STUDIES ON ADSORPTION OF AZOLES AND ALKANETHIOLS ONTO SOME ELECTRODE SURFACES

by

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Thesis submitted to Bangalore University for the award of the degree of Doctor of Philosophy



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CERTIFICATE

I certify that this thesis has been composed by Mr. R.Subramanian based on the investigations carried out by him at the Raman Research Institute Bangalore – 560080, under my supervision. The subject matter of this thesis has not previously formed the basis of the award of any Degree, Diploma, Associateship, Fellowship or any other similar title.

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DECLARATION

I hereby declare that the entire work embodied in this thesis is the result of the investigations carried out by me independently at the Raman Research Institute, Bangalore – 560080, and that no part of it has been submitted for the award of any Degree, Diploma, Associateship or any other similar title.

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PREFACE

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.

Chapter 1 is divided into two parts. The first part provides a general introduction to the topic of 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 compound in a solvent. There are different types of self assembly methods that yield organic monolayers. Normally, SAMs of alkanethiols on gold can be formed by simply immersing the gold substrate into the solution containing alkanethiol molecules. In this section, after describing the method of preparation of SAMs, various techniques which have been used for characterising self assembled monolayers on gold are presented. These include contact angle measurement, Infrared & Raman spectroscopy, photoelectron spectroscopy, x-ray diffraction, scanning tunneling and atomic force microscopy and electrochemistry. It is found that the alkanethiols possess a high degree of order and stability. The monolayer forms a ($\sqrt{3} \times \sqrt{3}$) R30[°] overlay structure with the underlying Au (111) substrate. The alkyl chains are tilted by approximately 30^{0} from the surface in order to maximise their Van der Waals interactions.

Since self assembled monolayers of alkanethiols can be formed on metal surfaces, the same metal can be used as the working electrode and SAMs characterised by electrochemical techniques. A measure of the degree of packing of the SAM on the gold electrode can be obtained by comparing its dielectric constant calculated from electrode capacitance.

The second part of the chapter deals with the corrosion inhibition of copper by heterocyclic compounds (azoles). The fundamentals of the process of corrosion are described. Organic compounds containing nitrogen or sulphur can effectively inhibit the corrosion reaction of copper. This is due to the chemisorption of the organic molecule onto the metal surface. Chemisorption of an organic molecule involves bonding between the metal and the inhibitor. There are various mechanisms by which an inhibitor can affect the corrosion of the metal.

The second chapter explains the details of the experimental set up used to carry out the experiments. The electrochemical cell which has been designed and fabricated is described here which is followed by different surface pretreatments employed in the preparation of the working electrode. A detailed description of the different experimental techniques used in our study such as cyclic voltammetry, electrochemical impedance spectroscopy, scanning tunneling microscopy is given.

Chapter 3 describes the study of the inhibition of copper corrosion in alkaline medium by azoles. Heterocyclic compounds such as Benzotriazole (BTA), Mercaptobenzothiazole (MBT) etc. act as inhibitors of the corrosion of copper. All these azoles contain nitrogen and/or sulphur atoms, and they coordinate with Cu(0), Cu(1) or Cu(2) through their lone pair of electrons. We have carried out electrochemical studies to investigate the adsorption properties and relative inhibition efficiency of different azoles such as Benzotriazole, Mercaptobenzothiazole, Benzimidazole, Mercaptobenzimidazole, Imidazole and Tetrazole on the corrosion of copper in 0.1 M NaOH. Copper exhibits well defined voltammetric characteristics in NaOH and this facilitates quantitative estimation of the effect of addition of inhibitors in this medium. Cyclic voltammetry and electrochemical impedance spectroscopy were used to characterise these systems. The influence exerted by concentration on their inhibiting efficiency has also been considered.

The cyclic voltammogram of copper in 0.1N NaOH solution shows three anodic and two cathodic peaks. The inhibitors reduce the corrosion rate of copper by adsorbing on the electrode surface and reducing the corrosion current i_{corr} . Addition of inhibitor leads to a reduction of charge measured from the cyclic voltammetric curve from which the surface coverage θ is calculated. We find that as the concentration of the inhibitor increases the current and consequently the charge under the oxidation-reduction curves progressively reduces. From impedance studies we can calculate the charge transfer resistance and double layer capacitance after adsorption of the azoles on copper. We find that all the azoles decrease the double layer capacitance and increase the charge transfer resistance of the interface to different extents depending on the nature of adsorption. In alkaline medium the azoles tend to from polymeric complexes by reacting with copper.

The adsorption of azoles onto copper in alkaline medium can be described by the Langmuir adsorption isotherm based on the variation of surface coverage θ with concentration c. The equilibrium constant k and free energy of adsorption AG can then be calculated from the plot of $\frac{c}{\theta}$ versus c. A relative comparison of the inhibition power of the different azoles studied can be obtained from the values of charge transfer resistance, double layer capacitance, equilibrium constant and free energy values measured. Based on these values the inhibition efficiency of the different azoles towards corrosion of copper in 0.1 M NaOH solution is of the order

$MBT > BIMD \approx MBIMD > BTA \approx IMD$

Chapter 4 deals with the effect of surface pretreatment on the adsorption properties of alkanethiols on gold, silver and copper. An understanding of the various factors that govern the formation, structure and properties of self assembled monolayers is important in the study of various interfacial phenomena. An important attribute of SAMs that has proved difficult to characterise is the defect sites. A small number of defect sites can have a major impact on the behaviour of the monolayer. One of the macroscopic properties of a monolayer that correlates with defectiveness is permeability; monolayers that are more permeable to small molecules eg. solvent, ions and electroactive solutes are more defective than monolayers that are not permeable to such species. We are interested in finding out the role of surface pretreatment in influencing the barrier properties of the monolayer. We have investigated the structural stability of octadecanethiol monolayer formed on polycrystalline gold subjected to the following kind of pretreatments: Mechanical polishing, Chemical etching, Electropolishing, Electrochemical formation of surface oxide and Evaporated gold on mica.

The effect of mechanical polishing is studied by gradually varying the particle size of the polishing materials. The topography of the substrate is thus changed in a controlled manner during each treatment. The blocking nature of the self assembled monolayer on the metal electrodes is determined by the cyclic voltammetry of the respective metal oxidation and reduction reaction in alkaline media. This method is used in characterising the films because the oxide stripping current affords a quick assessment of the area fraction of the pinholes since the oxidation of the metal can only occur if the redox species (hydroxyl ions in this case) can reach the electrode surface, through the pinholes. Also all the three metals studied exhibit well defined and reproducible oxidation-reduction peaks in alkaline media.

The cyclic voltammograms of octadecanethiol modified gold, silver and copper electrodes in 0.1 M NaOH for different surface treatments and roughness show marked decrease in the peak heights in all the cases *vis-a-vis* the respective bare electrode due to the physical barrier formed by the octadecanethiol monolayer that inhibits the electron transfer reaction. Measurement of charge involved in the redox reaction, by integrating the voltammetric peaks provide an

estimate of the extent of electrochemical reaction taking place on the surface. We find that the integrated charge measured on the octadecanethiol adsorbed substrate increases quite significantly with the decreasing particle size of the abrasive used for polishing. This shows that a surface roughened with 17 μ m emery blocks the charge transfer reaction more effectively than a surface treated with a 0.05 μ m alumina particles. Thus the surface polished with 0.05 μ m alumina is least effective as a barrier for faradic reaction compared with the one with 800 grit emery (17 pm). This clearly establishes a direct correspondence between the efficiency of the barrier film and the surface roughness.

We find that the increase in the roughness factor from the smoothest (0.05 μ m) polishing material to the coarsest (17 μ m particle emery) is only to the extent of 25%. The large increase in the barrier capability is thus not commensurate with the increase in measured roughness factor from 1.775 to 2.204 between alumina and 800 grit emery treated surfaces.

Optical micrographs of the electrode surfaces reveal that the macroscopic roughness increases gradually with the particle size of the polishing material. Scanning tunneling microscopy which probes the surface at the nanometer scale shows that at 200nm x 200nm range a gold surface after polishing with 0.05 μ m alumina, which appears smooth and bright visually through the optical microscope is granular with several nanometer level corrugations. Each such region is approximately 30nm in height and 60-80nm in diameter. The surface treated with 17 μ m particle emery is on the other hand surprisingly smooth on the same scale without similar regions of roughness and steps of comparable size in contrast to its macroscopic roughness. While at larger scales, the 17 μ m particle treated surface is rougher than the 0.05 μ m alumina treated surface, the situation is reversed on a much smaller scale.

We can infer that the defects are predominantly formed on the surface corrugation regions. These regions, which are present in large numbers on the alumina polished surface allow the redox species (hydroxyl ions in this case) to reach the electrode surface. The larger sized particles on the other hand create a smooth surface resulting in much less number of corrugations. Consequently this results in a lesser number of defect sites on such a surface which is reflected in lower charge values and hence better coverage.

It is found that a chemically etched surface shows the best barrier properties compared to all the other surface pretreatments even though it is rougher than 17μ m treated surface at the nanometer scale. We feel that the reason for this behavior lies in the fact that a chemically treated surface exposes a fresh pristine surface free from any surface contaminations and the monolayer formed on such a surface exhibits excellent blocking ability.

Impedance studies of Silver in 0.1N NaOH held at oxidation potential also show that the charge transfer resistance R_{ct} which is a measure of barrier efficiency varies as a function of surface pretreatment.

Our results clearly indicate that there exists a direct correlation between surface roughness and barrier efficiency. We also find that alkanethiols can form an effective monolayer even on oxidised metal substrates.

Chapter 5 deals with the study of the adsorption kinetics of alkanethiols on gold. Most of the studies on self assembled monolayers of alkanethiol molecules on gold have focused on investigating the fully covered substrates and their various applications. Though the general structure and molecular orientation of SAMs are well understood and not controversial, a variety of contradictory publications exist in the literature with respect to the formation kinetics and adsorption mechanism of SAMs from solution.

In our work we have studied the adsorption kinetics using electrochemical impedance spectroscopy. Adsorption processes in electrochemical systems can be studied by the measurement of capacitance of the electrical double layer. The adsorption of alkanethiol on the gold surface leads to a reduction in the double layer capacitance from the bare value to that of the monolayer covered surface.

The variation of double layer capacitance $C_{,,}$ as a function of time during alkanethiol adsorption is thus a measure of the kinetics of the adsorption process.

The gold – electrolyte interface can be modelled as a Randles circuit with a parallel combination of double layer capacitance and charge transfer resistance in series with the uncompensated resistance. The imaginary component of impedance of the cell can be expressed as,

$$Z'' = \frac{\omega C_{dl} R_{ct}^2}{1 + \omega^2 C_{dl}^2 R_{ct}^2}$$

where R_{ct} , R_s and C, are the charge transfer resistance, uncompensated resistance and double layer capacitance respectively. $\omega = 2\pi f$ where **f** is the frequency of the applied a .c potential. In a system where $\omega^2 C_{dl}^2 R_{ct}^2 >> 1$ the imaginary part of the impedance can be approximated as,

$$Z'' = \left(\frac{1}{C_{dl}\omega}\right)$$

An alkanethiol monolayer on gold has a capacitance value of the order of $1-5 \mu F cm^{-2}$. In the absence of redox species tlie gold-SAM-electrolyte interface behaves as an ideally polarisable interface. Thus R_{cl} for this system is very large (>10⁶ Ω). By substituting these values in the above equation it can be observed that by choosing an appropriate frequency of study the double layer capacitance C_{dl} can be directly obtained by measuring the imaginary component of the impedance. We have studied the evolution of the imaginary component of the impedance as a function of time at intervals of 160 nis and at a frequency of 520 Hz to follow the adsorption process. A lock in amplifier is used for the measurement.

It is found that the adsorption is so rapid at 1mM concentration that about 40% of coverage is completed within first 480 ms after dipping the electrode (in

this case for decanethiol). Any meaningful measurement of adsorption kinetics can only be carried out at lower concentrations (< 1 mM). The adsorption kinetics have been studied at three different concentrations namely, 1, 5 and 20 µM. The data were fitted to different adsorption models to get the best fit. There are two or three distinct time constants that can be discerned depending on the concentration studied. During the first fast step about 80% to 85% of the coverage is completed; the second and third step extends for the rest of the coverage. We find that the adsorption follows diffusion controlled Langmuir kinetics at low concentrations $(5\mu M)$ and Langmuir kinetics at higher concentrations (20 μM) and above. In the case of 1mM an indirect estimate of the rate of adsorption can be made. Since 40% of coverage is completed in a duration of 480 ms (within 3 sampling points) this corresponds to a rate constant k of 2.2 s⁻¹. The adsorption is found to follow Langmuir kinetics. This behaviour is true of all the five alkanethiols studied in this work. It is observed that the measured rate constant is not particularly dependent on the chain length of the alkanethiol. In the case of 1µM concentration we find that the adsorption is purely diffusion controlled in the initial stages following which it follows diffusion controlled Langmuir kinetics. For decanethiol the plot of rate constant with concentration is found to be linear yielding a value of $2980 M^{-1} s^{-1}$ for the concentration independent rate constant k_c . The plot of final capacitance versus inverse of the monolayer thickness yields a straight line from the slope of which a dielectric constant value of 2.21 is obtained which matches closely with that of bulk polyethylene suggesting that the monolayer is closely packed.

In the case of polycrystalline gold and silver surfaces we find that at $5\mu M$ concentration the coverage- time plots are found to fit well with the diffusion controlled Langmuir model. The final capacitances for the different pretreated surfaces after alkanethiol adsorption can be correlated to their real surface area.

Analysis of the second rate constants of the adsorption process indicate that they are around 4 - 5 times slower than the first rate constant. The third rate constant is in general found to be about an order of magnitude slower than the second rate constant.

A study of the capacitance of octanedithiol indicates that it is not bonded horizontally to the gold surface with both the sulphur atoms. It is likely to be bonded to gold with only one sulphur atom resulting in an upright orientation.

The study of adsorption kinetics of azoles on copper at 5mM concentration at a frequency of 1000 Hz reveals that at about 800 s more than 95% of the coverage is complete in all the cases. From the final capacitance values we find that the Benzimidazole covered copper surface has the least capacitance value whereas the Cu-BTA film shows the maximum value. These values are interpreted to correlate with the possible form of adsorbed azoles on copper.