

Chapter 1

Introduction

A molecule which comprises of two parts in such a way that, one part is hydrophilic(water loving) and the other part is hydrophobic(water hating) is called an amphiphilic molecule. These amphiphilic molecules when spread on water using an appropriate solvent form a two dimensional insoluble monolayer. These are referred as *Langmuir* monolayers. A typical

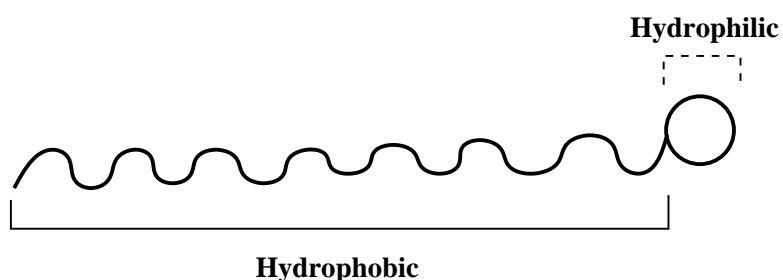


Figure 1.1: An amphiphilic molecule possessing a long hydrophobic tail and a hydrophilic polar head group.

amphiphilic molecule is shown in Figure 1.1. In general, the hydrophobic parts could be alkyl chains, fluorinated chains, or a combination of them (semi-fluorinated) or aromatic rings. The hydrophilic part comprises of polar groups like $-\text{COOH}$, $-\text{OH}$, $-\text{NH}_2$, $-\text{OCO}$ and $-\text{C}\equiv\text{N}$. The degree of stability of an amphiphilic molecule at air-water(A-W) interface is decided by its hydrophilic-hydrophobic balance. Different type of interactions exist between, the hydrophilic head groups and subphase, between the hydrophilic groups and also between the hydrophobic groups. The interactions that can exist between the polar heads can be of ionic-ionic, dipole-dipole and ion-dipole. There can be Van der Waals attractive interactions between the chains. Interactions due to hydrogen bonding and charge transfer can also play

an important role.

Though the calming of rough waves in seas were known to sailors, the first qualitative study of mono-molecular film dates back to 1774 by Benjamin Franklin [1] who estimated that a teaspoon of olive oil covered half an acre of a lake. Later Agnes Pockels [2] performed surface manometry experiments with stearic acid using a water bowl and a button. In 1899, Lord Rayleigh [3] estimated that the thickness of the layer covering the interface was that of a single molecule. The pioneering work in this field was carried out in 1917 by Irving Langmuir [4] who investigated the monolayer structure at the molecular level and showed that the molecules tend to orient at the A-W interface. The possibility of transferring these monolayers onto different substrates at the desired monolayer phases was first demonstrated by Katherine Burr Blodgett [5]. The film thus transferred onto substrates are known as Langmuir-Blodgett(LB) films. This technique has revolutionized the subject due to its potential device applications.

However, few exceptions to the traditional architecture of Langmuir monolayers have been reported. Semi-fluorinated molecules which were hydrophobic and did not have a polar hydrophilic group also tend to form a stable Langmuir monolayer [6, 7]. These experiments indicated that some of the semi-fluorinated molecules had their fluorinated chains pointing towards water and some others with the hydrogenated chains pointing towards water. An unusual way of forming the monolayer was reported for an urea lipid molecules in which the hydrophobic tails were in contact with water and the polar moiety was away from the water [8]. This was attributed to the strong hydrogen bonding network formation between the urea functional groups in air. Novel structures in Langmuir monolayer such as surface micelle formation have been reported for co-polymers [9] and semi-fluorinated alkane [10].

The study of Langmuir monolayer will reveal the molecular ordering in two dimensions. The subphase which is usually water, is an ideal smooth substrate (rms roughness of 5 Å). The monolayer properties are tunable by controlling the thermodynamic parameters; surface pressure(π), area per molecule(A/M) and temperature(t). These parameters define the state of the monolayer. Other factors that could affect the Langmuir monolayer are the polar head

groups, subphase, pH of the subphase, density, humidity, concentration of the molecules, compression rate and ionic strength [11].

Langmuir monolayers have many interesting properties. The richness in phases of these systems has attracted research groups to explore it in great detail using various experimental, theoretical and computer simulation techniques. It is also a good model for studying the biological systems. The Langmuir monolayer when spread over water, decreases the rate of evaporation. Thus it has been used in reservoirs to prevent evaporation. Langmuir monolayer of fatty acids with their dissociated polar heads has been used as a template to grow non-linear crystals. The crystals thus grown are much superior and highly directional. A thin layer of liquid in the alveolar sacks contains many amphiphilic materials in the mixed state and proteins. These are helpful in the respiration process. LB films which are artificially structured multilayered materials have been used in optical, electronic, chemical and bio-sensor devices. Friction, lubrication, wetting, anchoring of liquid crystals, adsorption, patterning, nano-electronics and photo lithography are a few other areas where the application of LB films are quite promising.

Apart from the Langmuir monolayers, there are also another type of adsorption of molecules at the A-W interface. This type of adsorption occurs in molecules which have a higher hydrophilicity. In this case, there exists a dynamic equilibrium between the molecules in the monolayer at the interface and the dissolved molecules in the subphase. These are known as Gibbs monolayers [11].

1.1 Experimental Techniques

1.1.1 Surface manometry

Surface manometry is a standard method to study the phase transition in Langmuir monolayers. Here the surface pressure(π) is varied as a function of the area per molecule(A/M) at constant temperature. The area per molecule is the inverse of surface density. The surface pressure is given by the difference in the surface tension of water in the absence of monolayer and in the presence of monolayer. There are various techniques to measure the surface

pressure which will be discussed later. The surface density of the molecules could be varied either by compression of the monolayer using barriers or by the addition of molecules on the water surface. Figure 1.2 shows a schematic diagram of the set up employed in our experiments to study the monolayers. The set up consists of a teflon trough with barriers.

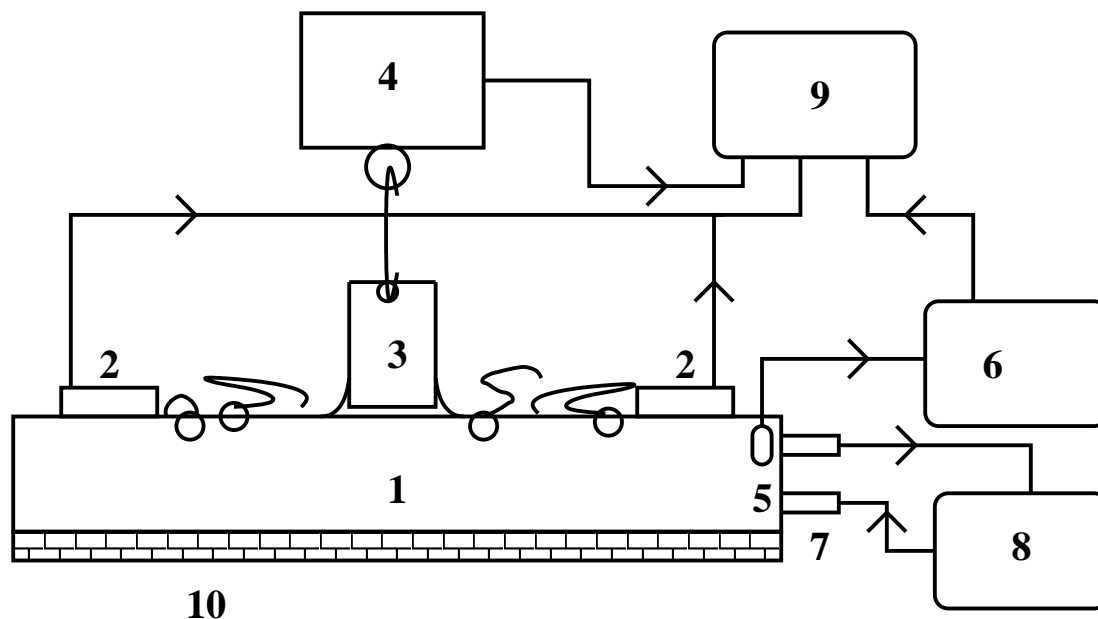


Figure 1.2: Schematic diagram of the experimental setup to measure the surface pressure - area per molecule at constant temperature. The different parts are listed as follows: 1.) Teflon trough, 2.) PC controlled motor driven barriers, 3.) Filter paper, 4.) Surface pressure sensor, 5.) Resistance Temperature Detector(RTD), 6.) Multimeter for measuring the resistance of RTD, 7.) Inlet and outlet for water circulation, 8.) Thermostat, 9.) Computer and 10.) Granite slab for vibration isolation.

The barriers are driven by a DC motor interfaced to a computer. Thus the area enclosed by the barriers can be changed. A Wilhelmy plate(filter paper) is used to measure the surface pressure. The temperature is maintained by circulating the water. The trough is kept on a granite slab to isolate vibrations. In our experiments the trough was cleaned with utmost care since traces of impurities reduces the surface tension. We employed the following procedure to clean the trough: Chloroform soaked tissue paper was used to remove the organic impurities. The trough was left with dilute chromic acid for half an hour for further cleaning. Copious quantity of distilled water was used to clean the trough to remove the traces of the acids. The trough was rinsed with Millipore Milli-Q water of high purity(specific resis-

tance was greater than 18.2 M Ω -cm). Finally, the trough was filled with Millipore water for carrying out the surface manometry studies.

The Wilhelmy plate method was used for measuring the difference in surface tension. Here a filter paper was cut to a known dimension(1 cm width and 2 cm length), cleaned by rinsing it in chloroform and dried. The filter paper acts as a Wilhelmy plate. It was suspended from the sensor head using a hook. The filter paper was immersed into the subphase and allowed to equilibrate. The principle of Wilhelmy plate method lies in measuring the vertical component of the force due to surface tension. The surface pressure, π , is given by

$$\pi = \gamma_0 - \gamma \quad (1.1)$$

where, γ_0 is the surface tension of pure water(about 72 mN/m at 20 °C), γ is the surface tension of water in the presence of the monolayer. The surface pressure is expressed in the units of mN/m. The sensor generates an electric signal proportional to the force acting on the filter paper which was calibrated with known weights. The sensitivity of the sensor was 0.1 mN/m. The material was dissolved in an appropriate solvent. The usual concentration was 1 mg per 1 ml. The solution was spread at the A-W interface using a Hamilton microsyringe. About 10 minutes was allowed for the solvent to evaporate. The solvent which is of volatile nature evaporates after spreading leaving the amphiphilic molecules at the A-W interface. The area per molecule was varied by compressing the barrier and the corresponding surface pressure was measured.

A typical $\pi - A/M$ isotherm is shown in the Figure 1.3. Here, the monolayer phases starts from gas(G), $G +$ low density liquid(L_1), L_1 , $L_1 +$ high density liquid(L_2), L_2 , Solid(S) and collapse into three dimensional(3D) structures. The description of the monolayer phases are given below. At very large A/M , the monolayer is predominantly in the gas(G) phase. In this phase, the molecules are far apart and have no interactions. At large A/M , the coexisting $G + L_1$ phases are also seen. In this region, the surface pressure is almost zero. At lower A/M , there is an increase in the surface pressure indicating a phase transition to L_1 phase. The L_1 phase is also referred as liquid expanded phase in the literature. At still lower A/M ,

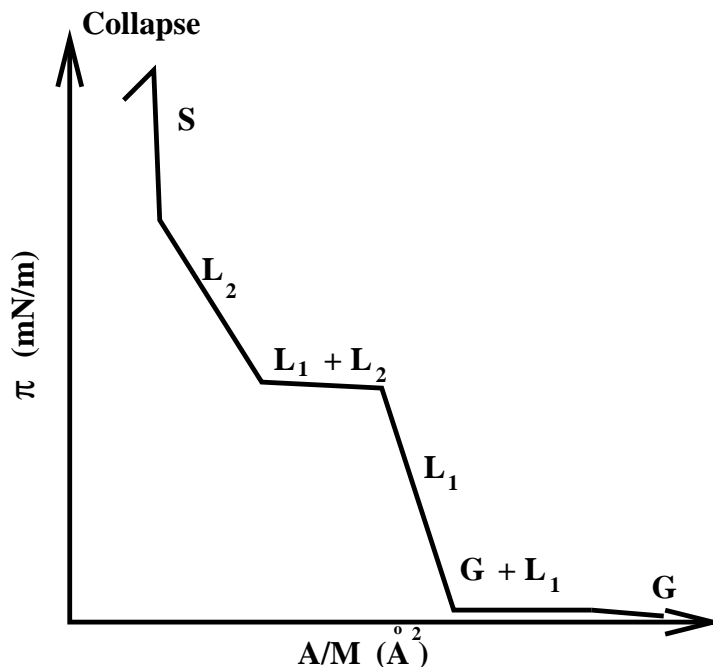


Figure 1.3: A schematic diagram of the variation of surface pressure as a function of area per molecule at constant temperature. The kink in the isotherm is associated with a phase transition.

the L_1 phase transforms to a coexisting $L_1 + L_2$ phase. This coexistence of L_1 with L_2 phase appears as a plateau region in the isotherm which indicates a first order phase transition. This coexisting phase transforms to the L_2 phase. In literature, L_2 phase is also referred as liquid condensed phase. At still lower A/M , there is a phase transition from the L_2 phase to a solid phase. Further compression, leads to collapse of the monolayers where it transforms to crystallites or multilayers. The schematic diagram showing the molecular arrangement in different monolayer phases during compression are depicted in Figure 1.4. In the G phase, the molecules are far apart. In the L_1 phase, the chains and the polar heads come closer and are randomly arranged. In L_2 phase, the chains have tilt and there is a quasi-long range order in the polar heads. In the S phase, the molecules are compactly packed and the chains are untilted.

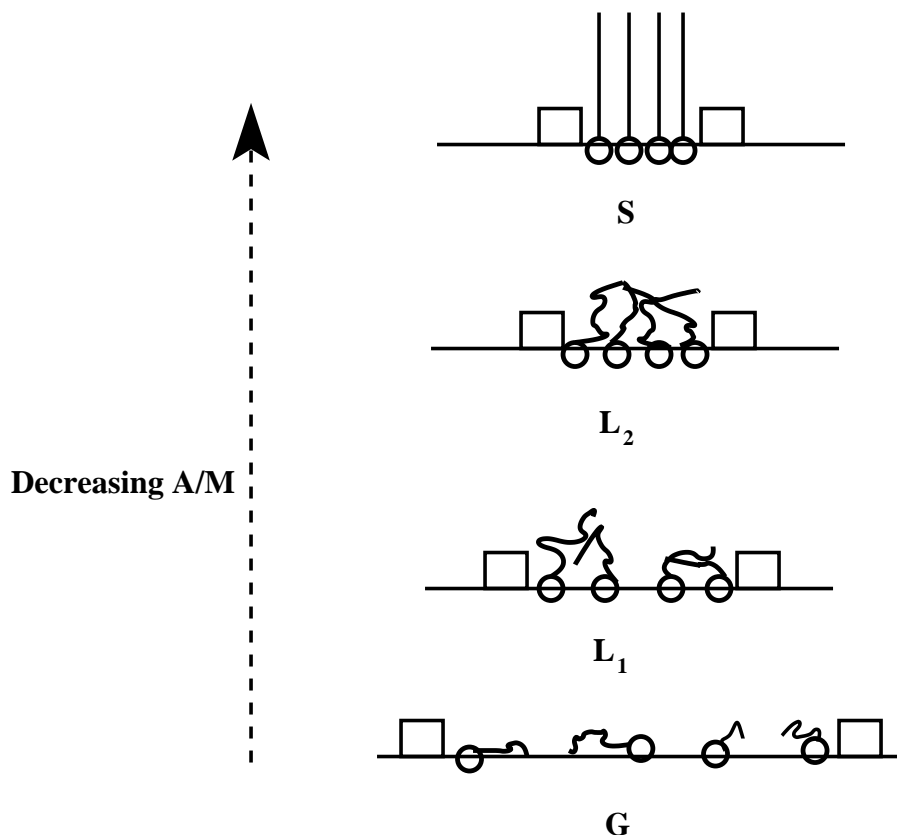


Figure 1.4: Schematic diagram of molecular arrangements in the different phases of a Langmuir monolayer with decreasing area per molecule (A/M).

1.1.2 Microscopy techniques

1.1.2.1 Epifluorescence microscopy

Using this technique, one can visually observe the monolayer phases at different surface densities [12, 13]. Here an amphiphilic fluorescent dye of 1% molar concentration is added as a dopant to the monolayer. The monolayer thus doped with the dye is directly observed under the microscope. The different monolayer phases exhibit different intensities. The contrast seen in different monolayer phases is attributed to differential solubility of the dye in the phases. In the G phase, where the molecules are far apart the monolayer appears dark due to quenching of the fluorescent dye. In the low density liquid phase (L_1), the dye molecules disperse uniformly and hence the monolayer appears bright. In the high density liquid phase (L_2), the molecules are densely packed and the dye is excluded from the L_2 phase. Hence, the monolayer appears dark. This technique allows a direct observation of the phases

in the monolayer, pattern formation, domain shape, domain size and phase coexistence. It is assumed here that the fluorescent dye do not affect the state of monolayer.

The schematic setup for epifluorescence microscopy is shown in Figure 1.5. Leitz Metalux 3 microscope was used for these studies. A white light from a mercury vapor lamp(100 W, HBO, Osram) was passed through the first filter and reflected downward by a half silvered mirror which was inclined at an angle of 45°. The bandwidth of the filter used for excitation of the dye was about 700 Å with peak wavelength centered around 4650 Å. The dyes used in most of our epifluorescence studies were 4-(hexadecyl amino)-7-nitrobenz-2 oxa-1, 3-diazole (NBDHDA) and 4-(octadecanoic acid)-7- nitrobenz-2 oxa-1, 3-diazole (NBDSA) whose excitation wavelength was around 4680 Å and it emits the fluorescence around 5330 Å. The resulting fluorescent intensity was very weak and was enhanced by the intensifier coupled to a charge coupled device(ICCD). We used cameras(Model P 46036A/V22, EEV, England) and later on another advanced and more sensitive ICCD(Cairns Ltd, UK). A composite signal from the ICCD was sent to a PCI-1411 frame grabber card(National Instruments). The images were grabbed at a rate of 25 frames/sec and were stored in a PC for later analysis.

1.1.2.2 Reflection microscopy

Multilayers which are sufficiently thick(of the order of 1 μm) could be observed under reflection microscope. Light striking normally on the thicker domains get interfered from the air-domain interface and domain-water interface leading to interference colors. The minimum thickness, d , of the film can be calculated using,

$$d = \lambda/2\mu' \quad (1.2)$$

where, λ is the wavelength of light in the visible region and μ' is the effective refractive index of the film. The minimum thickness which can be resolved is around 0.2 μm (taking $\mu'=1.5$ and $\lambda=5000 \text{ \AA}$). Using this technique, one can make out the shape of the domains. If the interference colors are uniform it indicates a flat domain. A pattern with concentric rings indicates a lens shaped domains.

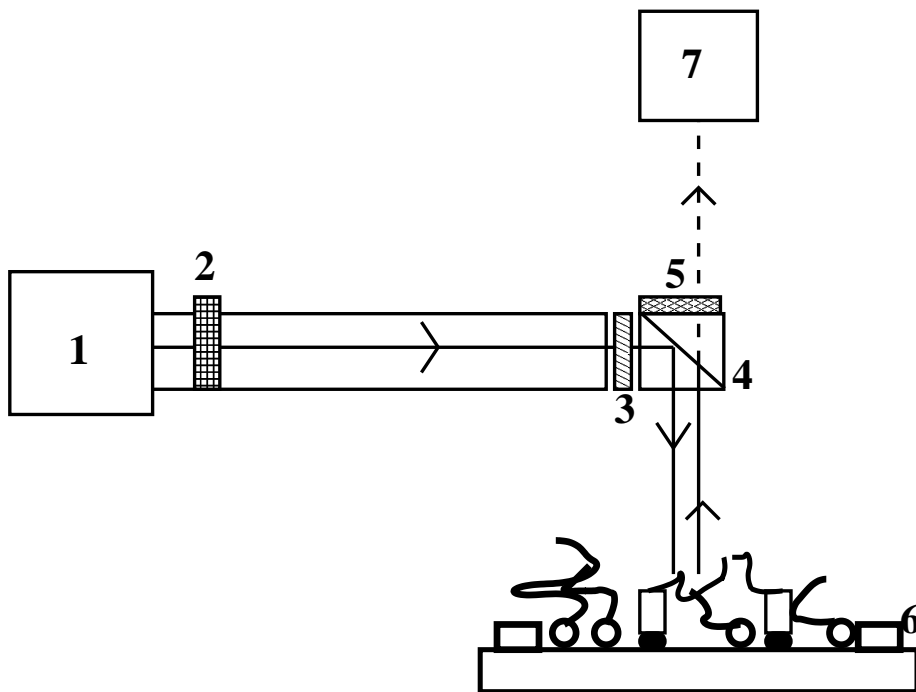


Figure 1.5: Schematic diagram to observe the monolayer under epifluorescence microscope. The different parts are listed as follows: 1.) Mercury lamp, 2.) Neutral density filters, 3.) Filter to allow excitation wavelength, 4.) Half-silvered mirror, 5.) Filter to cut-off excitation and allow emission 6.) Monolayer doped with fluorescent dye and 7) Detector (ICCD camera).

1.1.2.3 Polarising microscopy

To observe the textures of the thicker birefringent domains at A-W interface a Leitz orthoplan polarising microscope was used. The textures indicate the molecular ordering in the domains. An isotropic phase or a homeotropically aligned Smectic-A phase will appear dark under the microscope. An unaligned smectic or a nematic domain with defects show a pattern.

1.1.2.4 Brewster angle microscopy

Henon et.al., developed this technique [14, 15] which is now been widely used in studying the morphology of monolayers, both on liquid and on solid surfaces. It is employed to identify new phases [16, 17]. In this technique, there is no need of adding a dye to the monolayer which may affect the monolayer properties. At an interface, where the refractive index changes, the reflectivity of the in-plane polarization (p-polarised) component becomes

almost zero at the Brewster angle. The Brewster angle, θ_b , is given by,

$$\theta_b = \tan^{-1}[(n_2/n_1)] \quad (1.3)$$

where, n_1 and n_2 are the refractive indices of rarer and denser media. When the p-polarised laser beam is incident on the water surface at Brewster angle (53.1 °), the reflection from the water surface is negligible. The electric dipole oscillations of the p-component will be along the direction of propagation of the laser beam and therefore cannot contribute to the reflected ray. When the monolayer is spread, the Brewster angle condition is no longer satisfied and this results in some contrast due to increase in reflectivity. The reflectivity at the interface is dependent on the thickness of the monolayer, the roughness of the monolayer and the anisotropy of monolayers. Domains with different orientation or tilt give rise to different contrasts. There are other techniques like ellipsometry, surface potential measurements, second harmonic generation, Maxwell displacement current, grazing incidence X-ray diffraction and X-ray reflectivity to probe the monolayer phases.

1.2 Phases in two dimensional Langmuir monolayers

Langmuir monolayers are interesting because of its richness in phases in two dimensions. Traditionally, Langmuir monolayer phases are characterized as gas (G), Liquid expanded (L_1), Liquid condensed (L_2), Super Liquid (LS) and Solid (S) phases. This classification is based on the magnitude of compressional modulus [18] in these phases.

Gas phase : This phase occurs when the surface density of molecules are very low. The 2D equation of state,

$$\pi(A/M) = k_b T \quad (1.4)$$

is found to be obeyed in this gas state. The modified Van der Waals equation in this phase is given by,

$$(\pi + a/(A/M)^2)(A/M) - b = k_b T \quad (1.5)$$

where, a incorporates interaction between the molecules, b takes into account the excluded area, k_b is the Boltzmann constant and T the absolute temperature. This phase is highly

compressible.

L₁ phase : This is a low density phase where the molecules are randomly arranged. In the earlier literature, this phase was referred as *LE* phase. Recent experiments on the measurement of shear viscosity in *L₁* is reported to vary between around 10^{-10} - 10^{-9} Ns/m [19].

L₂ phase : The long standing controversy on whether the transition from *L₁* phase to *L₂* phase is first order has been resolved recently by observing their coexistence under fluorescence microscope. Monolayer is less compressible in *L₂* phase than the *L₁* phase. There are many variants of *L₂* phase. These phases are found to be classified based on their molecular ordering. These condensed phases are found to be crystalline with quasi-long range positional order. There are many variants in the condensed phase. At low surface pressure the phases which appear are *L₂*, *L'₂* and *O_v*. The molecules in the *L₂* phase has a collective tilt towards a nearest neighbor(NN) [20, 21]. *L'₂* and *O_v* phases tilt to a next-nearest neighbor(NNN) [20]. Peterson and co-workers reported a new intermediate-tilted phase within the *L₂* phase [22]. There are reports on the existence of two sub phases, *S'* and *L₂^{*}*, from the *L'₂* phase [23] based on the isotherms.

Solid phase : At high surface pressure, there are two untilted phases, the super liquid phase, *LS* [24, 25]. and the solid(*S*) phase [20], [26]. In the *LS* phase, a single peak is observed in X-ray diffraction which indicates a hexagonal structure. The viscosity suddenly drops during compression when this phase occurs. Hence, it is called as super liquid [27]. The phases, *CS* and *L''₂*, possess centered rectangular lattice with herringbone order. The difference between them lies in the tilt. *L''₂* is a two dimensional crystal with a NN tilt [20] and *CS* is untilted [20, 21], [26]. They show positional correlations larger than 500Å. These phases were summarized in detail in the recent review [28]. The monolayer phases discussed above with different positional and orientational orders are shown in Table 1.1.

1.3 Mixed Langmuir monolayers

Mixed Langmuir monolayers are model systems to mimic biological membranes [29]. For successful transfer of a monolayer on substrates, the stability of the monolayer is important

Table 1.1: Monolayer phases with different molecular order

Traditional 2D Phases	Refined phases	Tilt Azimuth	Azimuth of unit-cell distortion
G	G	Isotropic	–
LE	L_1	Isotropic	–
LC	$L_{2d}, L_{2h}, Ov, L'_2, L''_2$	NN, NN, NNN, NNN, NN	U, NNN, U, NN, NN
Super Liquid	LS	U	U
Solid	S, CS	U, U	NN, NN

which is governed by the interactions between the components. Many functional molecules which do not form a monolayer, when mixed with another amphiphilic molecule forms a stable monolayer. Lung surfactant is composed of a mixture of complicated lipids and proteins. The role played by them is of utmost importance in reducing the surface tension during expansion and contraction of lung without collapse [30]. A study of the mixed monolayer is helpful in identification and convergence of monolayer phases. Several monolayer phases are identified by optical and X-ray techniques when the concentration of the components in the mixed monolayer are systematically varied.

1.3.1 Miscibility in two dimensions

According to Crisp's phase rule, at equilibrium, the chemical potential, μ_i , is identical in all the phases. The number of independent variables or the degree of freedom(F) at constant temperature and external pressure, is given by,

$$F = C_b + C_s - P_b - q + 1 \quad (1.6)$$

where, C_b indicates the number of components in bulk, C_s the number of components at the surface, P_b is the bulk phase and q is the monolayer phase. Since, the number of bulk phases are known, the monolayer phases q can be determined from the value of F . The details applied to different systems will be discussed later.

1.4 Materials forming Langmuir monolayers

There are different materials which form Langmuir monolayers. They are fatty acids, their ester derivatives, biological lipids, proteins, polymers [31] and liquid crystals. In this thesis, we describe the studies on molecules which exhibit liquid crystalline phases in bulk.

1.4.1 Liquid crystals

Liquid crystals are intermediate state of matter between liquids and crystals [32, 33]. Traditionally, the molecules are rod shape, but, molecules which possess disc shape [34] or banana shape [35] are also mesogenic in nature. There are two classes of liquid crystals. They are thermotropic and lyotropic. In thermotropic, the phase transition is accompanied by the variation of temperature while in the lyotropic it is accompanied by concentration as well as temperature. A typical liquid crystalline phase sequence is: Crystal \longleftrightarrow Smectic-A; Smectic-A \longleftrightarrow Nematic; Nematic \longleftrightarrow Isotropic. The LC phases which are relevant to the

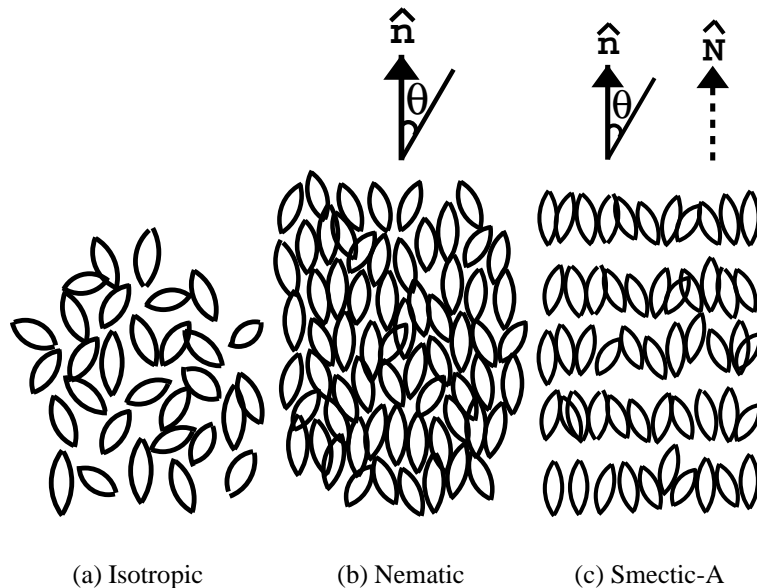


Figure 1.6: Ordering in mesogenic materials.

thesis are described below.

1. Isotropic: The molecules are randomly aligned as shown in Figure 1.6(a). In this phase, there is no registry of positional and orientational order.

2. Nematic liquid crystal: In nematic liquid crystal, the molecules possess orientational order and no positional order. This is shown in Figure 1.6(b). The average orientation of the molecules towards a particular direction is defined by a apolar, unit vector called *director*, \hat{n} .
3. Smectic-A liquid crystal: In smectic liquid crystals, the molecules are characterized by translational order in one dimension and liquid like positional order in the other two directions. The long molecular axes on an average are oriented collectively along one direction(\hat{n}) which is parallel to the layer normal(\hat{N}). This is shown in Figure 1.6(c). The rod like molecules form a density wave along the layer normal whereas in the layer plane it is isotropic.

1.4.2 Monolayer study on liquid crystalline molecules

The monolayer study of mesogenic, amphiphilic molecules have been reported for several systems. These systems are of considerable interest since many monolayer phases have liquid crystalline analogues. Many liquid crystalline materials with biphenyl alkyl chains and a cyano polar head group have been studied [36]. Apart from low molecular weight liquid crystals, some of the monomers [37] and polymers also form Langmuir monolayers [38, 39]. Monolayer formation of discotic liquid crystalline materials have also been reported [40]. Some liquid crystals with azo or biphenyl cores with symmetric alkyl chains on either sides form Langmuir monolayer though they were hydrophobic in nature [41]. The LC materials were found to undergo a transition from a 2D monolayer to 3D multilayers after collapse [36], [42]. This transition was also found to occur in another system with a siloxane moiety and with a cyano polar head [43]. These transitions from a monolayer to multilayers via a collapse are interesting and recent studies indicate that these explains the method of collapsing of pulmonary lung surfactant monolayers [44].

This thesis addresses on the monolayers and multilayers of mesogenic amphiphilic molecules at the air-water interface.

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