# CHAPTER 1

# Introduction

This thesis essentially deals with the electrochemical studies and molecular self-assembly on surfaces using the surfactant stabilized electrolytic systems. Recently, research work on surfactants and their structural aspects have gained widespread interest owing to their potential ability to mimic the biological and natural processes occurring in the human body. These studies are also useful in understanding the mechanism of biological electron transfer reactions, process of cell division and enzyme catalytic mechanisms. Above the critical micellar concentration (CMC), the surfactant molecules self-aggregate to produce a variety of structures that form an ideal system to study several biological processes involving the electron transfer reactions. Apart from these fundamental studies, the electron transfer processes also play a vital role in several technologically important phenomena such as energy conversion and modification of surfaces using electrodeposition.

Electrochemistry, which among other things deals with the study of various processes at the electrode | electrolyte interface of nanometers dimension, is a versatile area, which links different scientific disciplines such as chemistry, physics, biology and materials science. The electron transfer phenomenon occurring at the interface can be modeled to simulate the biological electron transfer processes. The behaviour of electrode | electrolyte interface can be controlled and regulated by the adsorbed species on the surface of the electrode. The orientation and chemical nature of the adsorbed species on the metal electrodes are important since it affects the heterogeneous electron transfer events. The interaction of these species with the metal electrodes may be merely electrostatic, for example in the case of adsorption of anions or cations on a surface of opposite charge, or charge-dipole in nature as in the case of adsorption of amines, thiourea etc., or due to the formation of covalent bond as in the case of self-assembled monolayers.

The first adsorption studies were carried out using mercury as a metal because the liquid mercury has several advantages in terms of uniform surface energy, surface smoothness and ease of purification. Moreover, the adsorption processes at mercury surfaces are completely reversible and faradaic in nature. Besides, mercury, other sp-metals such as Bi, Sn, Zn and Ga were used for the adsorption studies and found that the species are getting weakly adsorbed on these surfaces. Adsorption of organic molecules on d-metals namely platinum had been studied using electrochemical and spectroscopic techniques because of its importance in electrocatalysis. Apart from all these, adsorption of organic molecules with terminal thiol groups on noble metals such as gold, silver and copper attracted the attention of many researchers owing to their tendency to form a well ordered, oriented and highly dense monolayer on their surfaces. This technique is mainly used to modify the surface properties thereby finding potential applications in the field of sensors in biochemistry and environmental analysis. These monolayers also offer tailor made surfaces to study several phenomena such as wetting, lubrication, friction and other surface physical properties. The self-assembled monolayers are also used in the study of coulomb blockade, which involves a single electron tunneling through the molecular film. Recently, Willner et al. [1] reported the “write-read-erase” information storage system based on the principle of electron transfer reactions occurring at the electrode | electrolyte interface using the quinone functionalized electrode in conjunction with the hydrophobic magnetic nanoparticles.

Broadly, there are two methods of preparing the monolayer on the surfaces namely, the Langmuir-Blodgett method and molecular self-assembly method. The first method is commonly known as L-B film that consists of transferring the molecules to a substrate by compression at the air-water interface [2-4]. The orientation of the transferred monolayer depends on the wetting properties of the substrate. Multilayers can also be prepared using this technique by successive dipping of the substrate at the interface. The other method molecular self-assembly is based on the spontaneous adsorption of certain organic molecules on specific substrates to yield a structurally well defined, ordered monolayer [4-6]. Such organized molecular films exhibit several interesting properties and have potential applications in a variety of fields.

In this thesis, we discuss our experimental research investigation on the template electrodeposition, electron transfer studies and the study of self assembled monolayers of thiol compounds on gold surface using the self aggregated structures of surfactant molecules such as the hexagonal liquid crystalline phase and microemulsion phase. We have investigated the potential utility of the materials prepared using template electrodeposition in supercapacitor applications and as a hydrogen-evolving cathode in electrocatalysis. In addition to this, we have also studied the effect of applied magnetic field on mass transfer during the electrodeposition of nickel and investigated the structural morphology and electrochemical properties of the deposit using a variety of characterization techniques. Our experimental work and the characterization methods are mainly based on the electrochemical techniques such as cyclic voltammetry, electrochemical impedance spectroscopy, choronopotentiometry, chronoamperometry, capacitance measurements and gold oxide stripping analysis. Apart from these techniques, we have also performed microscopic techniques namely scanning electron microscopy (SEM) and scanning tunneling microscopy (STM) and surface analytical techniques like X-ray diffraction studies and grazing angle FTIR spectroscopy in our work.

This chapter has been mainly divided into three sections. In the first section, the chemistry of surfactant, the different self-aggregated structures such as micelles, reverse micelles, microemulsion phase and several liquid crystalline phases along with a general phase diagram of a ternary system have been explained in a detailed manner. The second section consists of a general introduction to the field of self-assembled monolayer and its characterization using a variety of techniques. In the third and final section, we have discussed the aims and scope of our present research work.

## I. Introduction to surfactant and its self-aggregated structures

**Surf**ace-**act**ive **a**ge**nts**, commonly known as ‘***surfactants***’, come under the category of amphiphilic molecules. It has two parts in its structure. One part is a polar hydrophilic head group (attracted to water) and the other part is a hydrophobic tail group (attracted to oil), as shown schematically in the following figure.

The essential function of a surfactant molecule is to reduce the surface tension at the interface or at the surface, thereby allowing easier spreading of molecules. Recently, the research works are mainly focused on mimicking the biological processes using the surfactants and their self-aggregated structures as a model system to understand the electron transfer reactions occurring in these low conducting media. Chang et al. reported an excellent review article on reverse micelles as life mimicking systems [7], where the self-aggregated structures of surfactants have been used to mimic different biological processes occurring in human life.

Critical micellar concentration (CMC) is a concentration of surfactant molecule at which the micelle formation begins. Above this CMC value, these surfactant molecules self aggregate to form different structures such as micelles, reverse micelles, emulsion phase and various liquid crystalline phases depending upon its concentration and the solvent. In general, the amphiphilic molecules such as surfactants, lipids, copolymers and proteins can associate into a variety of structures in aqueous solution, which can transform from one to another when the solution conditions namely the electrolyte concentration and pH of the medium are changed. In particular, if a surfactant is added to water, the hydrocarbon chains tend to self-associate to minimize their contact with the water molecules resulting in the formation of various aggregates [8]. If the water molecules are able to solubilize both the polar head groups and the alkyl chains equally, then no aggregates are formed. If the surfactant molecules have a very large polar head group and a small alkyl chain, then these molecules self-associate to form a spherical aggregate called as a normal micelle, in which the alkyl chains form the inner core (oil) and the head groups form the outer core (water). At low surfactant concentrations, the micelle is spherical in shape with a diameter fixed by the length of the alkyl chain and the size of the polar head group. If the surfactant molecule has a small polar head group and the branched hydrocarbon chains, then the spherical reverse micelles are formed, in which the polar groups form an inner core (water) and the alkyl chains form the outer core (oil). This is commonly termed as a water-in-oil droplet. The structure of this is exactly opposite to that of micelle described earlier. In contrast to normal micelles, the size of the reverse micelles increases linearly with the amount of water added to the system. In a surfactant system containing large amounts of both the oil and water phase, the shape and dimensions of the aggregates change with the formation of interconnected water channels or cylinders, leading to the formation of emulsion phases [9]. Adding more water induces a new phase transition with the surfactant molecules reorganize to form a planar or lamellar film. These phases are usually called as liquid crystalline phases, with the system becomes opalescent and exhibits birefringent. Figure 1 shows the various self-aggregated structures of surfactant molecules.

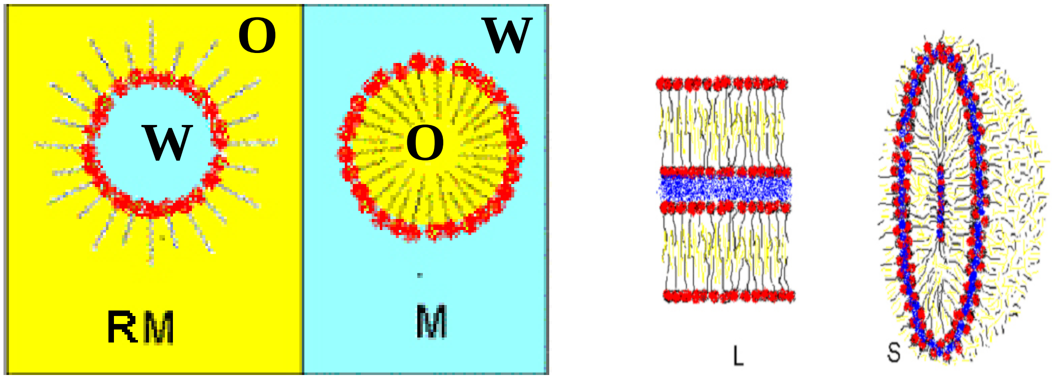

*Figure 1: Various self-associated structures of surfactant molecules.*
*M --- Micelles, RM --- Reverse micelles, L --- Lamellar phase, S --- Hemi spherical micelles, O --- Oil and W --- Water.*

There are two important factors that play a vital role in these self-assembled structures. They are the thermodynamics of self-assembly and the forces operating between these molecules within the aggregates. The forces that hold these molecules together are not due to strong covalent or ionic bonding, but due to a weak Van der Waals force, hydrogen bonding, hydrophobic or the electrostatic interactions. Thus, when the solution conditions such as the concentration of the electrolyte or pH of the medium is changed, the intermolecular forces between these aggregates are affected, thereby the size and shape of these structures have been modified.

These self-aggregated structures of surfactant molecules have been used in the synthesis of metallic and semiconductive nanoparticles [10-12] mainly to control their size and shape. The research interest in this field has further been motivated due to the unusual physical and chemical properties of nanoparticles that depend on their size, shape and packing density. Template electrodeposition of various metals and metal oxides with desired properties has been achieved using these self-aggregated structures as templates. These self-assembled structures of surfactant molecules come under the category of 'soft templates', which overcomes the problems such as the fabrication of templates and removal of the same after the deposition normally associated with hard templates. The most commonly used soft template for the electrodeposition of materials is the liquid crystalline phases formed by the surfactant molecules. Raimondi and Seddon have reported an excellent review article on liquid crystal templating techniques to produce porous materials [13]. Depending on the concentration of surfactant and water, different liquid crystalline phases namely hexagonal liquid crystalline phase, reverse hexagonal liquid crystalline phase and lamellar phases can be obtained. These phases have well-defined aqueous domains through which the deposition of materials occurs resulting in size and shape controlled nanoparticles that mainly depends on the nature and structure of the surfactants. Figure 2 shows the schematic representation of reverse hexagonal liquid crystalline phase and an individual aqueous nanocylinder formed by the aggregation of surfactant molecules.

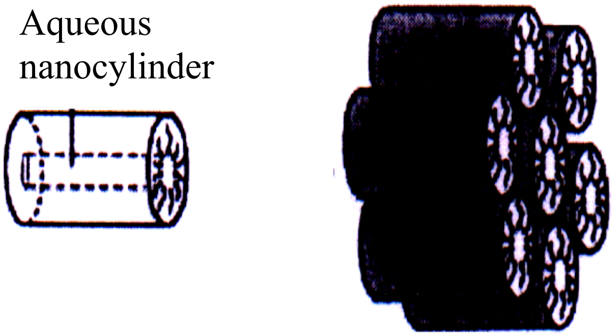

*Figure 2: Schematic representation of an individual aqueous nanocylinder and the reverse hexagonal liquid crystalline phase.*

The individual aqueous nanocylinder is also known as a micellar rod in which the aqueous phase constitutes the inner core and the hydrocarbon chains (oil phase) forms the outer core. The length of the micellar rod can be several hundreds of nanometers, depending upon the length of the hydrocarbon chain and the aqueous phase has the diameter in the order of nanometers depends on the size of the hydrophilic group. The hexagonal pattern of the liquid crystalline phase is also shown in the figure 2. In our work, we have mainly used hexagonal liquid crystalline phase for the template electrodeposition of nickel and in the studies of self-assembled monolayer formation and its characterization.

## 1.1. Winsor's classification

It is well known in the literature that the ternary mixture of oil, surfactant and water system forms different phases depending upon their concentration. A general phase diagram of a ternary mixture of oil, surfactant and water system is shown in figure 3.

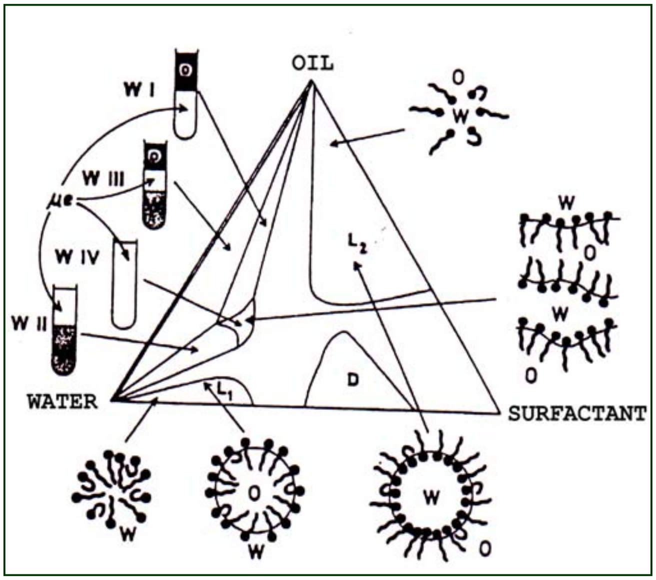

*Figure 3: A general phase diagram of a ternary system consisting of oil, surfactant and water compositions.*

It can be seen from the figure that the ternary system exhibits a variety of self-aggregated structures of surfactant such as micelles, reverse micelles, liquid crystalline phases and microemulsion phases depending on the concentration of the components. In the figure, O stands for oil phase, W for water/aqueous phase, $L_1$ and $L_2$ for isotropic micellar and reverse micellar solution respectively, D for liquid crystalline phases and μe for microemulsion phases respectively. WI, WII, WIII and WIV represent the Winsor's classification that deals with the different types of microemulsion phases [14,15]. WI represents the lower microemulsion phase coexisting with the upper oil phase. WII denotes the upper microemulsion phase coexisting with the lower aqueous phase. WIII stands for the middle part microemulsion coexisting with the upper oil phase and the lower aqueous phase. Finally, WIV represents the homogeneous microemulsion phase. From this diagram, it is clear that the concentration of the components of a ternary system plays a vital role in the self-aggregated structure formation. By changing the concentration of the desired components, we can obtain the desired phase by controlling the various parameters such as the length of the cylinder and the diameter of the aqueous phase etc., by choosing a proper surfactant molecule.

In our work, we have mainly used a hexagonal liquid crystalline phase consisting of water, Triton X-100 and PAA as a template for the preparation of high surface area materials based on nickel and as an adsorbing medium in the case of self-assembled monolayer in order to obtain a most blocking monolayer with defect free structure. We have also used a microemulsion phase formed from water, Triton X-100 and toluene to study the electron transfer reaction using disk/wire and macroelectrodes. We have chosen nickel as the material because of its importance as an electrocatalyst in many industrial processes and its use as batteries and supercapacitors in energy storage devices.

## II. Introduction to self-assembled monolayer (SAM)

Self-assembled monolayers are molecular assemblies of ultrathin organic films of few nanometers thickness, which are formed by the spontaneous chemisorption of organic molecules onto an appropriate substrate when it is immersed into a dilute solution containing organic molecules dissolved in an organic solvent. The ideal picture of an organic monolayer consists of molecules with the head and tail groups oriented perfectly on a smooth substrate. In general, monolayers can be deposited on substrates using two methods namely Langmuir-Blodgett and self-assembly.

The Langmuir-Blodgett method of preparing the monolayer consists of transferring the organic molecules that are spread on air-water interface onto a substrate by compression [2-4]. This kind of film formation is commonly known as L-B films. Usually, in these types of molecules the head group is hydrophilic and the tail group is hydrophobic in nature, so that the orientation of the molecules is achieved before transferring to the substrate. The orientation mainly depends on the wetting properties and the nature of the substrate used for the monolayer formation. Using the successive contacts of the substrate with the air-water interface where the organic molecules are spread, the multiple organized layers can be deposited. In this case, the bonding between the monolayer and the substrate is either by Van der Waals interaction or by hydrogen bonding. The L-B films have potential applications in variety of fields such as sensors, corrosions, photoresists and in the studies of non-linear optics.

Even though the phenomenon of self-assembly is known for the last 50 years, it is only in recent times that the researchers started exploring this field for a variety of studies involving the electron transfer reactions, single molecule electron tunneling, biosensors and switching properties etc. Self-assembled monolayers, the so-called SAM includes organosilicon on hydroxylated surfaces [16-18], alkanethiols and dithiols on gold [19,20], silver [21] and copper [22], dialkyl sulphide and disulphides on gold [23], alcohols and amines on platinum [24] and carboxylic acids on aluminum oxides [25] and silver [26]. The process of self-assembly in the case of SAM can be divided into three steps from the point of view of energetics. The first step is the chemisorption of the head group onto the substrate, which is an exothermic process. The very strong molecule-substrate interactions result in the pinning of the head group to a specific site on the surface of a substrate through a chemical bond. The bonding can be covalent as in the case of alkyltrichlorosilanes on hydroxylated surfaces, covalent but slightly polar for alkanethiol monolayers on gold or ionic bond for carboxylic acids on AgO/Ag. The energy associated with such chemisorption is of the order of tens of kcal/mol [27,28] (in case of thiolate on gold it is 40-50 kcal/mol). As a result of the exothermic process during the first step, molecules try to occupy every available bonding site on the surface and in this process they push together the molecules that have been already adsorbed. The second step is the inter chain Van der Waals interactions among the alkyl group. The energy associated with this process is only a few kcal/mol. The third and final step is the reorientation of the terminal groups. In the case of simple alkanethiol, methyl group is the terminal group. These surface groups are thermally disordered at room temperature that is evident from the helium diffraction [29] and FTIR studies on monolayers [30]. The energy associated with this process is of the order of a few kT, where k is the Boltzmann constant and T is the absolute temperature. Each gauche bond has a value of about 0.7 kcal/mol associated with it.

In 1983, Nuzzo and Allara [23] published the first paper on SAM, which deals with the formation of organized dialkyl sulphide monolayers on gold surface. It was clearly shown that the sulphur compounds bind very strongly to gold, silver and copper surfaces. Although several compounds on different surfaces have been reported for the monolayers, it is the alkanethiol monolayers on gold that has been extensively studied and characterized using a variety of techniques. This is because gold being a noble metal does not form a stable oxide layer on its surface as compared to other coinage metals and thus it can be used under ambient conditions. Figure 4 shows the steps involved in the process of self-assembly of alkanethiol molecules on gold surface.

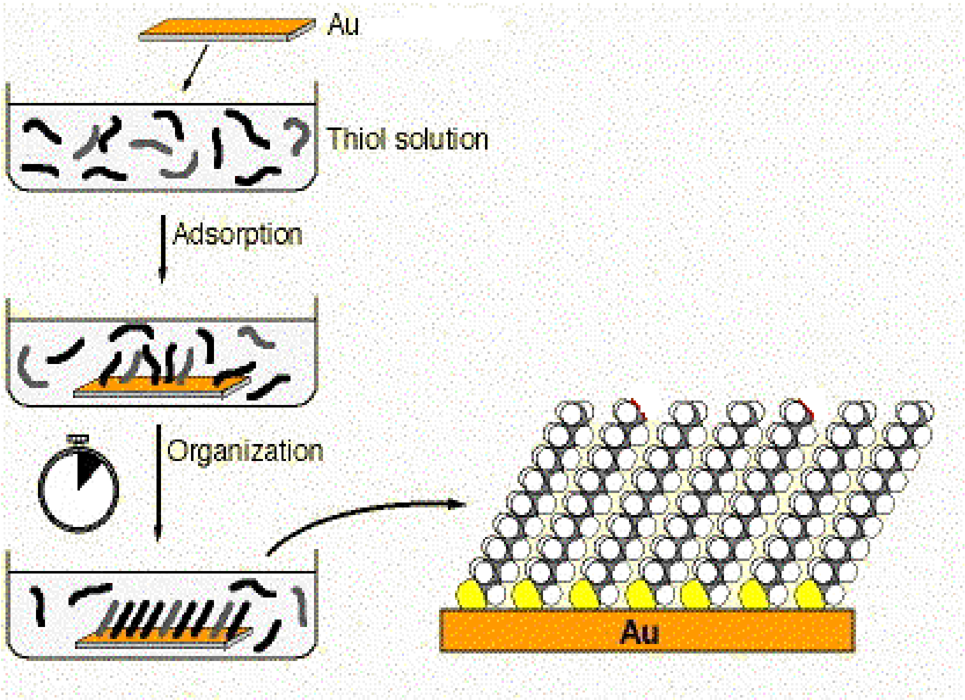

*Figure 4: Self-assembly of alkanethiol molecules on gold substrate*

## 1.2. Monolayer formation

The process of formation of SAM of alkanethiol on gold is quite simple. A very clean, fresh gold substrate is immersed into a dilute solution containing alkanethiol molecules dissolved in an organic solvent. The immersion time has been reported to be from several minutes to days. This results in the formation of a close packed, highly ordered and oriented monolayer. This simple procedure has been used to produce diverse structures including the commonly used alkanethiols with different terminal groups, with different substituents having large dipole moments, aromatic thiol monolayers, attached polymers, attached pendent groups, lipids, proteins, peptides etc. One of the primary aims of research on SAM is to produce the most blocking and highly oriented monolayers on gold substrates. There are several factors such as the substrate morphology, cleanliness of the substrate, purity of alkanethiol, solvent used for adsorption, concentration of thiol and deposition time etc.

As far as the morphology of substrate is concerned, it is the choice between either a polycrystalline sample or a single crystal. Most of the work on SAM formation has been performed on either evaporated or sputtered gold films on cleaved mica or single crystal silicon or glass under special conditions. The as prepared gold substrates exhibit predominantly (111) crystal face [31-33] under certain appropriate conditions. Although a single crystalline substrate containing a well defined crystal face is important for many surface analytical methods such as electron diffraction, scanning tunneling microscopy etc., there is no clear and consistent evidence that a single crystalline substrate is essential to obtain pinhole free SAMs.

The substrate cleanliness is very essential to produce a highly ordered and well-oriented monolayer. The very strong affinity of sulphur to gold implies that the weakly physisorbed materials will be displaced from the substrate during the process of self-assembly [34]. This indicates that the ultra high vacuum conditions are not required to prepare a high quality SAM. There are several procedures such as strong heating of the substrate, immersion of the sample in strong oxidizing agents, exposure of the substrate to argon or oxygen plasma, ozone or UV radiations and electrochemical cycling in dilute acid solution usually employed to clean the substrates before monolayer formation.

***"Piranha"*** solution, which is a mixture of concentrated sulphuric acid and 30% hydrogen peroxide in a 3:1 ratio, is a very common oxidizing agent to clean the Au substrate. The gold substrates are completely wetted by water after exposure to this kind of oxidizing agent. Since the wetting properties of bare gold samples are a sensitive test to the presence of organic contaminants, any partial dewetting of the gold surface by water indicates an incomplete cleaning. Prolonged exposure of the substrate to these kinds of oxidizing agents leads to the formation of a partial layer of gold oxide on the surface.

Although several commonly used organic solvents such as tetrahydrofuran (THF), n-hexane and acetonitrile are used for the preparation of SAMs, it is ethanol that has been mostly preferred and extensively used solvent due to its low toxicity, faint odour and availability in pure form [35]. Even now there is a lot of research is going on in the area of usage of solvents for SAM preparation and it is not clear whether good or bad solvents produce the most ordered monolayer films. Poor solvents will increase the driving force for adsorption of molecules onto the substrate, but at the same time it introduces disorderliness within the SAMs by intercalating into the organized film. The concentration of the thiol molecules and the immersion time of the substrate play a very important role in the self-assembly process and thereby in the formation of monolayer. Typically, the concentration of the thiol used is in millimolar (mM) levels, a range from micromolar (μM) to neat liquid thiols have also been employed for SAM preparation. It is also possible to form a monolayer in the absence of solvents using gas-phase deposition. An early work using gas-phase deposition for the monolayer formation was reported by Crooks et al. [36] in the year 1991 and after that there has not been much work on this method of preparing monolayer films.

## 1.3. Nature of bonding present in the monolayer

The nature of bonding between the alkanethiol molecules and gold substrate is still a matter of considerable research. Both the alkanethiols and disulphides adsorb onto gold substrate to form the same thiolate ($RS^-$) species [32,37]. The reaction of dialkyldisulphides with gold is an oxidative addition reaction, which is given as follows.

$$RS - SR + Au^0_n \longrightarrow 2\,R{-}S^-{-}Au^+ + Au^0_n$$

In the case of alkanethiol, the reaction may be considered as an oxidative addition of the thiol (S-H) bond to the gold surface, followed by a reductive elimination of hydrogen. When a clean gold surface is used for the monolayer preparation, the proton may probably end as a $H_2$ molecule. The chemical reaction occurs in this case is expressed as follows.

$$R{-}S{-}H + Au^0_n \longrightarrow R{-}S^-{-}Au^+ + Au^0_n + \tfrac{1}{2}H_2$$

The combination of hydrogen atoms at the gold surface to give $H_2$ molecule is an important exothermic step in the overall chemisorption energy involved in the process of self-assembly. During the chemisorption process, the thiolate species has been formed, as can be seen from the equation represented above, and it is verified by XPS [20,38,39], FTIR spectroscopy [40], FT-mass spectrometry [41], electrochemistry [42] and Raman spectroscopy [32]. The bonding of thiolate group to the gold surface is very strong and the bond strength is approximately 40 kcal/mol.

## 1.4. Self-assembled monolayers (SAMs) on silver and copper

Apart from gold, silver and copper are widely used as substrates for SAM preparation and its characterization. Silver is also known to form an organized monolayer after gold [43-48]. Unlike gold, silver surface rapidly forms an oxide layer when exposed to air/atmosphere. Despite of this factor, it is possible to form a close packed, highly oriented monolayer of thiol molecules on silver surfaces. SAMs on copper surfaces have also been reported in literature [49,50]. The air oxidation of copper is sufficiently rapid to prevent the formation of copper oxide during the process of deposition. X-ray photoelectron spectroscopy (XPS) studies reveal the presence of oxygen on the surface even after the monolayer deposition.

## 1.5. Characterization techniques used in the study of SAM

Several spectroscopic, microscopic and diffraction techniques have been used for the characterization of SAMs. Some of the issues involved in the research area of monolayers such as the monolayer structure, molecular conformation, orientation, distribution of pinhole defect density and the morphology have been studied and addressed using these techniques. In our work, we have extensively used electrochemical techniques namely cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and capacitance measurements to evaluate the barrier property of the monolayers on gold surface by studying the electron transfer reactions on these modified surfaces. Therefore, we have devoted a separate section in this thesis to explain elaborately the electrochemical techniques used for the characterization of SAMs.

### 1.5.1. Contact angle measurement

The phenomenon of wetting or non-wetting of a solid by a liquid is better understood by studying the contact angle measurements. One of the important properties of a monolayer is the wetting behaviour [19,51,52]. The wetting contact angle is measured by placing a small drop of a liquid on a horizontal solid substrate and measuring the angle subtended by the edge of the drop and the substrate. The drop of liquid forming an angle may be considered as resting in equilibrium by balancing the forces involved namely the interfacial tension between solid and liquid SL, between solid and vapour SV and between vapour and liquid LV as can be seen from the figure 5. The angle within the liquid is known as contact angle or wetting angle denoted by θ in the figure 5.

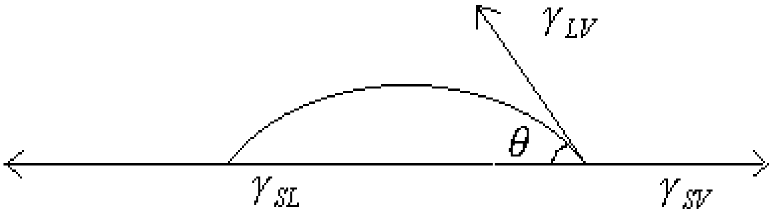

*Figure 5: Schematic representation of contact angle*

Both the advancing angle (drop volume increasing) and the receding angle (drop volume decreasing) are of interest, since the hysteresis in the contact angle is an indicative of the degree of order in the monolayer. For homogeneous monolayers, close packing and high degree of orientation generate a surface in which effectively only the terminal group of the tail is exposed outside. These types of surfaces exhibit strongly characteristic wetting properties. The tables are available for advancing contact angles as a function of terminal functional groups and contacting liquids. The highest values of contact angles are observed in case of alkanethiol monolayers with terminal $CH_3$ or $CF_3$ groups having water as a contacting liquid. These high wetting contact angles indicate that the monolayer chains are well oriented so that only the terminal group is exposed to the contacting liquid. On the other hand, the monolayers containing polar terminal groups such as -OH or COOH exhibit almost zero contact angle implying the complete wetting behaviour. Whitesides and his coworkers have extensively used contact angle measurements to study the structure of the monolayer films [53-55]. These measurements were also employed to follow the kinetics of thiol adsorption leading to a monolayer formation [19].

### 1.5.2. Ellipsometry

The term ‘ellipsometry’ arises from the fact that the most general state of the polarization of light is elliptic. The technique has been known for almost a century and it has been used for many applications now a days. As far as the characterization of monolayer is concerned, the thickness of the monolayer is an important parameter that has to be determined accurately. This plays a vital role in determination of orientation of the monolayer on the surface. At present, ellipsometry is the most common optical technique used to determine the thickness and refractive index of thin homogenous films [56]. Figure 6 shows an experimental setup used to measure the thickness of the SAM using an ellipsometer and the process is known as ellipsometry.

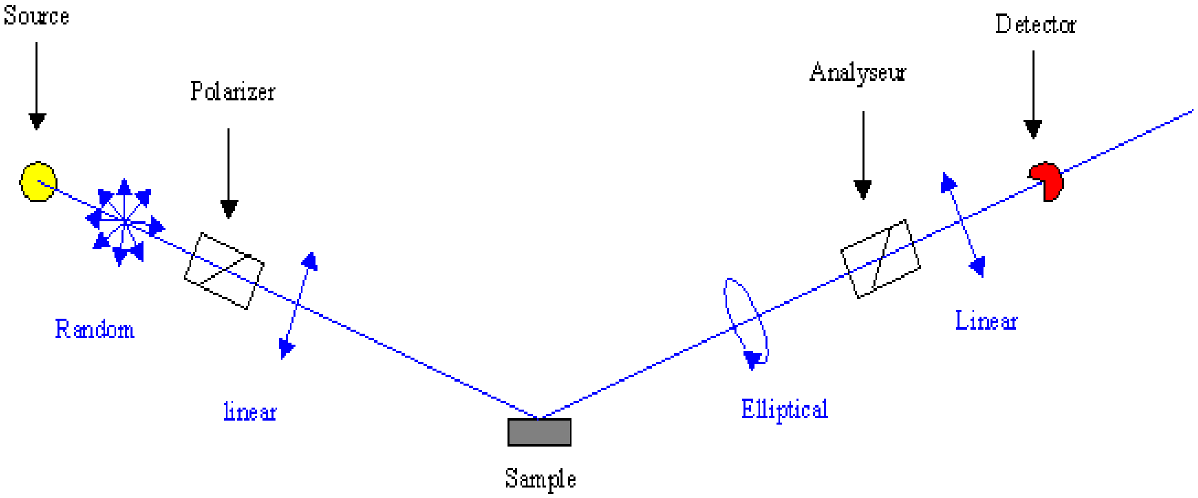

*Figure 6: Schematic diagram of an ellipsometer and its experimental setup*

In ellipsometry, a well-defined polarization state of light is reflected from the substrate and the changes in the polarization state are measured. The changes are well defined by two parameters $\Psi$ & $\Delta$. The parameter $\Psi$ is related to the change in the ratio of intensities for the in plane and out of plane components of the polarization, whereas the other parameter $\Delta$ is defined as the phase difference between the in plane and out of plane components of the reflected light. The thickness of a monolayer film can be measured by first measuring the values of the parameters $\Psi$ and $\Delta$ for the bare substrate and then repeating the measurement for a monolayer coated substrate. Using ellipsometry, it has been proved that a single molecular layer is formed during the self-assembly of alkanethiol molecules on gold surface resulting in a monolayer formation [57,58]. For the SAMs composed of alkanethiol molecules, the ellipsometric thickness increases linearly with the number of methylene units in the chain for $n > 5$, where n is the number of methylene units present in the alkyl chain. The ellipsometry is useful in monitoring the adsorption of protein molecules on the SAM modified surfaces and also in proving the stepwise deposition of bilayers and multilayers.

### 1.5.3. Surface plasmon resonance (SPR) spectroscopy

Surface plasmons are most commonly produced at the interface between a metal such as gold or silver and a dielectric material such as air or water. A surface plasmon generated by an optical radiation, consists of a resonant excitation of the electrons at the surface of a metal resulting in an associated surface bound and evanescent electromagnetic wave of optical frequency. The evanescent wave has a maximum intensity at the interface and decays exponentially with an increase in distance from the interface. Figure 7 shows a schematic representation of the experimental setup used in the surface plasmon resonance spectroscopic measurements.

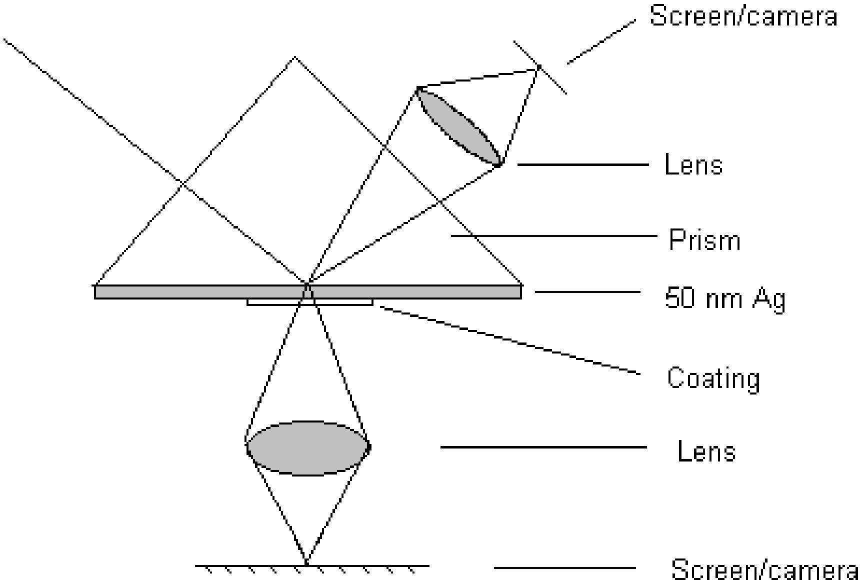

*Figure 7: Schematic representation of experimental setup of surface plasmon resonance spectroscopic measurements.*

Surface plasmon resonance spectroscopy [59] is based on the minimum in reflectance observed when a monochromatic light is reflected internally from a thin metal layer between two dielectric media. The change of position and the shape of the reflectance minimum measured as a function of incident angle can be transformed into the thickness of a film on a metal surface. This method is useful in the detection of volatile organic compounds present in gas, different liquid phases in polymers, oriented liquid crystals, and in the studies of biomolecular interaction on surfaces. This method has been used mainly to monitor the surface reactions of SAMs on gold surfaces in aqueous media [60,61]. Surface plasmon resonance spectroscopy has also been employed in the measurement of thickness of lipids and adsorption of proteins on SAMs.

### 1.5.4. Infrared (IR) and Raman spectroscopy

Infrared (IR) spectroscopy is a powerful tool to understand the molecular ordering, packing and orientation in ultrathin organic films deposited on an appropriate surface [20,62]. The spectrum is obtained using either internal or external reflection modes. The internal reflection mode is known as Attenuated Total Reflection (ATR) spectroscopy, whereas the external reflection mode is known as Reflection-Absorption or Grazing Angle spectroscopy. The grazing angle reflection measurements provide the greatest sensitivity for ultrathin organic films on reflective surfaces, especially that of metals. The reflection-absorption spectrum for a monolayer adsorbed on a metal surface is measured mostly at a higher angle of incidence in which only the p-polarization component of the incident light is allowed to pass through the sample [63]. The p-polarization component is parallel to the plane of incidence (or perpendicular to the substrate). The s-polarization component of the incident light is perpendicular to the plane of incidence. Hence the s-polarization component of the incident light does not interact with ultrathin film samples on metal and therefore does not contribute to spectral signal. This results in a very high quality, clean spectra. The spectrum obtained on a SAM modified metal substrate is ratioed with a suitable blank spectrum (taken on a bare substrate) to obtain the absorbance spectrum of the monolayer. The relative intensities of the absorption peaks in the spectrum are mainly affected by the average orientation of transition dipoles relative to the surface. A transition dipole parallel to the metal surface will exhibit a greatly attenuated peak relative to the transition dipole perpendicular to the metal surface. From these comparisons, the average orientation of the monolayer chains and the terminal groups can be determined. The peak positions also provide information about the dynamic behaviour of the monolayer. The pioneering work in the study of grazing angle FTIR spectroscopy on monolayers was carried out by Allara and Swalen [64]. The C-H stretching region is an important characteristic for the molecules containing long alkyl chains that provides an idea on the state of the monolayer film. The measured intensities of stretching modes of the $CH_2$ groups along with the intensities of stretching modes of $CH_3$ groups can be used to determine the average tilt of the alkyl chain axis from the surface normal [65]. Nuzzo et al. [23,38], Finklea et al. [66] and Porter et al. [19] have extensively used this technique to estimate the orientation of the alkyl chain, surface coverage, packing density & average tilt of the long alkyl chain in the monolayers of alkanethiols and disulphides on gold surface. Ulman et al. [21] used this technique to compare the monolayer formation of alkanethiols on gold and silver surfaces. It was found that on Au (111) substrate, the monolayers of alkanethiols exhibit all trans conformation with an average tilt of about $30^0$ from the surface normal. In addition to this, surface IR spectroscopy is also useful to determine the orientation of non-alkyl groups attached to the hydrocarbon chain. Allara and Nuzzo [25,65] have studied the adsorption of n-alkanoic acid on aluminium oxide surface using the surface IR spectroscopy.

Raman spectroscopy has been useful to probe the trans and gauche conformers present in alkanethiol SAMs on gold surface [67]. Both the Resonance Raman and IR spectroscopic studies have same set of selection rules, which can be stated as follows: ‘at the surface, transition dipoles that are parallel to the surface are not detected by a p-polarized light’. Usually the Raman spectrum is enhanced by mechanical or electrochemical roughening of the sample. Surface Enhanced Raman Scattering (SERS) was first observed for samples of pyridine adsorbed on roughened Ag surfaces [68,69]. Sandroff et al. have studied SERS of organic sulphides adsorbed on silver [70] and hexadecanethiol adsorbed on silver island films [71]. This monolayer has all-trans conformation, but on contact with chloroform there was a decrease in the number of trans bonds. It has been found that on silver the alkyl chains of alkanethiol and disulphide SAMs exhibit almost completely an all trans conformation. The Raman spectroscopy serves as a tool in understanding the process of self-assembly, order-disorder transitions and other molecular events in ultrathin organic films.

### 1.5.5. Measurement of surface potential

Surface potential is an important parameter for the analysis of electrical structures on the surfaces, which involve the distribution of polar and non-polar groups. The surface potential measurement can be performed on both the air-water interface and on the solid substrates. Evans et al. have measured the surface potential of alkanethiol monolayers on gold as a function of alkyl chain length [72].

### 1.5.6. Quartz crystal microbalance (QCM)

The Quartz crystal microbalance (QCM) consists of quartz crystal oscillators that can detect very small changes in both the current flow and weight of the electrode simultaneously [73,74]. This is a valuable tool for studying the reactions, which involve surface films, adsorbates, metal deposition, corrosion and monolayer formation. It is a very sensitive device that can detect even a fraction of a monolayer of most of the materials [75]. In this device, the monolayer-coated electrodes were placed in the opposite sides of a quartz crystal. When placed in a feedback loop of a radio frequency amplifier, the crystal oscillates at a precise frequency. Under certain conditions a change in frequency is proportional to the mass change of the monolayer film on the electrode. If one of the electrodes also functions as the working electrode of an electrochemical cell, then the device is known as an electrochemical quartz crystal microbalance. The QCM contains a piezoelectric device that has nanogram sensitivity in the measurement of mass of the material. The measured change in mass depends on the oscillation frequency of the crystal (usually disk shaped), its electrode and the contacting materials on its surface.

### 1.5.7. High vacuum surface techniques

The high vacuum surface techniques such as X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), high resolution electron energy loss spectroscopy (HREELS), low energy electron diffraction (LEED), helium atom diffraction and temperature programmed desorption were also used to characterize the monolayers formed on different surfaces. All of these methods require the SAM to be survived in the high vacuum environment and to the flux of photons or particles. The bond strength involved in the formation of SAMs especially in the case of alkanethiol SAMs on gold surface have the potential to withstand at these conditions that allow the analysis using these high vacuum methods.

Among these techniques, X-ray photoelectron spectroscopy (XPS) [76-79] is the most extensively used technique, which provides the evidence for the existence of monolayer on the surface and also used to determine the thickness of the SAM. For alkanethiol SAMs on gold, silver or copper, the XPS signals for the substrate element decay exponentially with the number of methylene units in the alkyl chain. The positions of the alkanethiol head group near the substrate and the terminal group at the exposed surface of SAM are confirmed by measuring the intensities of peaks associated with the elements in these two positions as a function of the photoelectron take off angle. XPS can be used to determine the mole fraction of each of the component in a mixed SAM provided the two components have different chain lengths. XPS is also useful in determining the presence of oxides on the substrates coated with the monolayers and the oxidation of sulphur by UV irradiation.

Various electron or atom diffraction methods [80,81] are useful in providing the information on the average spacing between the chains in a SAM and the registry of the SAM with the atomic structure on the substrate. Analysis of the diffraction intensity versus the angle of incidence suggests that the alkane chains have approximately a tilt angle of 30 degrees in the monolayer. This has been confirmed by extensive low energy electron diffraction studies on SAMs containing a wide range of alkanethiols. These molecules form a $(\sqrt{3} \text{ X } \sqrt{3})$ R $30^0$ overlayer structure on Au (111) surface with the thiols occupying every other three fold hollow site on the substrate.

Near edge X-ray absorption fine structure (NEXAFS) spectroscopy has been employed to study a series of SAMs on sputtered gold onto silicon for varying times [82]. The angular dependence of the C 1s edge spectrum provides information on the density of gauche verses trans conformations in the alkyl chains. During the initial stages of adsorption there is a high density of gauche conformations. Only after a very long time, the NEXAFS spectrum indicates the presence of a highly ordered all trans conformation in the monolayer.

### 1.5.8. Microscopic techniques

As far as the microscopic techniques are concerned, scanning tunneling microscopy (STM) and atomic force microscopy (AFM) have been extensively used for the structural characterization of the monolayer on various substrates [83-87].

STM is a powerful tool to investigate the very small areas of surfaces with extremely high level of precision and is a versatile tool in the area of surface science. It was invented by Gerd Binnig and Heinrich Rohrer [88] at the IBM research institute in Zurich. STM has the advantage of studying atomically smooth conducting surfaces in a variety of environments like ultra high vacuum (UHV), air, electrolytic media etc. The basic principle of STM is mainly based on the quantum tunneling of electrons. In a typical STM experiment, an atomically sharp metallic tip such as Pt/Ir, Pt/Rh or W is brought very close (~ < 1nm) to the surface. If a small potential difference (~1V) is applied between the surface and the tip, a tunneling current of the order of pA to nA [89,90] will flow due to the overlap of wave functions of atoms in the tip with the atom on the surface. In this method, the tip is scanned over the surface while the tunneling current is monitored. Since this current decreases by one order of magnitude per 0.1 nm change of the electrical gap width, the accuracy of the order of 0.1 Å can be achieved. The STM can be operated in two different modes namely the constant current mode and the constant height mode. The basic principle and modes of operation of STM have been explained elaborately in chapter 2. Actually the image obtained using STM corresponds to the local density of states (LDOS) of atoms on the surface.

The imaging of organic molecules adsorbed on conducting substrates by STM is challenging due to the low conductivity prevails in these kinds of organic films. Hallmark et al. [91] have studied the monolayers and multilayers of long alkyl chains containing octadecyltrichlorosilane and Cd arachidate. STM has been extensively used by various research groups to study the structure of alkanethiol SAMs on Au substrates [92,93]. While imaging the SAM coated surfaces using STM, damage to the monolayer and the substrate can be prevented by avoiding the prolonged scanning at high current densities. STM studies reveal that the alkanethiol monolayer on Au (111) substrate forms a $(\sqrt{3}\times\sqrt{3})$ R $30^0$ overlayer structure [62,92]. STM has also been used to demonstrate the phase segregations in mixed SAMs on gold that has been formed by varying the composition of two components.

In contrast to STM, the atomic force microscope (AFM) can image atoms on both the conducting and non-conducting surfaces [94]. In AFM, the tip of a flexible force-sensing cantilever stylus is scanned over the surface of a sample. The force acting between the cantilever and the sample surface causes deflections in the cantilever, which can be detected and utilized as the feedback signal.

For STM, the obtained images are a function of the surface topography and electron density, while for AFM the images combine the topography with the forces between the tip attached to the cantilever and the substrate. Even though both the methods can produce images with atomic resolution on a SAM coated surfaces, the resolution obtained using STM is always better than the AFM. These kinds of scanning probe techniques have been used mainly to determine the distribution of pinholes and defects density, the monolayer morphology and structure on the substrate.

### 1.6. Structure of the monolayer

The alkanethiol molecules are known to form a stable organic film (popularly called as either the monolayer or SAM) on gold surfaces with a high degree of order and orientation. These SAMs on gold substrates have been well characterized using a variety of surface analytical techniques. Most of the studies on SAMs of alkanethiol have been performed on evaporated or sputtered gold substrates deposited on freshly cleaved mica, polished single crystal silicon or glass under special conditions. These gold substrates exhibit predominantly Au (111) crystal face, as confirmed by X-ray diffraction studies [31-33]. Although a single crystalline substrate containing a well defined crystal face is important for many surface analytical methods like electron diffraction, scanning tunneling microscopy etc., there is no clear and consistent proof that a single crystalline substrate is essential to prepare the pinhole free SAMs. Electron diffraction and scanning tunneling microscopic studies reveal that the alkanethiol monolayer forms a $(\sqrt{3}\times\sqrt{3})$ R $30^0$ overlayer structure on Au (111) substrate [62,92]. The overlayer structure can be understood as follows. The vectors $a_1$ and $a_2$, shown in the figure 8, define the unit cell of Au (111) substrate and $b_1$ & $b_2$ (See figure 8) define the adsorbate unit cell. It can be seen from the figure 8 that the $b_1$ & $b_2$ vectors are longer than $a_1$ & $a_2$ vectors by a factor of $\sqrt{3}$ and the angle between $b_1$ & $a_1$ vectors (similarly between $b_2$ & $a_2$ vectors) is $30^0$. Thus the adsorbate unit cell is greater by $\sqrt{3}$ times and rotated by 30 degrees with respect to the substrate unit cell. Hence this overlay structure is classified as $(\sqrt{3}\times\sqrt{3})$ R $30^0$ structure and it is shown in figure 9.

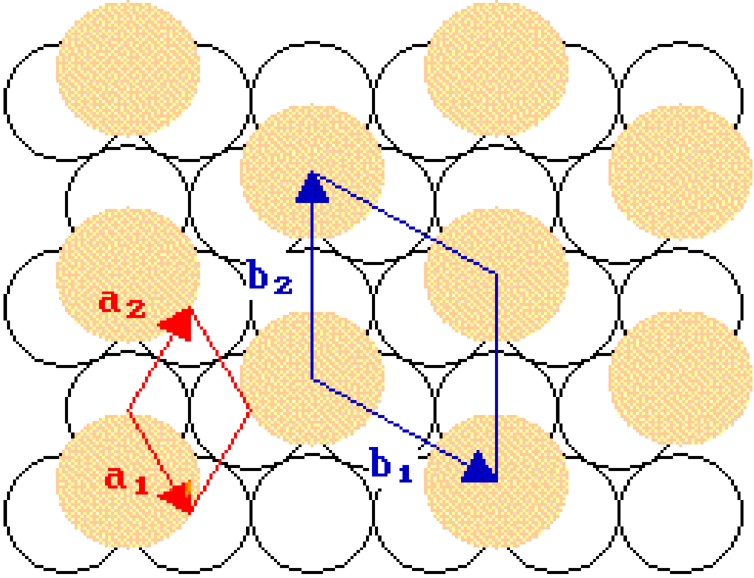

*Figure 8: Schematic representation of the unit cell of adsorbate*

The spacing between the adjacent sulphur atoms in this structure (4.99 Å) is about 3 times larger than the Van der Waals diameter of the sulphur atom

(1.85 Å), thereby minimizing the sulphur-sulphur interactions. This distance is also greater than the distance of closest approach of the alkyl chains (4.24 Å). Therefore the chains tilt by an angle of approximately about $30^0$ with respect to the surface normal in order to maximize their Van der Waals interactions [95]. Depending upon the chain length and the terminal group, various superlattice structures are superimposed on the $(\sqrt{3}\times\sqrt{3})$ R $30^0$ overlayer structure. The most common superlattice is the c(4×2) reconstruction, where the four alkanethiolate molecules of a unit cell exhibit slightly different orientations when compared with each other.

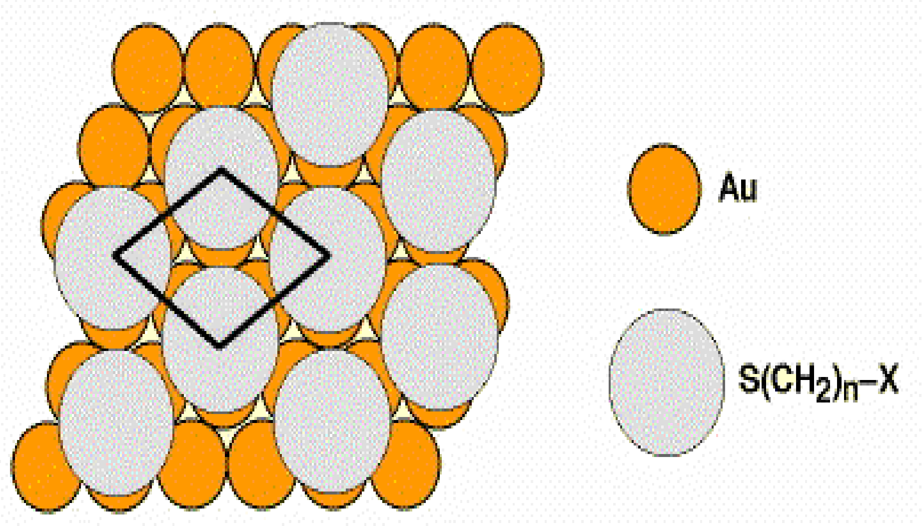

*Figure 9: $(\sqrt{3}$ X $\sqrt{3})$ R $30^0$ overlayer structure of alkanethiol SAMs on Au*

## 1.7. Characterization of SAMs using electrochemical techniques

Since the self-assembled monolayers are mostly formed on metal surfaces, the metal modified with the monolayer can be used as the working electrode in an electrochemical cell and these electrodes can be characterized using a variety of electrochemical techniques. Cyclic voltammetry, electrochemical impedance spectroscopy and capacitance measurements have been the most widely used electrochemical techniques in the characterization of

SAMs [6,8]. One of the main features of the monolayers on electrodes is their ability to inhibit the access of ions and the redox molecules to the electrode surface. Introducing a hydrocarbon layer between the metal electrode and the electrolyte ions in the solution phase leads to a substantial reduction of its interfacial capacitance value. The degree of packing of SAM on the gold electrode can be obtained by comparing the dielectric constant determined from the electrode capacitance value [96].

A monolayer, which is completely impermeable to a redox couple, prevents the electron transfer reaction on the metal electrode when it is coated with a monolayer. It also allows the study of electron tunneling over a well-defined distance and through a well-defined medium. The rate constants of these electron transfer reactions are greatly reduced and hence the kinetics can be studied over large range of overpotential values, which permits an excellent test of electron transfer theories. There are several methods have been reported in literature to determine the surface coverage of the monolayer on the electrode surface. Rubinstein and Sabatini [97] have used the characteristic gold oxide-stripping peak obtained in the cyclic voltammograms of gold electrodes and its corresponding SAM modified electrodes in sulphuric acid to measure quantitatively the fractional surface coverage ($\theta$) of the monolayer. This method assumes that the area covered by the dense monolayer is electrochemically inert. Porter et al. [98] have provided another method to determine the surface coverage of the monolayer based on the grazing angle FTIR spectroscopic studies. In alkaline medium, the monolayer can be desorbed quantitatively at very high negative potentials [99-102]. The position of the peak depends on the length of the alkyl chains. Longer the length of the alkyl chains, more negative is the potential where the desorption occurs. However, the area of the peak (90 μC) is independent of the alkyl chain and the peak is assigned to the reductive desorption of the alkanethiolate.

The monolayer-coated electrode used in the cyclic voltammetric studies dramatically brings down the charging current that becomes approximately a constant with the electrode potential. This observation is consistent with the presence of a layer with a low dielectric constant between the electrode and the electrolyte. In general, the monolayers on gold surface have an interfacial capacitance value in the order of 1-5 $\mu F/cm^2$ depending upon the medium used for the measurements and the measured value is significantly smaller than the bare gold electrode. The capacitance can be determined from the cyclic voltammetry in the absence of any redox species. The interfacial capacitance is the combination of at least two capacitances in series namely, the capacitance of the monolayer film $C_m$ and the double layer capacitance $C_{dl}$. The monolayer capacitance replaces the Helmholtz capacitance of the bare electrode and for electrolyte having the concentration above 0.1M, the double layer capacitance is much greater than the monolayer capacitance and hence the total capacitance is dominated by the monolayer capacitance $C_m$. The simplest expression for $C_m$ based on the Helmholtz model is given as follows [20].

$$C_m = \varepsilon_m \varepsilon_0 / d$$

where d is the thickness of the double layer, $\varepsilon_m$ is the static dielectric constant of the monolayer and $\varepsilon_0$ is the permittivity of free space ($8.854 \times 10^{-12}$ F/m). This expression is consistent with the nearly constant capacitance with respect to electrode potential observed in cyclic voltammetry.

A plot of the reciprocal of the interfacial capacitance versus the chain length is linear for thiol molecules with alkyl chains containing 10 or more methylene units. From the slope of this plot the effective dielectric constant of the monolayer can be determined. If the thickness increment is assumed to be 1.3Å per methylene group (corresponding to all trans alkyl chain with $0^0$ tilt), then the effective dielectric constant of the monolayer is found to be 2.6. On the other hand for a thickness increment of 1.1Å per methylene group (corresponding to all trans alkyl chain with $30^0$ tilt), the effective dielectric constant of the monolayer film is determined to be 2.3 [20]. For comparison, the typical dielectric constant values for a pure aliphatic hydrocarbon & polyethylene are 2.0 and 2.3 respectively. The excellent agreement between these values indicates that the long chain alkanethiols have very low permeability for ions in the aqueous medium. The interfacial capacitance of the monolayer-coated electrode is affected by the presence of various terminal groups in the thiol molecules [62]. The packing density of the monolayer affects its ionic permeability to a large extent. Grazing angle FTIR spectroscopic studies of the peak positions for the $CH_2$ stretching modes of these monolayers suggest that the –COOH terminated SAM is more of liquid like, while the $–CF_3$ or $–CH_3$ terminated SAM is more crystalline. From these observations, we can conclude that the SAM with the terminal –COOH group is more permeable to ions than the other SAM with $–CF_3$ terminal group.

Cyclic voltammetry and electrochemical impedance spectroscopy have been extensively used to probe the presence of pinholes & defects in the monolayer. A pinhole is defined as a site at which the electrode surface is accessible to the redox molecules and ions. Not only the adsorbed molecules are absent in a pinhole, but also the tails of nearby adsorbed molecules do not block this site. A defect is defined as a site where the ions and redox molecules can approach the electrode surface at a distance shorter than the thickness of the monolayer. The close packed and highly ordered SAMs on electrodes block a variety of faradaic processes such as metal oxidation, underpotential deposition of metals, oxidation and reduction of solution species, which requires the diffusion of species from the solution to the electrode surface. The presence of pinholes in the monolayer can be identified from the deviation of electrode from the perfect blocking behaviour. As mentioned earlier, one of the important manifestations of a close packed SAM on faradaic processes is the passivation of surface oxidation. It is reported in literature [6,97] that the gold oxide stripping current in acidic or alkaline medium offers the estimation of the area fraction of the pinholes present in the SAM coated gold electrodes. The oxidation of gold can occur only if the water molecules or hydroxyl ions can directly access the electrode surface through the pinholes. The measured charge from the area under the oxide-stripping peak is proportional to the amount of gold oxide formed in the positive sweep. This is an indication of the presence of pinholes in the SAMs. The ratio of the peak areas of a SAM modified electrode and a bare gold electrode with equal surface areas yields (1-$\theta$) value. The typical values of area of fraction of pinholes present in the long chain SAMs range between 0.01 and 0.0001 [6]. If a SAM coated electrode is subjected to repeated CVs into the oxide forming and stripping regions, the oxide stripping current grows with each successive scan. The increase in pinhole area is gradual, which is indicative of the slow growth of existing pinholes and the formation of new pinholes under the oxidation conditions. The stability of the monolayer is worse for the shorter chain SAMs.

The second main effect of a blocking SAM is the inhibition of the metal deposition on the gold surface. The metal deposition includes both the bulk deposition of the metal at potentials close to the thermodynamic potentials and the underpotential deposition (UPD) at potentials, which is very positive to that of thermodynamic potentials. The area under the underpotential deposition or stripping peak is proportional to the surface area of the electrode. The third main effect of the blocking SAMs is the suppression of simple redox reactions in which both the oxidized and reduced forms of the redox couple are soluble. This phenomenon is due to the unfavourable energetics of forcing a redox ion through a close packed domain of hydrocarbon chains. Several factors such as the heterogeneous rate constant for the electron transfer reaction, the size and solvophilicity of the redox species, mechanism of electron transfer (inner sphere versus outer sphere) affects the apparent blocking properties of the SAMs. These factors complicate the interpretation of suppressed faradaic current in terms of pinholes, defects and electron tunneling across the monolayer. The current due to faradaic reactions at pinholes are limited by mass transfer at relatively low overpotentials compared to kinetically controlled currents due to tunneling. Hence the factors that affect the mass transfer should affect the observed currents if they are dominated by pinhole currents. This point of mass transfer controlled or kinetically controlled process for the electron transfer reactions can be resolved using electrochemical impedance spectroscopic studies. Fawcett et al. [103,104] have extensively used impedance spectroscopic studies on the SAM modified electrodes to analyze their blocking properties to the electron transfer reactions.

From the literature, we find that while there have been a detailed and exhaustive studies on the structure and properties of aliphatic thiols on gold surface, there have been a relatively less attention that has been paid to the study of structure and blocking properties of aromatic thiol SAMs on gold surface. Moreover, the ultimate aim of researchers who work in the area of SAM is to obtain a completely blocking and almost defect free structure of the monolayer. With this in view, we have studied the monolayers of aromatic thiols on gold surface and evaluated the structure, integrity and interfacial properties of these monolayers using different electrochemical and nonelectrochemical techniques. We have also tried to improve the barrier properties of these SAMs by forming them in a medium containing the self-aggregated structures of surfactant.

## III. Aims and scope of the present work

1. To study some of the electrochemical reactions and molecular self-assembly of thiol molecules on Au surface using surfactants self-aggregated structures as electrolytic media.
2. To study the template electrodeposition of nickel using a hexagonal liquid crystalline phase and a microemulsion phase as templates.
3. To study the redox reactions and to understand the electron transfer processes occurring in the surfactants self-aggregated systems.
4. To study and characterize the self-assembled monolayers of thiol molecules on gold surface prepared using a hexagonal lyotropic liquid crystalline phase as an adsorbing medium.
5. To compare the electrochemical blocking ability and the structural arrangement of the monolayers prepared using the hexagonal liquid crystalline phase as an adsorbing medium with that of the corresponding monolayers formed from the commonly used organic solvents (conventional method).
6. To understand the electron transfer mechanism of two different redox probes viz., $[Fe(CN)_6]^{3-|4-}$ and $[Ru(NH_3)_6]^{2+|3+}$ on the SAM modified surfaces that have been used to evaluate the barrier properties of the monolayers on Au surface.

We find from literature that although the chemistry of surfactants and their structural aspects are known for quite sometime, there is relatively less attention that has been paid to the electrochemical studies on surfactants and their self-aggregated structures as electrolytic media. The electrochemistry involved in these surfactant stabilized electrolytic systems is novel from the point of view of conductivity, solubility, chemical stability of redox probe molecules and the structural integrity, which makes the study more interesting and useful in terms of understanding several processes that are occurring in biological systems. There are also several possibilities in terms of technological applications. For example, there has been quite a lot of interest in the synthesis of metallic and semiconducting nanoparticles using template deposition techniques. This kind of research has been highly motivated by the unusual physical and chemical properties of these particles, which essentially depends on their size, shape and packing density. Soft template deposition technique involves mainly the usage of surfactant and its self-aggregated systems. Keeping this in mind, we have carried out a detailed study using the self-aggregated structures of surfactants as a medium to prepare nanoparticles and high surface area materials.

We have carried out template electrodeposition of nickel using a new hexagonal liquid crystalline phase and a microemulsion phase as templates. We have chosen nickel as the material for the study because of its importance as a catalyst in many electrochemical processes. A new hexagonal liquid crystalline phase is a ternary mixture consisting of Triton X-100, water and poly(acrylic acid) at a particular composition. The microemulsion phase is also a triphase system containing Triton X-100, water and toluene at a specific composition. In this context, we have obtained a very high surface area nickel material by template electrodeposition using the hexagonal liquid crystalline phase as a template. The roughness factor for the nickel deposit obtained is of the order of 3600, which makes it an ideal candidate for many potential applications. We have investigated its utility in the applications of supercapacitors as an electrode material and in electrocatalysis as a hydrogen-evolving cathode.

We have used a variety of surface, microscopic and electrochemical characterization techniques in our study. The materials prepared using the template electrodeposition have been characterized using scanning electron microscopy (SEM), scanning tunneling microscopy (STM) and X-ray diffraction studies. Apart from these techniques, we have also used electrochemical techniques such as cyclic voltammetry, electrochemical impedance spectroscopy, Tafel plot analysis and capacitance measurements. In addition to this, we have also studied the effect of applied magnetic field on the electrodeposition of nickel. Using the above-described surfactants aggregate systems such as the hexagonal liquid crystalline phase, microemulsion phase and micelles as the electrolytic media, we have carried out some preliminary work on the electron transfer reactions of some redox probe molecules.

We have also investigated the formation of self-assembled monolayers of thiol molecules on gold surface using the surfactant-stabilized system as an adsorbing medium. Ever since the discovery of self-assembled monolayers (SAM) on noble metal surfaces, several research groups have been aiming to obtain the most blocking and almost defect free monolayer. A lot of efforts have been taken to achieve this aim due to the importance of such a film in several technological applications. The various factors such as the substrate morphology, thiol purity, adsorption solvent, deposition time and concentration of thiol molecules have been controlled and adjusted to achieve this. In this thesis, we have investigated the monolayer formation and its structural characterization using the surfactant stabilized system as an adsorbing medium and compared our results with that of the conventional methods of preparing the monolayers using organic solvents like ethanol (most commonly used solvent), acetonitrile etc. This overcomes the problems normally associated with the organic solvents such as the toxicity and volatility. Based on the experimental results, we have proposed a plausible mechanism of monolayer formation in the hexagonal liquid crystalline phase that has been used as an adsorbing medium.

We have studied the monolayer and mixed monolayer formation of aliphatic thiols, aromatic thiols and thiol molecules containing both the aliphatic and aromatic parts in their structure on gold surface. We have carried out the comparative studies on the above-mentioned SAMs prepared using ethanol as a solvent and hexagonal liquid crystalline phase containing the thiol molecules as an adsorbing medium. The barrier properties have been evaluated and their structure and orientation have been characterized using electrochemical techniques such as cyclic voltammetry, electrochemical impedance spectroscopy, gold oxide stripping analysis and capacitance measurements. Apart from these techniques, we have also used scanning tunneling microscopy and grazing angle FTIR spectroscopy in our studies.

We have evaluated the blocking ability of these monolayers using two different redox probes viz., $[Fe(CN)_6]^{3-|4-}$ and $[Ru(NH_3)_6]^{2+|3+}$ to study the electron transfer reactions on these SAM modified surfaces. Our studies on the electron transfer process are also aimed at understanding the differences in the behaviour of these two redox species. Based on these studies we have proposed a possible electron transfer mechanism for the case of ruthenium redox reaction. We have also carried out a detailed study on the monolayer formation of 2-naphthalenethiol on gold surface.

It is felt that the studies conducted during the course of this research investigation arrived at a better understanding of the processes occurring in surfactant systems, which are very important in the fundamental studies of electron transfer reactions in biological systems and in a variety of technological applications.

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