under the condition of photostationary equilibrium, the rate of activation excited triplet states is equal to the rate at which \(T_1\) deactivates. Hence,

\[ [T_1] (K_P + K_{ISC}^T) = K_{ISC} [S_1] \]

\[ \Rightarrow [T_1] = \frac{K_{ISC} [S_1]}{K_P + K_{ISC}^T} \]

\[ \Rightarrow [T_1] = I_a (\frac{K_{ISC}}{K_f + K_{IC} + K_{ISC}}) \frac{1}{K_P + K_{ISC}^T} \]

Thus the expression for the phosphorescence quantum yield \(\phi_p\) reduces to the form as,

\[ \phi_p = \frac{K_P}{K_P + K_{ISC}^T} \cdot \frac{K_{ISC}}{K_f + K_{IC} + K_{ISC}} \]

\[ \Rightarrow \phi_p = \phi_T \frac{K_P}{K_P + K_{ISC}^T} \]

Where, \(K_{ISC}^T\) is the rate constant for the inner-system crossing from triplet to the ground state singlet, \(\phi_T\) is the quantum efficiency for the triplet formation.

1.4.2.1.2. Non-Radiative Transition:

In non radiative transition, the energy is released as phonons, more commonly known as heat. Non radiative relaxation occurs when the energy difference between the levels is very small, and these typically occur on a much faster time scale than radiative transitions. For many materials (for instance, semiconductors), electrons move quickly from a high energy level to a meta-stable level via small nonradiative transitions and then make the final move down to the bottom level via an optical or radiative transition. This type of conversion is an intrinsic property of polyatomic molecule. Wavy arrows as
shown in the figure 1.21 conventionally denote the non – radiative transition. There are two major type of non – radiative transitions:

* Internal conversion (IC).

* Inter – system crossing (ISC).

1.4.2.1.3. Delayed Fluorescence:

Delayed fluorescence is a non-collisional energy transfer process, which actually give long-lived emission of radiation: the processes were known as α- and β-phosphorescence. Thus the long-lived delayed emission of the excitational energy possessed by an excited molecule shows very different spectral characteristics from that of the fluorescence. The spectra of several delayed emissions are found to coincide exactly with that of the prompt fluorescence from the lowest singlet state, with only difference being in their lifetime. This result in emission with the same spectral distribution as normal fluorescence but with a much longer decay time constant because the molecules stay in the triplet state before emitting from Singlet. Studies of delayed fluorescence in a variety of aromatic hydrocarbons show that the intensity of delayed fluorescence is proportional to the square of the intensity of the exciting radiation and to the square of the phosphorescence intensity, indicating that it is a biphotonic process involving two triplet states. These processes are known as the delayed fluorescence.

Delayed fluorescence can be broadly classified into three groups:

1. E-type delayed fluorescence
2. P-type delayed fluorescence and
3. Recombination fluorescence.

1. E-type delayed fluorescence:

E-type delayed fluorescence show features characteristics of the normal, short-lived, fluorescence. It is observed when the singlet-triplet energy gap (ΔE_{ST}) be small. The process in which the first excited singlet (S_1) becomes populated by thermally activated
radiationless transition (reverse intersystem crossing) from the first excited triplet ($T_1$) state, consequently its efficiency increases with increasing temperature. Here the molecules initially excited to the singlet energy level, cross over to the triplet level by intersystem crossing.

2. **P-type** delayed fluorescence: The process in which the first excited singlet state is populated by a collision between two molecules in the triplet state (triplet-triplet annihilation) [172] can provide enough energy to allow one of them to return to the excited singlet state. Such triplet-triplet annihilation thus leads to a delayed fluorescence emission called **P-type** delayed fluorescence. In this biphotonic process the lifetime of delayed fluorescence is half the value of the concomitant phosphorescence [172].

3. **Recombination fluorescence**: The first excited singlet state becomes populated by recombination of radical ions with electrons or by recombination of radical ions of opposite charge [173] i.e by cation-anion recombination when both one and two photon process exist [174].

### 1.4.2.2. Bimolecular process:

The primary condition for a biomolecular process is close approach of two molecules i.e. the collision of two molecules is required for the occurrence of a bimolecular process. The closeness of approach is a variable term, which depends on the nature of the interaction between the two colliding molecules. The external perturbation opens several pathways for the deactivation of the access excitational energy. The process, which constantly competes with the spontaneous emission process and thereby shortens the lifetime of the emitting molecule, is known as quenching. The bimolecular reactions such as quenching may be classified as follows:

1. **Self – Quenching**: The quenching of an excited atom (etc) by interaction with another of the same type of atom in the ground state

2. **Impurity – Quenching**: Addition of other substances leads to this type of quenching.
3. **Solvent – Quenching:** It may involve other physical parameters as well such as solute – solvent interactions.

4. **Electronic energy transfer:** It is very important bimolecular deactivation process. In this process a molecule initially excited by absorption of radiation, transfers its excitation energy by non radiative mechanism to another molecule. The second molecule, thus excited, can undergo various photophysical and photochemical processes according to its own characteristics.

1.5. **Formation of excimer and excimeric emission:**

Many molecules that do not interact significantly in their ground states appear to form reasonable stable complexes when excited. The complexes are called excimers, word derived from excited dimer. An excimer (originally short for excited dimer) is a short-lived dimeric or heterodimeric molecule formed from two species, at least one of which has completely filled valence shell by electrons (for example, noble gases). In this case, formation of molecule is possible only if such atom is in an electronic excited state (by schematic representation it shown in the fig. 1.22). Thus, an excimer is produced by the interaction of an excited molecule with a ground-state molecule of the same identity. Heteronuclear molecules and molecules that have more than two species are also called exciplex molecules (originally short for excited complex). Excimers are often diatomic and are composed of two atoms or molecules that would not bond if both were in the ground state. The lifetime of an excimer is very short, on the order of nanoseconds. Binding of a larger number of excited atoms form Rydberg matter clusters, the lifetime of which can exceed many seconds. Excimers were observed while studying the effect of increasing concentration on the fluorescence spectra of some molecules. The fluorescence intensities of some molecules increase initially with increasing concentration but further increase of concentration make the intensities to fall. When the concentration is sufficiently high then this fall in the fluorescence intensity is accompanied with the appearance of a new band at the longer wavelength region, the intensity of which increases with increasing concentration [175-176]. Actually, emission from the excimer occurs at lower energy than of the monomer, and is typically broad.
and structureless because emission leads to a continuum resulting from repulsion of the ground-state molecule. Some aromatic hydrocarbon such as pyrene shows this behavior distinctly.

Figure 1.22: Schematic representation of the excimer formation.

Under the molecular orbital formalism, a typical ground-state molecule has electrons in the lowest possible energy levels. According to the Pauli principle, at most two electrons can occupy a given orbital, and if an orbital contains two electrons they must be in opposite spin states. The highest occupied molecular orbital is called the HOMO and the lowest unoccupied molecular orbital is called the LUMO; the energy gap between these two states is known as the HOMO/LUMO gap. If the molecule absorbs light whose energy is larger than this gap, an electron in the HOMO may be excited to the LUMO. This is called the molecule's excited state. Excimers are only formed when one of the dimer components is in the excited state. When the excimer returns to the ground state, its components dissociate and often repel each other. The wavelength of an excimer's emission is longer (smaller energy) than that of the excited monomer's emission. An excimer can thus be measured by fluorescent emissions.
The mechanisms involved in the formation of excimer for a molecule $A$ and its emission are as follows:

<table>
<thead>
<tr>
<th>Step followed</th>
<th>Process</th>
<th>Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. $A(S_0) + h\nu \rightarrow A^*(S_1)$</td>
<td>Absorption</td>
<td>$I_a$</td>
</tr>
<tr>
<td>2. $A^*(S_1) \rightarrow A(S_0) + h\nu_f$</td>
<td>Normal fluorescence</td>
<td>$K_f[A^*]$</td>
</tr>
<tr>
<td>3. $A^<em>(S_1) + A(S_0) \rightarrow A(S_0).A^</em>(S_1)$</td>
<td>Excimer formation</td>
<td>$K_{xc}[A^*][A]$</td>
</tr>
<tr>
<td>4. $A(S_0).A^*(S_1) \rightarrow A(S_0) + A(S_0) + h\nu$</td>
<td>Excimer fluorescence</td>
<td></td>
</tr>
</tbody>
</table>

The emission from the excimer is initially to $A(S_0).A(S_1)$ pair possessing the same geometry as the excimer, but since there is no attraction between the ground-state molecules, it has the same energy as that of an isolated $A(S_0)$ molecule and hence immediately gets separated. The excimer on the other hand is stabilized with respect to an isolated $A(S_1)$ molecule, and so the emission from the excimer lies at the longer wavelength region than that of the normal fluorescence. Again excimeric emission is structureless because the lower state of the transition is essentially a continuum resulting from the repulsion of the ground state molecule. Excimeric fluorescence is commonly observed in solutions and in liquids. However, this type of fluorescence can also be observed in the solid phase if the crystalline structure of that allows a close overlap of the two molecular planes, which is a must for the formation of the excimer.

1.6. Dimer and Dimeric emission:

Due to some strong attractive interactions two molecules are combined to form a dimer. It may be between two molecules of the ground state as well as in the excited state. When the dimer is formed in the excited state it is called excimer. Due to the presence of strong attractive interactions one molecule of the ground state come very close to the
other molecule of the same state there by forms a complex. Several compounds forms dimer in the ground state such as flat aromatic hydrocarbon, several aromatic dyes etc. Some changes in the absorption spectra is noticed during the formation of dimer in the ground state.

1.7. **Exciplex formation and decay:** In bicomponent and multicomponent molecular solids (chemically different molecular mixtures – molecular blends), especially for electron donor (D) and electron acceptor (A) molecules, the formation of bimolecular excited states by electron transfer from donor to acceptor is highly facilitated, in analogy to single-component systems: they are called exciplexes [177]. A complex may be formed between the excited fluorescence molecule and the added foreign molecule. Thus the exciplex may be defined as an excited state complex of two molecules of different species, one in the ground state and the other in the excited state [178]. The mechanisms involved in the formation and emission of the exciplex are as follows: Exciplex emission has been seen in the solution of the mixed solutes. In recent years, the formations of exciplex in pyrene and perylene molecules are extensively studied [178]. In some cases, the formation of excited aggregates of three interacting species has also been reported [179].

![Exciplex formation and decay diagram](image)

Exciplex emission has been seen in the solution of the mixed solutes. In recent years, the formations of exciplex in pyrene and perylene molecules are extensively studied [180-181]. In some cases, the formation of excited aggregates of three interacting species has also been reported [182].
Chapter 1: Introduction

References


22. Z.Jia, G.Shwn Tyng,A.Hui Ling, M.P.Srinivasan, Colloids and Surface

23. J.J.Giner-Casares, G.De Miguel, M.Perez-Morales, M.T.Martin


Films.284,(1996),162.


Commun.15,(1994),405.


36. P.N.Prasad, D.J.Williams, Nonliner Optical Effects in Molecules and Polymers;John
56. L. Rayleigh, Phil. Mag. 48, (1899), 321.


64. G. L. Gaines, “Insoluble Monolayers at the Liquid-Gas Interfaces” (New York; Wiley Inter Science)(1966).


100. G. Decher, science., 277, (1997), 1232.


Chapter 1: Introduction

121. G.F. Schneider, V. Subr, K. Ulbrich, G. Decher, Nano Lett. 9, (2009), 636.
138. X. Yang, X. Han, Y. Zhu, Colloids and Surfaces A. 264, (2005). 49,