

CHAPTER 1

Introduction:

Several technologically important processes such as corrosion of metals, the operation of sensors, charging and discharging of batteries, etching of semiconductors, plating of metals etc., are all greatly dependent on the properties of the interface between the electrode and electrolyte. The behaviour of the interface can in turn be controlled and regulated by the adsorbed species on the surface of the electrode. The orientation and chemical nature of interaction of these molecules at metal electrodes is of considerable interest in electrochemistry due to the ability of the interfacial molecular structure to influence the heterogeneous electron transfer events. The character of adsorption of an organic molecule at the metal – solution interface is the net result of competing interactions between the molecule and two phases, the metal and solution. The adsorption process is generally determined by the interaction of the organic molecule and the metal with the solvent. The interaction may be merely electrostatic (e.g. the adsorption of anions or cations on a surface of opposite charge) or charge – dipole in nature (e.g. the adsorption of amines, thiourea etc.) or due to the formation of a covalent bond. Electrode reactions are most strongly affected when the adsorbate is the electroactive species, a reaction intermediate or the product. The adsorption of species not directly involved in the electrode process can also change the rate of electron transfer and the final product. Unless adsorption effects are taken into account it is not possible to understand the mechanisms of the various processes occurring at the electrode surface. The double layer structure and properties of the double layer are also of significant theoretical interest. The problems of electrical double layer structure on ideally polarised electrodes and reversible adsorption of ions and neutral organic molecules on electrodes are of considerable interest for various research groups.

Historically the first adsorption studies were carried out on mercury. A considerable amount of work on the adsorption of organic substances in relation to the structure of the electrical double layer has been done on mercury electrodes. The liquid mercury electrode offers advantages because its surface is energetically uniform, devoid of roughness and easy to clean. In addition most adsorption processes at mercury surfaces are completely reversible and uncomplicated by faradic reactions. The calculation of adsorption parameters can be readily obtained from capacitance measurements. Besides mercury, adsorption in other sp-metals such as Ga, Bi, Sn or Zn have been studied in great detail onto which organic molecules are weakly adsorbed.

Adsorption of organic compounds on d- metals such as Platinum have been studied by electrochemical and spectroscopic techniques mainly due to their ability to strongly interact with organic molecules and often causing dissociative adsorption. In combination with other metals such as ruthenium and tin, platinum exhibits electrocatalytic properties which find applications in fuel cells. The behaviour of direct methanol fuel cell is largely determined by the adsorbed intermediates on the catalytic surface. The adsorption of organic molecules on noble metals of Group IB such as gold, silver and copper are of great interest because they exhibit marked tendency to form well ordered monolayers on their surfaces. Thin films of organic molecules on these metals are often used to modify the chemical nature of surfaces aiming at tailor made properties and such films are often the basis for the development of highly selective sensors in biochemistry and environmental analysis. Organic molecules on single crystals of these metals have become model systems for the study of structural transitions in adlayers for self assembled molecules on surfaces.

Adsorption of organic compounds is widely used for regulating processes during metal electrodeposition because as additives, they improve the quality of metallic coatings such as brightness and porosity. The action of corrosion inhibitors is also based on adsorption effects. Corrosion inhibitors are organic or inorganic species added to the solution in low concentration that

reduce the rate of corrosion. These compounds adsorb onto the metal surface thus reducing the rate of metal dissolution reaction. The corrosion inhibitors are generally heterocyclic compounds containing nitrogen and sulphur which can bond to the metal surface through their lone pair of electrons. The adsorbed organic molecule may be simply chemisorbed or form a polymeric film on the electrode surface.

There is another type of adsorption process known as molecular self assembly which enables the formation of structurally well defined monolayers[1,2]. In recent years there has been an upsurge of activity in the fabrication of these organic monolayers on solid surfaces with the goal of studying a wide variety of interfacial processes such as surface passivation, adhesion, biological membrane systems etc. In surface electrochemical research, these monolayers make possible the systematic study of the dependence of electron transfer dynamics on the electrode-reactant distance and on the interfacial structure. One type of structurally well defined organic monolayer can be formed on gold surfaces by the self assembly of alkanethiols. Such ordered structures on electrode surfaces have several interesting properties and technological applications.

In broad terms this thesis deals with the study of self assembled monolayers of alkanethiols on gold, silver and copper and the adsorption behaviour of –N and –S containing heterocyclic compounds (azoles) on copper. More specifically, we focus on the kinetics of formation and barrier properties of alkanethiol monolayers which are studied using electrochemical techniques such as cyclic voltammetry and electrochemical impedance spectroscopy.

This chapter is divided into two parts. In the first part the formation and study of self assembled monolayers of alkanethiols on gold is discussed in detail. We also briefly review different techniques that are used to study self assembled monolayers. The second part presents a general introduction on the process of corrosion and adsorption study of heterocyclic compounds (azoles) on copper surface and their use as corrosion inhibitors.

I. Introduction to self assembled monolayers

1.1 Self assembled monolayers:

Self assembled monolayers are molecular assemblies that are formed spontaneously by the immersion of an appropriate substrate into a solution of a surfactant in an organic solvent. There are different types of self assembly methods that yield organic monolayers. The ideal picture of an organic monolayer consists of molecules with head and tail groups aligned perfectly on a smooth substrate. Monolayers can be deposited on substrates in general by two methods: Langmuir-Blodgett and self assembly.

The Langmuir-Blodgett method consists of transferring to a substrate by contacting a substrate with a compressed organised monolayer spread on the air-water interface [3,4]. The head group is hydrophilic and the tail group is hydrophobic, so that the orientation of the molecules is achieved before the transfer to substrate. The orientation of the transferred monolayer with respect to the substrate surface depends on the wetting properties of the substrate. Multiple organised layers can be deposited by successive contacts of the substrate with the air-water interface. The monolayer –substrate bond is either by Van der Waals interaction or by hydrogen bonding. Langmuir-Blodgett films have technical applications in sensors, corrosion, photoresists, non linear optics etc.

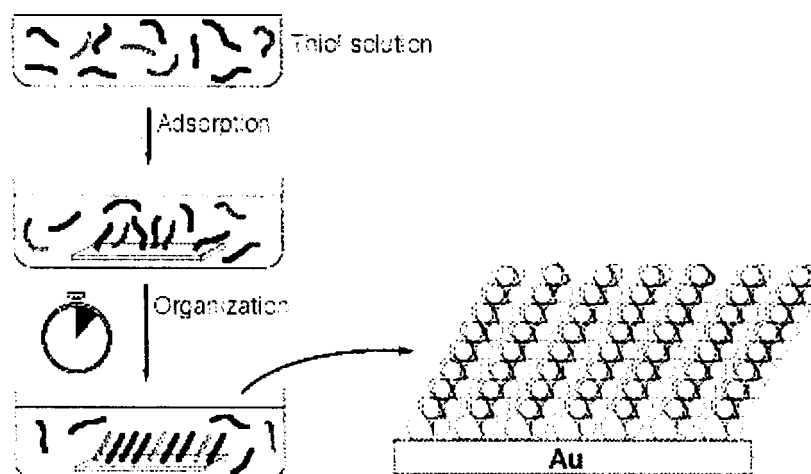
Self assembled monolayers include organosilicon on hydroxylated surfaces, alkanethiols on gold, silver and copper, alcohols and amines on platinum and carboxylic acids on aluminium and silver [5-8]. From the energetics point of view a self assembling molecule can be divided into three parts. The first part is the head group that provides the most exothermic process which is chemisorption onto the substrate. The very strong molecule-substrate interactions result in the pinning of the head group to a specific site on the surface through a chemical bond. The bonding can be covalent as in the case of alkyltrichlorosilanes on hydroxylated surfaces, covalent but slightly polar for alkanethiols on gold or ionic bond for carboxylic acids on AgO/Ag. The

energies associated with chemisorption are of the order of tens of Kcal/mole [9,10]. As a result of the exothermic head group - substrate interactions molecules try to occupy every available binding site on the surface and in this process they push together molecules that have already adsorbed. The second molecular part is the alkyl chain. The energies associated with its inter chain Van der Waals interaction are of the order of few Kcal/mole(exothermic). The third molecular part is the terminal functional group which in the case of a simple alkyl chain is a methyl group. The surface groups are thermally disordered at room temperature. Evidence for this comes from helium diffraction [11] and FTIR [12] studies on monolayers. The energies associated with this process are of the order of a few kT s where k is the Boltzmann constant and T is the absolute temperature. Each gauche bond has a value of about 0.7Kcal/mole associated with it.

In 1983 Nuzzo and Allara [13] published the first paper showing that dialkyl sulphides form oriented monolayers on gold surfaces. It was found that sulphur compounds coordinate very strongly to gold, silver and copper surfaces. Most of the work on alkanethiol monolayers has been done on gold surfaces because gold does not form a stable oxide layer on its surface and thus can be used under ambient conditions.

1.1.1 Monolayer formation:

The procedure for formation of the monolayer is quite simple. A clean, fresh hydrophilic gold substrate is immersed into a dilute solution of the alkanethiol in an organic solvent. The immersion time can vary from several minutes to several hours. This results in the formation of a close packed oriented monolayer. This simple procedure has been used to create diverse structures including alkanethiols with different terminal functional groups, alkanethiols with groups having large dipole moments, aromatic monolayers, attached polymers, lipids, proteins, peptides etc.



Self assembly of alkanethiol on gold

There have been a lot of efforts to achieve the most blocking and highly oriented monolayers on gold substrates. This has led to a consideration of various factors in the self assembly process such as substrate morphology, cleanliness of substrate, alkanethiol purity, deposition solvent, solution concentration, deposition time etc.

The first choice in terms of morphology is a polycrystalline substrate versus a single crystal. Most of the work on self assembled monolayer (SAM) formation has been done on evaporated or sputtered gold films on cleaved mica, single crystal silicon or glass. The gold films show essentially (111) crystal face when deposited [14-16] under appropriate conditions. While a well defined crystal face is important for many surface analytical methods (electron diffraction, scanning tunneling microscopy etc.) there is no consistent evidence that a single crystal surface is required to form pin hole free SAMs.

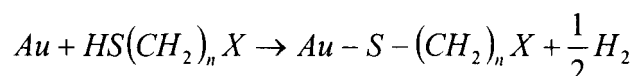
The strong affinity of sulphur for gold implies that the more weakly adsorbed materials will be displaced from the substrate during the self

assembly step [17]. Thus ultra high vacuum conditions are not required for the preparation of high quality monolayer films. The usual cleaning procedures are strong heating of the substrate, immersion of the substrate in strong oxidising agents, exposure of substrate to argon or oxygen plasma, ozone or UV radiation or electrochemical cycling in dilute acid solution. Polycrystalline gold can be cleaned by heating it in a gas –air flame to the point of incandescence. Piranha solution which is a mixture of concentrated sulphuric acid and 30% hydrogen peroxide in a 3:1 ratio is a commonly used oxidising cleaner. Gold substrates are completely wetted by water after exposure to these oxidising agents. Since the wetting properties of bare gold are a sensitive test to the presence of organic contaminants any partial dewetting of the gold surface by water indicates incomplete cleaning. Prolonged exposure of the substrate to UV/ozone, oxygen plasma, piranha solution leads to the formation of a partial layer of gold oxide on the surface.

All of the common organic solvents have been used to prepare SAMs. Ethanol is the preferred solvent because of its low toxicity, faint odour and availability in pure form [18]. It is not clear whether good or poor solvents for alkanethiols yield the most ordered SAMs. Poor solvents will increase the driving force for adsorption of alkanethiol onto the substrate, but at the same time a long alkane chain may introduce disorder within the SAMs by intercalating into the organised monolayers. The concentration of the alkanethiol and the time of immersion of the substrate also influence the formation of the monolayer. Typically the concentration of alkanethiol used is in the millimolar level though concentration ranges between micromolar and liquid alkanethiol have been used. Lower concentrations of the alkanethiol (micromolar range) require longer deposition times because of mass transfer effect of alkanethiol molecules to the surface [19]. It is also possible to form a monolayer in the absence of solvent via gas phase deposition.

1.1.2 Nature of bonding:

The nature of bond between the gold substrates and the alkanethiol is not fully understood. Both alkanethiols and disulphides adsorb to form the same species. The presumed adsorption chemistry is shown in the following equation:



where n is the number of methylene groups and X is the terminal group ($X = CH_3, CH_2OH, COOH$) etc. Extensive X-ray photoelectron spectroscopy (XPS) [18,20] experiments have shown that the organosulphur species formed from the adsorption of either alkanethiol or disulphide is a gold alkanethiolate ($Au-S-(CH_2)_nX$). No $S-H$ stretching vibration (2600 cm^{-1}) is seen in either infra red or Raman spectrum of adsorbed alkanethiols. This observation is confirmed by laser desorption Fourier transform mass spectroscopy studies. In X-ray photoelectron spectroscopy 2p peaks of Sulphur consistently appear at 162 eV, a value characteristic of metal alkanethiolate. Although the desorption of molecular hydrogen has not been detected, adsorbed hydrogen atoms readily recombine and desorb from gold surfaces at temperatures above 120 K. The formation of ordered monolayers from alkanethiols under UHV conditions on Au (111) substrates indicates that this reaction might be occurring. The desorption of water from the reaction of the alkanethiol with trace oxidants is also possible in studies involving immersion of the crystal in solution.

1.1.3 Monolayers on silver and copper:

After gold, silver has received the most attention as a substrate for the formation of organised monolayers [21-26]. Unlike gold, silver rapidly forms an oxide layer when exposed to air. Despite these factors it is possible to form a close packed highly oriented monolayer of alkanethiol on silver surfaces. SAMs have also been formed on copper surfaces [27,28]. Air oxidation of

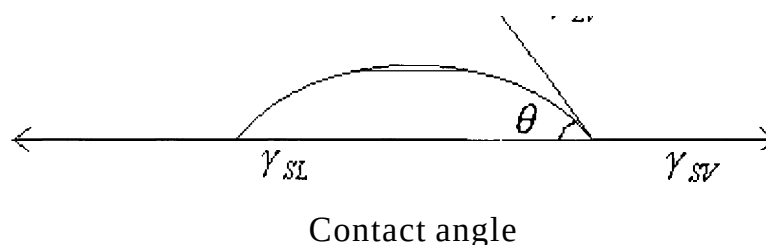
copper is sufficiently rapid to prevent the formation of copper oxide during the deposition step. X-Ray photoelectron spectroscopy reveals the presence of oxygen on the surface after monolayer deposition.

1.2 Methods of characterisation:

Several techniques have been employed in the characterisation of alkanethiol monolayers. Some of the issues addressed in the characterisation of monolayers are monolayer structure, pinhole defect density, molecular conformation, orientation and monolayer morphology.

1.2.1 Contact Angle:

One of the important properties of a monolayer is the wetting behaviour [29,30]. The wetting contact angle is measured by placing a small drop of a probe liquid on a horizontal substrate and measuring the angle subtended by the edge of the drop and the substrate. 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 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. Tables are available for advancing contact angles as a function of terminal functional group and contacting liquid. The highest values are observed for water in contact with alkyl monolayers with the $-\text{CF}_3$ terminal group. These high wetting contact angles show that the monolayer chains are well oriented so that only the terminal group is exposed to the contacting liquid. Monolayers possessing very polar terminal group like $-\text{COOH}$ show zero contact angle (complete wetting).



1.2.2 Infra red and Raman spectroscopy:

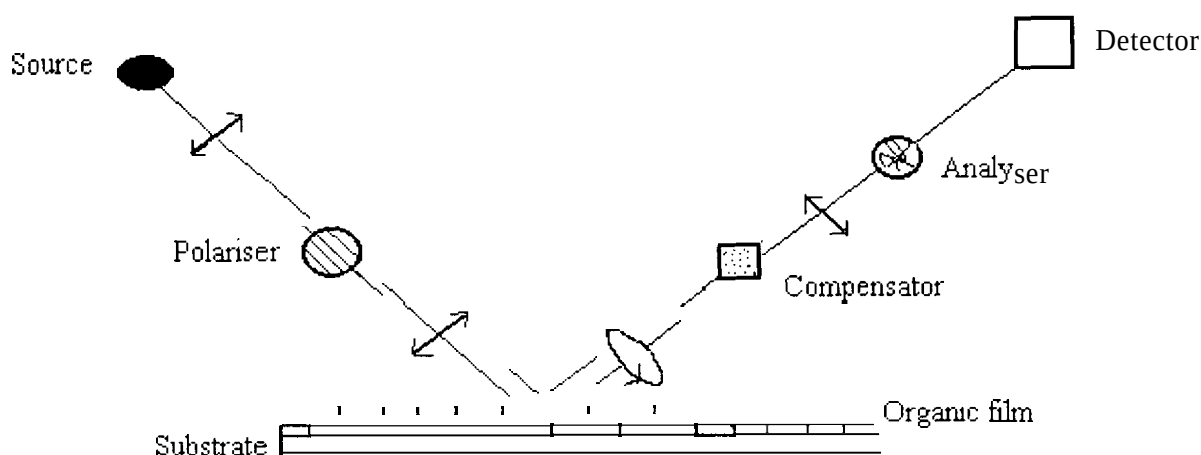
Infra red spectroscopy is a powerful tool in understanding the structure of monolayers [31-34]. The spectrum is obtained using either internal or external reflection geometries. The spectrum obtained on a SAM coated substrate is ratioed with a suitable blank spectrum (taken on a bare substrate) to obtain the absorbance spectrum of the monolayer. The IR spectrum is usually polarised in the plane of reflection (almost perpendicular to the substrate) because the intensity of electric field component parallel to a metal surface is essentially zero while the component perpendicular to a metal surface is enhanced. Consequently the relative intensities of the absorption peaks in the spectrum are affected by the average orientation of the transition dipoles relative to the surface. A transition dipole parallel to the metal surface will exhibit a greatly attenuated absorption peak relative to a transition dipole perpendicular to the metal surface. From these comparisons the average orientation of the monolayer chains and of the terminal groups are obtained. Peak positions also yield information about the dynamic behaviour of the monolayer. For alkanethiol SAMs, the intensities of stretching modes for CH_2 groups along the alkane chain relative to CH_3 stretching modes yield an average tilt for the alkyl chains. On an Au (111) substrate alkanethiols exhibit an all trans confirmation with an average tilt of about 30° from the surface normal. Surface IR spectroscopy is also useful for monitoring the orientation of non alkyl groups attached to the hydrocarbon chain.

Raman Spectroscopy has been useful to probe trans and gauche conformers in alkanethiol SAMs [35]. The Raman spectrum is usually

enhanced by mechanical or electrochemical roughening of the substrate. It is found that on silver the alkyl chains of alkanethiol SAMs exist almost completely in an all trans conformation.

1.2.3 Ellipsometry:

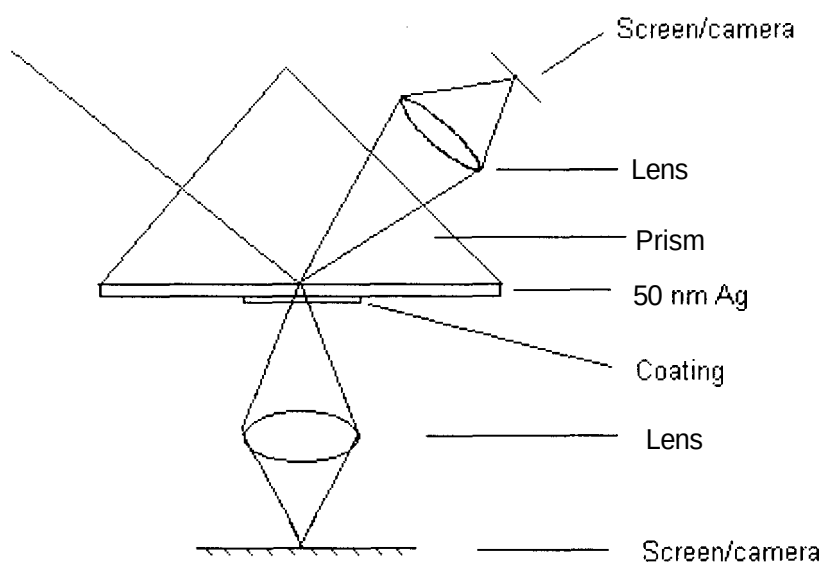
In ellipsometry, light [36] with a well defined polarization state is reflected from the substrate and the changes in the polarisation state are determined. The changes are defined by two parameters ψ and Δ . The parameter ψ is related to the change in the ratio of intensities for the in plane and out of plane polarisation components, and Δ is equal to the phase difference between the in plane and out of plane components of the reflected light. To measure the thickness of a film on a substrate, it is necessary to first measure ψ and Δ for the bare substrate and then to repeat the measurement on a coated substrate. The first result obtained from ellipsometry is that self assembly really deposits only one layer of molecules [37-39]. For SAMs composed of alkanethiols the ellipsometric thickness increases linearly with the number of methylene units in the chain for $n > 5$. Ellipsometry is also useful for proving the stepwise deposition of bilayers and multilayers and for monitoring the adsorption of proteins on SAM surfaces.



Schematic diagram of ellipsometer

1.2.4 Surface plasmon spectroscopy:

Surface plasmons are surface electromagnetic modes that travel along a metal – dielectric interface as bound non radiative waves with their field amplitudes decaying exponentially perpendicular to the interface. Surface plasmon spectroscopy [40] is based on the minimum in reflectance observed when monochromatic light is internally reflected from a thin metal layer between two dielectric media. The position and shape of the reflectance minimum as a function of the angle of incidence can be transformed into the thickness of a film on the metal surface. This method has been used to monitor surface reactions of SAMs on gold surfaces in aqueous media [41,42]. Surface plasmon spectroscopy has also been applied to the measurement of thickness of lipids and adsorption of proteins on SAMs.



Schematic setup of surface plasmon microscopy

1.2.5 High vacuum surface methods:

High vacuum surface methods include x-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), high resolution electron energy loss spectroscopy (HREELS), Low energy electron diffraction spectroscopy

(LEED), helium atom diffraction, temperature programmed desorption spectroscopy etc. All of these methods require the SAM to survive both the high vacuum environment and the flux of photons or particles. Alkanethiols on gold possess the necessary strength of bonding to the substrate to permit analyses by high vacuum methods.

X-ray photoelectron spectroscopy [43-46] provides another means for estimating the thickness of SAMs. For alkanethiol SAMs on gold, silver or copper, 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 elements in the two positions as a function of the photoelectron take off angle. X-ray photoelectron spectroscopy can be used to determine the mole fraction of each component in a mixed SAM provided that the two components have different lengths. XPS is also useful for determining the presence of oxides on reactive substrates coated with SAMs and the oxidation of sulphur by UV irradiation.

Various electron or atom diffraction methods [47-48] have provided both the average spacing between the chains in a SAM and the registry of the SAM with the atomic structure of the substrate. Electron diffraction study of $\text{HSC}_{21}\text{CH}_3$ SAM shows that on Au (111) the sulphur head groups form a hexagonal array with a $5.0\text{\AA}$ spacing. Analysis of the diffraction intensity versus the angle of incidence suggests that the alkane chains have approximate tilt angle of 30 degrees. This has been confirmed by extensive low energy electron diffraction study of SAMs containing a wide range of alkanethiols. The alkanethiols form a $(\sqrt{3}\times\sqrt{3})\text{R}30^\circ$ layer on Au(111) with the alkanethiols occupying every other three fold hollow site on the substrate.

Helium diffraction experiments probe the outermost layers of the SAM. At low temperature ($<100\text{ K}$) [49,50]. He diffraction has verified that the outer layers of the SAMs on gold retain the symmetry of the head groups. On Au

(111) the diffraction pattern is consistent with a hexagonal packing with a $5.0 \text{ \AA}$ spacing in a $(\sqrt{3} \times \sqrt{3})R30^\circ$ layer.

Near-edge x-ray absorption fine structure (NEXAFS) spectroscopy has been applied to a series of SAMs on sputtered gold onto silicon for varying times [51]. The angular dependence of the C 1s edge spectrum yields information about the density of gauche versus trans conformations in the alkane chains. During the initial stages of adsorption there is a high density of gauche conformations. Only after 10^4 hours the NEXAFS spectrum indicates the presence of a highly ordered all trans conformation in the SAM.

1.2.6 Scanning tunneling and atomic force microscopy:

Scanning tunneling microscopy (STM) is a powerful tool for investigation of very small areas of surfaces with extremely high level of precision. Scanning tunneling microscopy (STM) and atomic force microscopy (AFM) have been extensively applied to gold substrates coated with alkanethiol SAM [52-56].

In a typical STM experiment an atomically sharp metallic tip is brought very close ($< 10 \text{ \AA}$) to the surface. If a small potential difference ($\sim 1 \text{ V}$) is applied between the surface and the tip, a tunneling current will flow. This process of tunneling occurs due to the fact that the wave functions extend into vacuum and there is an overlap between atoms on the tip and atoms on the surface. In an STM experiment, the tip is scanned over the surface even while the tunneling current is monitored. Since this current decreases by one order of magnitude per $\sim 1 \text{ \AA}$ change of the electrical gap width, accuracy of the order of $0.1 \text{ \AA}$ can be achieved. There are two ways to carry out an STM experiment, the first being the constant current and the second the constant height approach. In the first method, the tip height above the sample is adjusted maintaining the current constant and the image is obtained as a map of the tip height z , versus the lateral coordinates x and y . In the latter approach, the height is kept constant and the current I is recorded as a function of the lateral coordinates.

While imaging SAM coated metals using STM, damage to the monolayer and the substrate can be prevented if prolonged scanning at high current densities is avoided. At tunneling currents less than 10nA an Au (111) substrate coated with alkanethiol yields images of spots with hexagonal symmetry and a spacing consistent with the $(\sqrt{3} \times \sqrt{3}) R30^\circ$ structure obtained by diffraction experiments. The images obtained are independent of chain length, and are attributed to the alkanethiolate head groups. STM has also been used to demonstrate phase segregations in varied composition two component SAMs on gold.

The Atomic force microscope in contrast to STM can image both conductors and non conductors with atomic resolution. Here the atoms in the tip interact with those on the surface, and the resulting attractive or repulsive force deflects the spring. Atomic force microscopy can be operated in two modes. In the first mode the tip is rastered across the substrate usually at a constant force to generate an image, while in the second mode, the force distance curve is monitored as the tip is pushed into the substrate. In the first mode images can be obtained on Au(111) coated with alkanethiol with chain lengths greater than three carbon atoms. The images possess the expected hexagonal symmetry with $5.1\text{\AA}$ nearest neighbours and $9.1\text{\AA}$ next nearest neighbours of the $(\sqrt{3} \times \sqrt{3}) R30^\circ$ overlay. The hexagonal pattern of the SAM is commensurate with the Au (111) lattice.

For STM, the observed images are a function of surface topography and electron density, while for AFM the images combine topography with the forces between the AFM tip and the substrate. Both methods can generate images with atomic resolution on a SAM coated substrate. Scanning probe techniques have been used to determine pinhole defect density, monolayer morphology and monolayer structure on the substrate.

1.2.7 Quartz crystal microbalance:

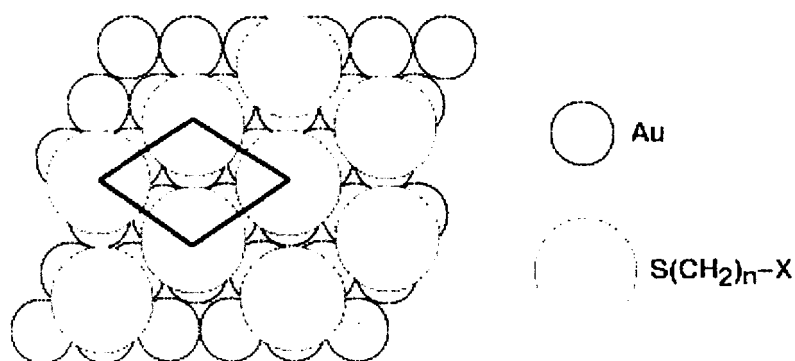
The quartz crystal microbalance (QCM) is one of a class of quartz oscillators able to detect very small changes in surface films [57-59]. In this device, two electrodes coat the opposite sides of a quartz crystal. When placed in a feedback loop of a radio frequency amplifier, the crystal oscillates at a precise frequency. Under certain conditions a change in frequency is proportional to the mass change of the surface film on the electrode. If one of the electrodes also functions as the working electrode of the electrochemical cell, the device is known as an electrochemical quartz crystal microbalance. This device can detect mass changes corresponding to fraction of a monolayer of molecules.

1.3 Monolayer structure:

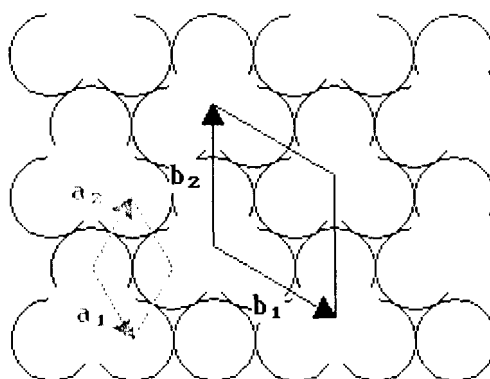
The high degree of order and stability of alkanethiol films allow them to be characterised by various physical and chemical methods. SAMs have been thoroughly characterised using a large number of surface analytical tools. We concentrate on the structures formed on Au (111) surface because these monolayers are the best studied.

Most experiments dealing with the formation of alkanethiol monolayers are performed on evaporated gold films on either mica, silicon or glass substrates. X-ray diffraction studies of gold films on mica and silicon show these to be highly (111) textured (grain size $1000\text{\AA}$). As discussed above the bonding of the sulphur head group to the gold substrate is extremely strong (-44Kcal/mole). Electron diffraction and Scanning tunneling microscopy reveal that the monolayer forms a $(\sqrt{3}\times\sqrt{3})R30^\circ$ overlay structure [60,61]. The structure order can extend over hundreds of square nanometers. The overlay structure can be understood as follows. The vectors a_1 and a_2 define the unit cell of the substrate [Au (111)]. The adsorbate unit cell is defined by the two vectors b_1 and b_2 . It can be easily shown that the vectors b_1 and b_2 are longer than a_1 and a_2 by a factor of $\sqrt{3}$. The angle between b_1 and a_1 vectors (and between b_2 and a_2 vectors) is 30 degrees. Thus the adsorbate unit cell is $\sqrt{3}$

times greater and rotated by 30 degrees with respect to the substrate unit cell. Hence this overlay structure is classified as $(43 \times \sqrt{3}) R 30^\circ$ structure.



The $(\sqrt{3} \times \sqrt{3})$ structure of alkanethiol on Au(111) substrate



Unit cell of adsorbate

The spacing between the adjacent sulphur atoms in this structure ($4.99\text{\AA}$) is nearly three times that of the Van der Waals diameter of the sulphur atom ($1.85\text{\AA}$), thus sulphur-sulphur interactions are believed to be minimal. This distance is also greater than the distance of closest approach of the alkyl chains ($4.24\text{\AA}$), therefore the chains tilt by approximately 30° to maximise their Van der Waals interactions [62,63]. Depending on chain length and chain-terminating group, various superlattice structures are superimposed on the $(43 \times \sqrt{3}) R 30^\circ$ overlay structure. The most commonly seen superlattice is the

c(4×2) reconstruction, where the four alkanethiolate molecules of a unit cell display slightly different orientations when compared with each other.

1.3.1 Structure of polymethylene chains:

The structure of the polymethylene chains has been studied quantitatively by ellipsometry, infrared spectroscopy, Raman spectroscopy, x-ray diffraction etc. It is found that the chains are fully extended, tilted with respect to the surface normal and in a nearly all trans configuration. These conclusions are supported by molecular dynamics simulations. Increasing the chain length of the adsorbed alkanethiols from 9 to 21 carbon atoms increases the measured thickness linearly. Other measurements of film thickness including infrared spectroscopy, differential capacitance, [64] surface potential, x-ray photoelectron spectroscopy all show linear changes with increasing polymethylene length. One convenient method of checking a SAM for well-ordered and dense structure is infrared reflection-absorption spectroscopy (IRAS). The C-H stretching vibrations of the alkyl chain are very sensitive to packing density and to the presence of gauche defects, which makes them ideally suited as probes to determine SAM quality. A quantitative analysis of both infrared and Raman data indicates that the optimum angle is around 25 – 30 degrees.

In addition to the tilt the alkanethiol also has a twist angle β [65]. The measured value for alkanethiols is -52° which implies that the gold surface-sulphur-carbon bond is near to 120° . This value is close to the optimum for a sp^2 hybridised sulphur atom. The actual tilt and twist angles of the chain are constrained by the geometry imposed by the metal-sulphur bond and thus has more effect on the structure of the monolayer than simply pinning the chains with a characteristic spacing.

From the view point of surface chemistry the structure and orientation of terminal group is very important. This is the portion of the substrate molecule that dominates the interactions that occur between the monolayer and the contacting phase, because the structures are sufficiently compact that

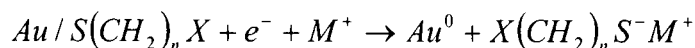
deeper contacts are sterically precluded. The gold lattice and the polymethylene chains merely anchor, orient and when suitably chosen order the group. The most widely studied chains are those terminated with methyl groups. The only requirement for good orientation is that the surface projection of the tail group be small enough to pack efficiently at $\sim 5\text{\AA}$ distance.

1.4 Electrochemical techniques:

Since self assembled monolayers of alkanethiols can be formed on metal surfaces, the metal can be used as the working electrode and *SAMs* characterised by electrochemical techniques [66]. Electrochemical techniques were among the first employed to characterise alkanethiol monolayers. Cyclic voltammetry and capacitance measurements have been the most widely used techniques. One desirable feature of monolayers on electrodes is their ability to limit access of solution phase molecules (both electrolyte ions and redox couples) to the electrode surface. Inserting a hydrocarbon layer between the electrode and the electrolyte ions leads to a substantial reduction of interfacial capacitance. A measure of the degree of packing of the **SAM** on the gold electrode can be obtained by comparing the dielectric constant calculated from electrode capacitance [67].

A monolayer that is completely impermeable to a redox couple allows the study of electron tunneling over a well defined distance and through a well defined medium. The electron transfer rate constants are greatly reduced, hence kinetics can be studied over large values of overpotential which permit an excellent test of electron transfer theories. Several methods have been employed to determine surface coverage of the monolayer on the electrode surface. Rubinstein [68] has used the characteristic gold oxide formation/removal peaks in cyclic voltammograms of gold electrodes immersed in H_2SO_4 for quantitative measurement of the fractional surface coverage θ . This method assumes that areas covered with the dense monolayer are electrochemically inert. Porter [69] has provided another method to quantitatively measure the surface coverage of the monolayer.

In alkaline medium a **SAM** will be quantitatively desorbed at a potential of -0.7 to -1.4 V vs. Ag/AgCl [70-73]. The position of the peak depends on the length of the alkane chain, longer chains yield more negative potentials. However the area of the peak (90 μC) is independent of the length of the alkyl chain. The peak is assigned to the reductive desorption of the alkanethiolate.



A cation from the electrolyte is included in the desorption reaction since the peak potential is sensitive to the identity of the cation. With an estimated roughness area of 1.2, the peak area corresponds to a coverage of $7.8 \times 10^{-10} \text{ mol cm}^{-2}$ in good agreement with a coverage expected for a $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ overlay structure on Au (111). The reproducibility of the results depends critically on the crystallinity of the gold surface.

When a **SAM** with a long alkane chain is deposited on a electrode, the charging current in the cyclic voltammogram drops dramatically and becomes approximately constant with electrode potential. This observation is consistent with the presence of a layer of low dielectric constant between the electrode and electrolyte. The total interfacial capacitance is obtained by dividing the charging current by the scan rate v . In general the interfacial capacitance for most SAMs with 10 or more methylene groups lie in the 1 to 5 $\mu\text{F cm}^{-2}$ range significantly smaller than the typical capacitances for bare gold [74]. The interfacial capacitance is composed of at least two capacitances in series, the capacitance of the monolayer C_m , and the double layer capacitance C_d . The monolayer capacitance replaces the Helmholtz capacitance of the bare electrode. For electrolyte concentrations greater than 0.1 M the double layer capacitance is much greater than the monolayer capacitance, hence the total capacitance C , is dominated by the monolayer capacitance C_m . The simplest expression for C_m , based on the Helmholtz model of double layer is,

$$C_m = \frac{\epsilon_m \epsilon_0}{d}$$

where d is the thickness of the double layer, ϵ_m is the static dielectric constant of the monolayer and ϵ_0 is the permittivity of free space ($8.854 \times 10^{-12} \text{ F m}^{-1}$). This expression is consistent with the nearly constant capacitance with respect to electrode potential seen in cyclic voltammetry.

The reciprocal of the interfacial capacitance is linear with chain length when the alkane chain has more than 10 or more methylene units. The slope yields an effective dielectric constant of around 2.6 if the thickness increment is $1.3 \text{ \AA}$ (corresponding to an all trans alkane chain with 0° tilt) and 2.3 if the thickness increment is $1.1 \text{ \AA}$ (corresponding to a chain tilt of 30°). For comparison typical dielectric constants for a pure aliphatic hydrocarbon and for polyethylene are 2.0 and 2.3 respectively. The excellent agreement suggests that long chain alkanethiols have very low permeabilities for water and ions when they are in contact with aqueous solutions. The terminal group affects the capacitance of a SAM coated electrode. The packing density of the monolayer affects the ionic permeability of the monolayer. IR study of the peak positions for the CH_2 stretching modes suggests that the $-\text{COOH}$ terminated SAM is liquid like while $-\text{CH}_3$ terminated SAMs are more crystalline, hence the $-\text{COOH}$ terminated SAM should be more permeable.

Pinholes and defects in the monolayer can be probed by cyclic voltammetry. A pinhole can be defined as a site at which an electrode surface is exposed to the electrolyte. Not only is an adsorbed molecule not present at a pinhole but the tails of nearby adsorbed molecules do not block this site. A defect is defined as a site at which molecules and ions from the electrolyte can approach the electrode surface at a distance shorter than the thickness of the SAM. Close packed SAMs on electrodes block a variety of faradic processes (metal oxidation, underpotential deposition of metals, oxidation and reduction of solution species) all of which require the solution species to diffuse to the

electrode surface [75]. Evidence for pinholes is obtained by the departure of the electrode from perfect blocking behaviour. As discussed earlier one of the main manifestations of close packed SAMs on faradic processes is the passivation of surface oxidation. When a gold electrode is subjected to a positive potential sweep from the double layer region to potentials that cause the oxidation of gold in aqueous acid solution, the surface oxidation yields a set of well defined anodic peaks whose shape and position are indicative of the crystallinity of the gold and the presence or absence of surface contaminants. When the potential is returned in the negative direction a well defined cathodic peak appears at potentials negative to the start of oxidation. This peak corresponds to the stripping or reduction of gold oxide. Its area is proportional to the amount of gold oxide formed in the positive sweep. When a long chain SAM is present the gold oxidation and subsequent oxide stripping currents are strongly suppressed [76]. Often there is no anodic current present during the positive scan. It is evident that the SAM passivates the oxidation of gold. Inhibition of gold oxidation is caused by the exclusion of water from the gold surface rather than by bonding of SAM to the gold surface, since the passivation of gold surface occurs on silane coated electrodes also. The oxide stripping current is evidence for the presence of pinholes in the monolayer since gold can be oxidised only if water reaches the electrode surface. The area fraction of the pinholes can be estimated from the area of the oxide stripping peak. The oxide stripping current offers a quick assessment of the area fraction of the pinholes. The ratio of the peak areas of the coated and clean gold electrodes with equal surface areas yields $1-\theta$. The typical values for long chain SAMs range between 0.01 and 0.0001. The formation and stripping of the gold oxide perturbs the SAM. If a SAM covered electrode is subjected to repeated CVs into the oxide forming region 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 formation of new pinholes under oxidation conditions. The instability of the monolayer is worse for shorter chain SAMs. A second effect of a blocking SAM is the inhibition of metal

deposition on gold electrode. Metal deposition includes both bulk deposition of the metal at potentials close to the thermodynamic potential and underpotential deposition (UPD) at potentials well positive of the thermodynamic potential. The areas under the underpotential deposition or stripping peaks are proportional to the surface area of the gold electrode.

When a monolayer is partly formed then UPD peaks are observed. The area fraction of pinholes can be estimated from the area of the underpotential deposition or stripping peak. It is possible that blocking SAMs on gold do not show any Cu or Pb UPD peaks even though oxide stripping peaks are visible. This discrepancy might be caused by the need for a gold substrate that is completely free of organic material in order for underpotential deposition to occur. The third main effect of a blocking SAM is the suppression of simple faradic processes in which both the oxidised 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. Interaction of the alkane chains with the solvent is important for blocking behaviour. An alkanethiol coated gold electrode in water can be extremely blocking to $\text{Fe}^{+2/+3}$ couple and yet exhibit no perceptible blocking properties to the ferrocene/ferricinium redox couple in acetonitrile. Factors influencing the apparent blocking behaviour include the heterogeneous rate constant for electron transfer, the size and hydrophilicity of the redox ions, mechanism of electron transfer (inner sphere versus outer sphere). These factors complicate the interpretation of suppressed faradic currents in terms of pinholes, defects, or electron tunneling across the SAM.

Pinholes can be presumed to be present if the SAM is not strongly blocking and there is significant faradic current at relatively low overpotentials. Current peaks are strong evidence for pinhole controlled faradic process. Currents due to faradic reactions at pinholes are limited by mass transfer at relatively low overpotentials compared to kinetically controlled currents due to tunneling. Hence factors that affect mass transfer should affect the observed currents if they are dominated by pinhole currents.

From the study of literature we find that while there have been detailed and almost exhaustive studies on the structure and properties of equilibrated alkanethiol assemblies on Au, there have been relatively few studies of the kinetics of the formation process using electrochemical techniques. Besides, the effect of the surface morphology on the properties of the self assembled monolayers have not been studied in detail so far. In this work we have used electrochemical impedance spectroscopy to study the kinetics of formation of alkanethiol monolayers on gold, silver and copper surfaces. In addition to this we have also investigated the effect of surface morphology and pretreatment on the formation of the monolayer as they have a significant effect on their blocking properties.

II. Corrosion and organic corrosion inhibitors:

In this section we present a general introduction on the process of corrosion and the role of organic compounds in inhibiting the corrosion reaction.

1.5 Introduction to corrosion:

Corrosion is a process of spontaneous degradation of a metal by its reaction with the environment [77,78]. Corrosion of metals in aqueous environments is almost always electrochemical in nature. It occurs when two or more electrochemical reactions take place on a metal surface. As a result, some of the elements of the metal or alloy change from a metallic state to a non metallic state. The products of corrosion may be dissolved species or solid corrosion products; in either case the energy of the system is lowered as the metal converts to a low energy form. Rusting of steel is the best known example of conversion of a metal (iron) into a non metallic corrosion product (rust) The change in the energy of the system is the driving force for the corrosion process. Corrosion processes can be broadly classified into uniform and localised corrosion. The uniform corrosion is assumed to be due to the occurrence of an anodic metal dissolution reaction over the entire surface of the

metal and one or several cathodic conjugate reactions also taking place uniformly on the surface of the metal. The dissolution of a metal in acid solution is an example of uniform corrosion. When the corrosion process is confined to a few small places of the metal (pits, grain boundaries, crevices and cracks) the process is known as localised corrosion. Pitting corrosion, crevice corrosion, intergranular corrosion and stress corrosion cracking are some examples of localised corrosion. In simplest terms corrosion can be described in terms of the metal oxidation half cell reaction,



coupled with a reduction reaction,



Generally in corrosion systems, the reverse reactions of (1) and (2) are negligible. In such a case, a steady state is attained when the net rate of one of the reactions becomes equal to the net reaction rate of the other. For example in acid solutions this happens when the net rate of metal dissolution equals the net rate of discharge of hydrogen ions. The potential of the corroding metal is the mixed potential of anodic and cathodic reactions (1) and (2) and the net current is zero. This potential is known as the 'corrosion' potential or 'rest' potential. According to the homogeneous theory of corrosion [79] the entire surface of the metal acts as both the cathode as well as the anode. In other words, cathodic and anodic areas are not spatially separated on the metal surface. Both the conjugate reactions (1) and (2) take place over the entire metal surface and hence corrosion is assumed to be uniform.

Evans [80] advocated the theory of local cells to explain corrosion process. According to this theory, the corrosion process is considered to be due to the existence of micro cathodes and anodes which are short circuited by the bulk metal. When current flows, the different cathodes and anodes on the surface of the metal get polarised in such a way that they assume a mixed potential known as the corrosion potential. On the basis of this theory, uniform

corrosion would be expected whenever the anode area is very much greater than the cathode area.

A study of the kinetics of corrosion processes is quite useful in the evaluation of corrosion resistance of materials and methods of protection against corrosion. Such a study calls for determination of corrosion rate and Tafel slopes. A knowledge of these parameters also helps to suggest suitable inhibitors to reduce corrosion damage.

1.6 Measurement of corrosion rate:

Measurements of corrosion rate can be carried out using electrochemical or non electrochemical methods. The non electrochemical methods are direct methods and are mainly based on:

- 1) Weight loss measurements
- 2) Solution analysis and
- 3) Gasometric titrations

While these are quite useful, since they lead to direct determination of the corrosion rate, they also suffer from several disadvantages. Due to long exposure times needed, these methods are quite time consuming and provide only average corrosion rates. Besides the accuracy and reproducibility of these methods are poor when corrosion products form as a layer on the surface.

Measurement of corrosion rate by electrochemical methods has the basis in Faraday's law which correlates the mass flux density with the corrosion density.

$$i_{corr} t = \frac{nFw}{M} \quad (3)$$

where,

i_{corr} is the corrosion current in amperes

t is the time in seconds

nF is the number of coulombs required to convert 1 mole of metal to corrosion product where n is the no. of electrons involved in the reaction and F is 96500 coulombs.

M is the molecular weight in grams

w is the mass of the corroded metal in grams

The electrochemical methods of measuring the corrosion rate are quite fast and accurate when compared to non electrochemical methods. They also provide information on **in situ** corrosion rate which is useful in corrosion monitoring. The theoretical basis for the electrochemical methods of investigation of corrosion systems is the standard rate expressions employed in the study of electrode kinetics.

1.7 Rate equation for corrosion process:

When concentration polarisation is absent (i.e. when the mass transport of the reactants and products are sufficiently fast) and when the reverse reactions of (1) and (2) are neglected, the steady state current- potential relation corresponding to this pair of reactions is given by the following relationship in electrode kinetics,

$$I = I_{corr} \left[\exp\left(\frac{\alpha_A nF}{RT} \eta\right) - \exp\left(\frac{-\alpha_C nF}{RT} \eta\right) \right]$$

where ,

I is the current

I_{corr} is the exchange current density

α_A, α_C are transfer coefficients for the anodic and cathodic reactions respectively.

η is the overpotential i.e deviation of the potential from its equilibrium value.

which is the well known Butler- Volmer equation in electrode kinetics [78]. This rate expression forms the basis of almost all electrochemical techniques used in corrosion kinetics, since measurement of I_{corr} provides a means of measuring weight loss from equation [3].

1.8 Inhibition of corrosion in aqueous solutions:

Metals which are in common use, such as aluminium, copper, iron, zinc etc. are inherently unstable. Their ionic solutions and their salts are more stable than the free metal under the many conditions to which these metals are exposed. The free energy change for the conversion of these metals to a compound is a large negative value, and the thermodynamic driving force to convert the elemental metal to an oxide or salt is great. Thus to retain a required physical property of the metal such as strength, thermal conductivity, magnetic nature etc. it is essential to protect the metal from the environments to which it is expected to be exposed. The objective of all protective systems is to reduce the rate of corrosion to a value that is tolerable or that will allow the material to attain its normal or desired lifetime. The concept of barrier protection involves protecting the metal from its environment by coating it with a barrier that resists penetration by aggressive environmental constituents. There are different types of barrier coatings used to prevent corrosion. One of them is the use of inhibitors. In many cases the role of inhibitors is to form a surface coating of one or several molecular layers thick that serve as a barrier. Many effective organic inhibitors have a reactive group that interacts with the metal surface.

For the corrosion inhibitor to be effective it must protect all the exposed metal from corrosive attack, must be effective at low concentration, must not cause deposits on the metal surface, remain effective under a broad range of pH, temperature etc. Inhibitors can broadly be classified according to the rate processes being controlled. Anodic inhibitors suppress anodic reactions, i.e. the rate of metal ions transferred to the aqueous environment is reduced. Cathodic

inhibitors impede the cathodic reaction. Mixed inhibitors hinder both reactions. The performance of an inhibitor can be asserted by its effectiveness in reducing the corrosion rate.

Numerous organic compounds have been found to be effective as inhibitors [77] by adsorbing on the electrode surfaces. The adsorption may be electrostatic or by chemisorption. It has been found that most of the inhibitors have Oxygen, Nitrogen or Sulphur in their structure which will donate electrons for bonding with the metal surface.

Electrostatic adsorption depends on the potential of zero charge (pzc) of the metal surface and the position of corrosion potential with respect to pzc . The adsorption of organic inhibitor depends on the sign and magnitude of the corrosion potential and on the sign of the charge on the inhibitor molecule. Adsorption of cationic compounds requires a negative potential whereas a positive potential is required for adsorption of anionic compounds.

Chemisorption of an organic molecule involves a bonding between the metal and the inhibitor. It depends on the nature of the metal, the molecular structure of the inhibitor and the chemical nature of the bonding atom. In addition factors such as lattice parameters of the metal and inter atomic distance between two or more bonding atoms in the inhibitor molecule are important factors in chemisorption.

1.9 Nature of inhibition of corrosion:

Inhibitors can affect the corrosion reaction of the metal in several ways.

1.9.1 Formation of a diffusion barrier:

The adsorbed inhibitor may form a surface film which acts as a physical barrier to restrict the diffusion of ions or molecules to or from the metal surface thus retarding the corrosion reaction. This effect occurs particularly when the inhibitor species are large molecules e.g. gelatine, agar-agar etc. Similar effects

also occur when the inhibitor can undergo reaction to form a polymeric film on the surface.e.g. acetylinic compounds and sulphoxides.

1.9.2 Blocking of reactive sites:

The interaction of adsorbed inhibitor with surface metal atoms may prevent these metal atoms from participating in either the anodic or cathodic reactions of corrosion. This blocking effect decreases the number of surface metal atoms at which these reactions can occur, and hence the rates of these reactions decrease in proportion to the extent of adsorption. The mechanism of the reactions is not affected. The Tafel slopes of the polarisation curve remain unchanged. Behaviour of this type is observed for iron in sulphuric acid solutions containing 2-6 dimethyl quinoline, β naphtha quinoline and aliphatic sulphides.

1.9.3 Participation in the electrode reaction:

The electrode reactions of corrosion involve the formation of adsorbed intermediate species with the surface metal atoms e.g. adsorbed hydrogen atoms in the hydrogen evolution reaction. The presence of adsorbed inhibitors will interfere with the formation of these adsorbed intermediates and hence the electrode processes may then proceed by alternative paths through intermediates containing the inhibitor e.g. phenyl thiourea, benzaldehyde.

The adsorbed inhibitor may also influence the corrosion reaction by increasing the separation between the reaction zone and the electrode surface and by changing the potential distribution in the double layer.

1.10 Study of azoles as corrosion inhibitors:

Heterocyclic compounds such as Benzotriazole (BTA), Mercaptobenzothiazole (MBT) etc. are well known inhibitors of the corrosion of copper. All these azoles contain nitrogen atoms, and they coordinate with Cu (0), Cu(1) or Cu(2) through the lone pair of electrons to form certain complexes. These complexes

are generally believed to be polymeric in nature and form an adherent protective film on the copper surface which acts as a barrier to aggressive ions such as chloride. The inhibitor action of these compounds may also be due to their chemisorption on the copper surface.

Aruchamy et al. [81] using SERS find that in the case of BTA the inhibition action is found to be due to the substitution of hydrogen of the $-NH$ group of BTA and the formation of coordination links with the lone pair of electrons on one of the nitrogen atoms. For MBT a water insoluble thin polymeric film of $Cu(I)+MBT$ is formed on the surface by a surface reaction of the $Cu(I)$ ion with adsorbed MBT and this film acts as a barrier against corrosive environment. Several surface analytical techniques such as IRRAS, XPS and SERS have been employed to investigate the process of reaction of these azoles on a copper surface.

Weaver et al [82] studied the adsorption of Benzotriazole (BTA) on copper using SERS as a function of solvent, pH and electrode potential in order to examine the adsorbate species, surface bonding and the potential dependent onset of $Cu-BTA$ film formation. They find that in acidic media at $pH > 1$, the monoprotonated acid $BTAH$ constitutes the predominant adsorbate, being replaced by the diprotonated $BTAH_2^+$ species by $pH 0$ and the basic BTA^- form in alkaline electrolytes. Insight into the adsorbate molecular geometry and mode of surface attachment is obtained by examining the adsorption induced alterations in frequency, bandwidth and relative intensity of the various benzotriazole ring modes. The SERS spectral features for $BTAH$ and BTA^- suggest that surface attachment is *via* a pair of triazole nitrogens with a tilted or vertical orientation. The transformation from adsorbed benzotriazole to a $Cu(I)-BTA$ film at higher potentials is readily diagnosed from the SERS spectra. They also study the structure of benzotriazole films in air. They find that a $Cu(I)-BTA$ layer is formed via a coupled oxygen induced electrochemical pathway.

Aramaki et al [83] studied the inhibition mechanism of BTA and its 5-methyl, 5-chloro and 5-nitro derivatives for copper corrosion in sulphate

solutions at several values of pH by impedance and SERS technique. All benzotriazoles were found to readily form protective films of the respective complex polymers with Cu(I) ion at high pH ; and they chemisorb on the copper surface at low pH. Poling [84] carried out infrared reflectance studies of benzotriazole on copper which indicated the formation of a highly inert Cu benzotriazole polymer. The spectra also indicated that such films continue to grow beyond the chemisorbed monolayer stage to form films upto several Å⁰ thick. The mechanism for growth of Cu-BTA films beyond the chemisorbed monolayer involves transport of Cu ions through the surface films which then react with physically adsorbed BTA molecules to precipitate insoluble Cu-BTA complex on the film surface. Polarisation curves showed that the Cu –BTA films act as physical barrier layers. These barriers markedly inhibit both the anodic and cathodic corrosion reactions in neutral, aerated or deaerated solutions. Infra red reflectance studies of films formed on copper by imidazole and benzimidazole showed that in both cases Cu replaced the protons on the >N-H groups during film formation.

Chadwick et al. [85] carried out X-ray photoelectron spectroscopy (XPS) studies on surface films formed by adsorption of BTA on copper and copper alloys in NaCl solution. It is found that on both copper and copper-nickel alloys, benzotriazole forms a Cu(I)-BTA surface complex. It is also found that the presence of Cu₂O facilitates formation of surface film. Ohsawa et al. [86] studied the mechanism of corrosion inhibition of Cu by Mercaptobenzothiazole (MBT) using UV visible reflection spectra, Infra red reflection and XPS on potentiostatically polarised Cu electrodes. The UV – visible reflection spectra of potentiostatically polarised Cu electrodes observed in- situ, showed that a water insoluble film of Cu(I)-MBT forms on the surface which inhibits the corrosion of the metal. Infra red spectra of Cu(I)-MBT indicate that MBT coordinates to cuprous ion through S (=C) atom and forms a S-bridged polymeric complex. Modestov et al [87] studied the electrochemical behaviour of copper electrodes in alkaline solutions containing Benzotriazole, 6-tolyl triazole and 1-(2,3-dicarboxypropyl)-benzotriazole by

photocurrent response method and intensity modulated photocurrent spectroscopy. The photocurrent observed from a Cu electrode in 0.1M NaOH solution where the electrode surface was covered with Cu_2O was the result of the recombination of the photoexcited electrons through the photoreduction of Cu^+ ions which was then followed by a dark oxidation. In the case where both Cu_2O and CuO were present on the electrode surface, the photocurrent was attributed to the photoreduction of CuO as well as the recombination process mentioned above. Chemisorption of the corrosion inhibitor BTA, 6-TTA on the Cu electrodes in 0.1M NaOH with the formation of multilayers such as $\text{Cu/Cu}_2\text{O/Cu(1)-BTA}$ significantly decreases the photocurrent caused by the photoexcitation of electrons in Cu_2O . This is ascribed to a lack of unbonded Cu^+ ions at the $\text{Cu}_2\text{O/}$ chemisorbed inhibitor interface. The ability of the inhibitors in decreasing the photocurrent in the system correlates with their inhibition efficiency for Cu corrosion. The presence of inhibitors on the surface of Cu electrode prevents electrochemical reduction of Cu_2O layer at negative potentials.

They also studied Cu electrode behaviour in Cl^- and benzotriazole containing acidic or neutral solutions by voltammetry, photocurrent response, impedance measurements and chemical analysis of BTA content [88]. It was observed that the rate of formation of Cu-BTA films in acidic solution is controlled by the transport of CuCl_2^{-1} ions through the pores in the film at an early stage of film formation and later by the volume diffusion rate in the film. The photocurrent measurements revealed that Cu-BTA formation is accompanied by simultaneous deposition of a Cu_2O underlayer. The main portion of the polarisation resistance of the passive layer was ascribed to the Cu_2O underlayer. They proposed that the role of the Cu-BTA overlayer is to stabilise the Cu_2O underlayer and maintain its high resistance by preventing it from being doped by Cl^- ions resulting in the formation of solid CuCl on top of Cu_2O .

Perrin et al. [89] prepared an insulating film using 2-MBT on copper surface by oxidising it in alkaline water-metlanol solutions. The film formed

on the surface was investigated using voltammetric experiments, elemental analysis, infrared spectroscopy and mass spectroscopy. Boden et al. [90] made measurements on the adsorption isotherm of BTA on copper. It showed that the inhibitor molecule is weakly held on the oxide covered surface until a critical solution concentration of BTA is reached above which good corrosion inhibition results. The chemical nature of the complexes formed were found by XPS to correspond closely to Cu(1)-BTA. Han et al. [91] studied the corrosion behaviour of copper with various organic inhibitors in aerated solutions. The inhibitors studied included benzotriazole, hydroxy benzophenoximes, L-hydroxy-5-nonyl acetophenone oxime and sodium octyl hydroxamate. BTA was shown to be most effective of the inhibitors tested. The morphology of the copper substrate after corrosion in the presence and absence of BTA was examined using Scanning electron microscopy (SEM). FTIR was used to identify the spectra of the adsorbed complex. The surface film was identified as a polymeric Cu(1)-BTA complex that totally covered the copper surface, exhibiting strong corrosion inhibition. The formation of Cu(1)-BTA was found to have been accomplished after the adsorption of BTA on the copper surface.

McCorry-joy et al [92] used cyclic voltammetry and chronocoulometry to study the anodic oxidation of copper in acetate buffered media, and the effect of pretreatment of copper surface by immersion in azole solutions on the anodic reactions. They compared the effects of Benzotriazole (BTA), Imidazole (IMD) and Benzimidazole (BIMD) on the inhibition of the anodic reaction of copper. It was found that the degree of inhibition of anodic oxidation reaction produced by azole pretreatment decreases in the order BTA > BIMD – IMD.

Ito et al. [93] used polarisation modulated infrared reflection absorption spectroscopy to measure the infra red spectra of surface films on copper grown in methanol or aqueous solutions containing benzotriazole. They find that the surface protective films prepared in methanol containing benzotriazole are composed of infinite chains in which the Cu-BTA complex is connected by strong charge transfer interactions between benzotriazole molecules. The

polymer structure of the film grown in aqueous solution also resembles the former structure except for a small difference of the triazole five membered ring. BTA-BTA charge transfer interactions are important in forming a tight, inert and infinite polymer sheet parallel to the surface. The Cu-BTA film grows in proportion with time if copper ions and BTA are fully supplied.

Bohn et al. [94] have studied the adsorption of BTA on Cu_2O and CuO surfaces from a variety of aqueous and non aqueous solutions using XPS, Auger electron spectroscopy (AES) and transmission UV measurements. At solution concentrations of $\text{BTA} < 5 \times 10^{-3} \text{ M}$ a chemisorbed layer is formed on both surfaces within 500 seconds. They consider two possible structural models: 1) An adsorbed monolayer of pure BTA. 2) A thicker mixed Cu-BTA layer. AES and XPS studies show that at low concentrations of BTA (0.1 mM – 5 mM) and short adsorption times a single layer of BTA is formed on copper oxide surfaces. Comparison of solution and adsorbed UV band structures indicate the dissociation of BTA into BTA' and H^+ upon adsorption.

Brusic et al [95] studied the capacity of BTA to provide a protective and stable surface film on copper surface. They characterised the film by electrochemical techniques, *in situ* ellipsometry, *ex situ* time of flight static secondary ion mass spectrometry, high temperature mass spectrometry etc. They find that the spontaneous reaction of Cu and BTA leads to the formation of Cu-BTA with copper being in the Cu^{+1} state. The formation of a Cu-N bond could be clearly identified from the Cu LMM Auger lines. The film could be formed on both an oxidised and oxide free Cu surface, in contrast to other reports suggesting that the presence of Cu_2O is a prerequisite for the buildup of Cu-BTA. Under oxidising conditions the growth of a three dimensional Cu-BTA film was shown to proceed by a logarithmic or parabolic growth law. The protectiveness of the film is found to be proportional to the degree of polymerisation. The build up of a polymerised network of BTA-Cu chains is more strongly favoured on an oxidised copper surface, in solutions in which the Cu oxides are stable. They also find that once the film is formed on the surface

it provides very effective and durable protection even in an environment without BTA.

Fleischmann et al [96,97] studied the synergetic inhibition of copper corrosion by BTA and Benzyl amine (BZA) in chloride and cyanide media by voltammetric and ac impedance measurements. BZA enhances the performance of the strong inhibitor BTA by accelerating the growth of a protective surface layer; used alone BZA is ineffective as an inhibitor. The competitive adsorption of aggressive anions and inhibitors is studied by Surface enhanced Raman scattering (SERS). The dramatic increase in corrosion caused by low concentrations of cyanide ions is shown to be due to the displacement of BTA from the copper electrode surface. Fleischmann et al. also studied the efficiency of four selected corrosion inhibitors (Benzotriazole, 1-Hydroxybenzotriazole, Benzimidazole and 2-mercaptobenzoxazole) for the corrosion inhibitor of copper in aqueous chloride media using electrochemical and SERS techniques. They found that to a first approximation the rate of loss of SERS intensity at open circuit is related to the rate of corrosion. A competitive adsorption of halide and corrosion inhibitors as well as of mixtures of inhibitors is observed. BTA and 2-Mercaptobenzoxazole are found to exclude the aggressive chloride ion from the surface.

Babic et al. [98] studied the electrochemical behaviour of Cu and Cu-10Ni alloy in 1M sodium acetate solution (pH 5.8) in the presence of benzotriazole by cyclic voltammetry, photopotential measurements and impedance spectroscopy. Polarisation and impedance studies showed that BTA forms a multilayer structure Cu/Cu₂O-Cu(1)-BTA on the electrode surface at higher concentration of the inhibitor (>1 mM) and at longer immersion time. At lower inhibitor concentration and shorter immersion time molecules of the inhibitor are adsorbed chemically on the electrode surface. Photopotential measurements showed that the surface layer formed on Cu in the presence of BTA is stoichiometric.

We find from literature that the electrochemistry of corrosion of copper in alkaline medium in the presence of azoles has not been studied in detail. In

this work, we have carried out electrochemical studies to investigate the adsorption properties and relative inhibition efficiency of different azoles like Benzotriazole, Mercaptobenzothiazole, Benzimidazole, Mercaptobenzimidazole, Imidazole and Tetrazole on the corrosion of copper in 0.1 M NaOH. Our choice of alkaline medium is dictated by the fact that copper exhibits well defined voltammetric characteristics in NaOH and this facilitates quantitative estimation of the effect of addition of inhibitors in this medium. We have employed cyclic voltammetry and electrochemical impedance spectroscopy to characterise these systems.

REFERENCES

1. Abraham Ulman *Chemical Reviews* 96 (1996) 1533-1554.
2. A. Ulman *An introduction to ultrathin organic films*, Academic Press: San Diego, 1991.
3. G.L.Gaines *Insoluble monolayers at Gas-Liquid interfaces*, Interscience Publishers, New York 1966.
4. G.G.Roberts, *Langmuir-Blodgett films*, Plenum Press New York 1990
5. E.E.Polymeropoulos, J.Sagiv *J.Chem Phys.* 69 (1978) 1836.
6. J.Sagiv *J.Am.Chem..Soc.* 102 (1980) 2.
7. J.Sagiv *Israel J. Chem* 18 (1979) 339.
8. J.Sagiv *Israel J.Chem* 18 (1979) 346.
9. L.H.Dubois, B.R.Zegaski, R.G.Nuzzo *Proc. Natl. Acad. Sci. U.S.A.* 84 (1987) 4739.
10. L.H.Dubois, B.R.Zegarski, R.G.Nuzzo *J.Am. Chem. Soc.* 112 (1990) 570.
11. K.R.Stewart, G.M.Whitesides, H.P.Godfried, I.F.Silvera *Surface Science* 57 (1986) 1381.
12. R.G.Nuzzo, E.M.Korenic, L.H.Dubois *J.Chem.Phys.* 93 (1990) 767.
13. R.G.Nuzzo, D.L.Allara *J.Am.Chem.Soc.* 105 (1983) 4481.
14. Y.Golan, L.Margulis, I.Rubinstein *Surface Science* 264 (1992) 312.
15. C.A.Widrig, C.Chung, M.D.Porter *J.ElectroanaChem.* 310 (1991) 335.
16. S.D.Evans, K.E.Goppert-Bearducci, E.Urankar, L.J.Gerenser, A.Ulman *Langmuir* 7 (1991) 2700.
17. E.B.Troughton, C.D.Bain, G.M.Whitesides, R.G.Nuzzo, D.L.Allara, M.D.Porter *Langmuir* 4 (1988) 365.
18. C.D.Bain, E.B.Troughton, Y.T.Tao, J.Evall, G.M.Whitesides, R.G.Nuzzo *J.Am.Chem.Soc.* 111 (1989) 321.
19. H.A.Biebuyck, C.D.Bain, G.M.Whitesides *Langmuir* 10 (1994) 1825.
20. C.J.Zhong, M.D.Porter *J.Am.Chem.Soc.* 116 (1994) 11616.

21. M.M.Walczak, C.Chung, S.M.Stole, C.A.Widrig, M.D.Porter *J.Am.Chem.Soc.* 113 (1991) 2370.
22. P.E.Laibinis, M.A.Fox, J.P.Folkers, G.M.Whitesides *Langmuir* 7 (1991) 3167.
23. S.C.Chang, I.Chao, Y.T.Tao *J.Am.Chem.Soc.* 116 (1994) 6792.
24. R.L.Sobocinski, M.A.Bryant, J.E.Pemberton *J. Am. Chem. Soc.* 112 (1990) 6177.
25. M.A.Bryant, J.E.Pemberton *J. Am. Chem. Soc.* 113 (1991) 8284.
26. M.A.Bryant, J.E.Pemberton *J.Am. Chem. Soc.* 113 (1991) 3629.
27. P.E.Laibinis, C.D.Bain, G.M.Whitesides *J.Phys.Chem.* 95 (1991) 7017.
28. P.E.Laibinis, G.M.Whitesides *J.Am.Chem.Soc.* 114 (1992) 1990.
29. L.H.Dubois, R.G.Nuzzo *Annual Reviews of Physical Chemistry* 43 (1992) 437.
30. C.D.Bain, G.M.Whitesides *Science* 240 (1988) 62.
31. M.D.Porter, T.B.Bright, D.Allara, C.E.D.Chidsey *J.Am.Chem.Soc.* 109 (1987) 3559.
32. C.E.D.Chidsey, D.N.Loiacono *Langmuir* 6 (1990) 682.
33. L.H.Dubois, B.R.Zegarski, R.G.Nuzzo *J.Chem.Phys.* 98 (1993) 678.
34. R.G.Nuzzo, E.M.Korenic, L.H.Dubois *J.Chem.Phys.* 93 (1990) 767.
35. C.J.Sandroff, S.Garoff, K.P.Leung *Chem.Phys.Lett.* 96 (1983) 547.
36. R.M.A.Azzam and N.M.Bashara *Ellipsometry and polarised light*, North-Holland, New York 1987.
37. C.J.Miller, P.Cuendet, M.Gratzel *J.Phys.Chem.* 95 (1991) 877.
38. H.O.Finklea, D.A.Snider, J.Fedyk *Langmuir* 6 (1990) 371.
39. S.D.Evans, A.Ulman *Chem.Phys.Lett.* 170 (1990) 462.
40. J.G.Gordon II, J.D.Swalen *Optics Communications* 22 (1977) 374.
41. L.Haussling, H.Ringsdorf, F.J.Schmitt, W.Knoll *Langmuir* 7 (1991) 1837.
42. F.J.Schmitt, L.Haussling, H.Ringsdorf, W.Knoll *Thin Solid Films* 210/211 (1992) 815.
43. C.Pale-Grosmange, E.S.Simon, K.L.Prime, G.M.Whitesides *J. Am.Chem.Soc.* 113 (1991) 12.

44. P.E.Laibinis, G.M.Whitesides *J.Am.Chem.Soc.* 114 (1992) 1990.
45. R.Losch, M.Stratmann, H.Viefhaus *Electrochim Acta* 39 (1994) 1215.
46. C.D.Bain, H.A.Biebuyck, G.M.Whitesides *Langmuir* 5 (1989) 723.
47. L.Strong, G.M.Whitesides *Langmuir* 4 (1988) 546.
48. L.H.Dubois, B.R.Zegarski, R.G.Nuzzo *J.Chem.Phys.* 98 (1993) 678.
49. C.E.D.Chidsey, G.Y.Liu, P.Rowntree, G.Scoles *J.Chem.Phys.* 91 (1989) 4421.
50. N.Camillone, C.E.D.Chidsey, P.Eisenberger, P.Fenter, J.Li, K.S.Liang, G.Y.Liu, G.Scoles *J.Chem Phys.* 99 (1993) 744.
51. G.Hahner, Ch.Woll, M.Buck, M.Grunze *Langmuir* 9 (1993) 1955.
52. C.A.Widrig, C.A.Alves, M.D.Porter *J.Am.Chem.Soc.* 113 (1991) 2807.
53. Y.T.Kim, R.L.McCarley, A.J.Bard. *J.Phys.Chem.* 96 (1992) 7416.
54. L.Haussling, B.Michel, H.Ringsdorf, H.Rohrer *Angew. Chem. Intl. Ed. Engl.* 30 (1991) 569.
55. L.Sun, R.M.Crooks *J.Electrochem Soc.* 138 (1991) L23.
56. R.M.Crooks, C.Xu, L.Sun, S.L.Hill, A.J.Ricco *Spectroscopy* 8 (1993) 28.
57. J.W.Grate, S.J.Martin, R.M.White *Anal.Chem.* 65 (1993) 940 A and 987A.
58. D.A.Buttry, M.D.Ward *Chem. Rev.* 92 (1992) 1355.
59. H.C.De Long, D.A.Buttry *Langmuir* 8 (1992) 2491.
60. C.E.D.Chidsey, D.N.Loiacono *Langmuir* 6 (1990) 682.
61. C.A.Widrig, C.A.Alves, M.D.Porter *J.Am.Chem.Soc.* 113 (1991) 2805.
62. A.Ulman, J.E.Eilers, N.Tillman *Langmuir* 5 (1989) 1147.
63. B.Wunderlich *Macromolecular Physics* Vol.1 1973. New York Academic.
64. M.D.Porter, T.B.Bright, D.L.Allara and C.E.D.Chidsey *J.Am.Chem.Soc.* 109 (1987) 3559.
65. R.G.Nuzzo, L.H.Dubois and D.L.Allara *J.Am.Chem.Soc.* 112 (1990) 558.
66. H.O.Finklea in *Electroanalytical Chemistry*, Marcel Dekker, New York 1996 Vol.19 pp.105 – 335.
67. C.J.Miller, P.Cuendet and M.Gratzel *J.Phys.Chem.* 95 (1991) 877.
68. E.Sabatini, I.Rubinstein *J.Phys.Chem.* 91 (1987) 6663.

69. M.M.Walczak, D.D.Popence, R.S.Deinhammer, B.D.Lamp, C.Chung and M.D.Porter *Langmuir* 7 (1991) 2687.
70. C.A.Widrig, C.Chung and M.D.Porter *J.Electroanal.Chem.* 310 (1991) 335.
71. C.J.Zhong, M.D.Porter *J.Am.Chem.Soc.* 116 (1994) 11616.
72. D.E.Weisshaar, M.M.Walczak and M.D.Porter *Langmuir* 9 (1993) 323.
73. M.D.Porter, T.B.Bright, D.Allara and C.E.D.Chidsey *J.Am.Chem.Soc.* 109 (1987) 3559.
74. A.J.Bard and L.R.Faulkner *Electrochemical methods – Fundamentals and applications* Wiley, New York 1980 p.508.
75. S.Steinberg, Y.Tor, A.Shanzer and I.Rubinstein *Organic Thin Films and Surfaces* (A.Ulman ed.) Academic Press, New York 1995 p183.
76. E.Sabatini, I.Rubinstein, R.Maoz and J.Sagiv *J.Electroanal.Chem.* 219 (1987) 365.
77. M.G.Fontana and R.W.Staehle(Editors) Volume1 *Advances in corrosion science and technology* Plenum Press New York – London 1970.
78. J.O'M.Bockris and A.K.N.Reddy *Modern Electrochemistry* Vol.2, p 682, Plenum Press, New York (1970).
79. C.Wagner, W.Traud *Z.Elektrochem.* 44 (1938), 391.
80. U.R.Evans *An Introduction to metallic corrosion*, Edward Arnold (London) 1963.
81. A.Aruchamy, A.Fujishima, A.Ibrahim, B.H.Loo *J.Electroanal. Chem.* 281 (1990) 299-304.
82. Ho Yeung H. Chan, M.Weaver *Langmuir* 15 (1999) 3348-3355.
83. K.Aramaki, T.Kiuchi, T.Sumiyoshi, H.Nishihara *Corrosion Science* Vol.32, No.5/6, (1991) 593-607.
84. G.W.Poling *Corrosion Science* 10 (1970) 359-370.
85. D.Chadwick, T.Hashemi *Corrosion Science* 18 (1978) 39-51.
86. M.Ohsawa, W.Suetaka. *Corrosion Science* 19, (1979) 709-722.
87. A.D.Modestov, Guo-Ding Zhou, Hong-Hua Ge, B.H.Loo *J. Electroanal. Chem.* 375 (1994) 293-299.

88. A.D.Modestov,G.D.Zhou,Y.P.Wu,T.Notoya,D.P.Schweinsberg *Corrosion Science* Vol.36, No.11, (1994), 1931-1946.
89. F.X.Perrin, J.Pagetti *Corrosion Science* Vol.40 No.10 (1998) 1647-1662.
90. P.G.Fox, G.Lewis, P.J.Boden *Corrosion Science* 19 (1979) 457-467.
91. Y.Ling, Y.Guan, K.N.Han *Corrosion Science* Vol.51 No.5 (1995) 367-375.
92. C.McCrory-Joy, J.M.Rosamilia *J. Electroanal Chem.* 136,(1982),105-118.
93. M.Ito, M.Takahashi *Surface Science* 158 (1985) 609-615.
94. Zhi Xu, Sharon Lau, P.W.Bohn *Langmuir* 9 (1993) 993-1000.
95. V.Brusic, M.A.Frisch, B.N.Eldridge, F.P.Novak, F.B.Kaufmann, B.M.Rush, G.S.Frankel *J. Electrochemical Soc* Vol.138, No.8, (1991) 2253-2259.
96. M.Fleischmann, G.Mengoli, M.M.Musiani, C.Pagura *Electrochimica Acta* Vol.30, No.12, (1985) 1591-1602.
97. M.Fleischmann, I.R.Hill, G.Mengoli, M.M.Musiani, J.Akhavan *Electrochimica Acta* Vol.30, No.7 (1985) 879-888.
98. R.Babic, M.Metikos-Hukovic, M.Loncar *Electrochimica Acta.* 44 (1999) 2413-2421.