CHAPTER-5

Study of adsorption kinetics of alkanethiols on gold:

In this chapter we discuss the kinetics of adsorption of alkanethiol molecules on gold that has been studied using electrochemical impedance spectroscopy.

5.0 Introduction:

Immersion of gold substrate in a dilute solution of alkanethiol or alkyl disulphide leads to the formation of well ordered self assembled monolayers [1-3]. Such SAMs not only provide excellent model systems to study fundamental aspects of wetting, surface reactions, adsorption, adhesion etc. but also they are promising candidates for potential applications in the fields of biosensors, biomimetics, corrosion inhibition etc. A variety of analytical techniques such as infrared spectroscopy (IR), scanning tunneling microscopy (STM), Helium atom scattering (HAS), grazing incidence x-ray diffraction (GIXD), sum frequency generation (SFG), metastable induced electron spectroscopy (MIES), atomic force microscopy (AFM), near edge X-ray absorption fine structure spectroscopy (NEXAFS), etc. have been applied in studies of these self assembled monolayers to elucidate their molecular scale structural properties. These studies have shown that the interface is composed of densely packed virtually all trans aliphatic chains that are tilted at -30° with respect to the surface normal. The films are found to have a $(\sqrt{3} \times \sqrt{3})R30^{\circ}$ overlay structure. Most SAM studies have focused on investigating the fully covered substrates and their various applications. Whereas the general structure and molecular orientation of SAMs are well understood and not controversial, a variety of contradictory publications exist concerning the formation kinetics and adsorption mechanism of SAMs from solution.

There are several techniques which have been used to study the adsorption process of alkanethiols on gold. These include measurement of mass change as reflected in the frequency shift using Quartz crystal microbalance (QCMB), measurement of contact angle, ellipsometry, reflectance absorption infrared spectroscopy, surface plasmon resonance etc. The first kinetics experiments were carried out by Bain et al. [4] who adsorbed octadecanethiol from ethanol solution with concentrations ranging from 10^{-4} to 1 mM. Using ellipsometry to measure the layer thickness they found two distinct adsorption steps. The first step in which more than 80% of the monolayer is formed is completed within minutes. The second step extends over several hours (10-20 hours) and is almost independent of concentration. Films with a thickness of one monolayer could be formed in a variety of different solvents. Bain et al. [4] proposed that, at first an imperfect partial molecular assembly forms and this relatively disordered structure reorganises in the second stage into a more perfectly ordered monolayer.

The first more quantitative kinetic study of alkanethiol adsorption from solution was done by Buck et al. [5] using second harmonic generation (SHG). The amplitude of the signal is sensitive mainly to the quantity of adsorbed sulphur atoms and the coverages well below a monolayer could be detected. The results of the experiments showed excellent agreement when compared with photoelectron spectroscopic data. In this *in situ* investigation they found the first adsorption step being consistent with a Langmuir adsorption model. They obtained a rate constant of 3300 $M^{-1} s^{-1}$. In a subsequent ex *situ* study Hahner et al. [6] used near edge X-ray absorption fine structure (NEXAFS) spectroscopy to investigate the intermediate steps in the self assembly of the long chain alkanethiol CH₃(CH₂)₂₁SH on gold surfaces. This technique is sensitive to the orientation of alkyl chains. They find that the self assembly process by which the alkanethiol molecules form well ordered monolayers on gold substrates proceeds through two steps with time constants differing by roughly two orders of magnitude. In the first step the molecules adsorb on the gold surface, replacing possible hydrocarbon

contamination and forming bonds between the terminating S atom and the gold surface atoms. They find that at this stage the alkyl chains are tangled with a very high concentration of gauche conformations. The slow second step could be identitied as an ordering process where the alkyl chains initially containing gauche defects are gradually straightened out and assume an all trans conformation. For a 3μ M C₂₂ alkanethiol solution, the time constant for sulphur adsorption (first step) was estimated to be less than 10 minutes, whereas the orientational ordering (second step) was proposed to last more than 10 hours.

After immersion of the gold substrates into air saturated ethanolic solutions of $C_{18}SH$ with concentration of 1mM for 6 days, Kim et al. [7] detected the formation of multilayers using scanning tunneling microscopy and quartz crystal microbalance (QCM). Multilayer formation was attributed to the low solubility of oxidised sulphur species in the air saturated ethanol. Ex *situ* measurements using a combination of X-ray photoelectron spectroscopy (XPS) and ellipsometry as well as Fourier transform infra red reflection absorption spectroscopy (FT-IRRAS) studies confirmed the two step mechanism first observed by Bain et al. [4].

Besides these mainly *ex situ* investigations, there have been a variety of *in situ* kinetic measurements from different solvents with conflicting results. Shimazu *et al* [8] were the first to use an electrochemical quartz crystal microbalance (EQCM) to follow the adsorption of ferrocenylundecanethiol from hexane to gold surfaces *in situ* for a concentration of 0.5 mM. They also find two adsorption steps with 40-50% of the adsorption occurring very rapidly within -10 seconds. This was followed by slow adsorption completing in about 10-100 minutes. The magnitude of the frequency shift suggested a monolayer formation. Since these first *in situ* QCM measurements, several other studies in different solvents and for a variety of alkanethiols have been conducted. In a comparative study of the adsorption of C_{18} SH from hexane and ethanol, a two step process was reported [9] for concentrations as high as 1 to 5mM which was proven independently for the adsorption from ethanol for lower concentrations. Formation

of multilayers in acetonitrile and of layers with 20% higher coverage than a monolayer in ethanol was reported. Pan et al. [10] also observe a two step process using QCMB for the adsorption of 5mM 1-Dodecanethiol and Mercaptoundecanethiol onto gold from ethanol. They find the first time constant of about 300 min⁻¹ to be more or less in agreement with that of Bain et. al. [4].

Kim et al. [11] studied the adsorption of 1mM dodecanethiol and hexadecanethiol from n-hexane and 10^{-2} mM octanethiol and dodecanethiol from ethanol solution respectively. They find that the entire adsorption time for full monolayer coverage decreases with increase in the alkyl chain length. The adsorption is found to proceed by two separate steps with octanethiol but only step adsorption process is observed with dodecanethiol and single hexadecanethiol. They observe that at the initial stages of monolayer formation octanethiol shows more rapid adsorption than dodecanethiol in ethanol solution. They conclude that short chain alkanethiols with 10 or less methylene groups form monolayers through two separate steps while longer chain alkanethiols form monolayers through thermodynamically controlled single step adsorption. The adsorption rate of alkanethiols is also found to depend on the solvent used.

Contrary to the studies summarised above, the QCM measurements of Karpovich et al. [12] did not identify a second step in the formation of SAMs of C_8SH (Octanethiol) and $C_{18}SH$ (Octadecanethiol) adsorbed from hexane and cyclohexane for concentrations varying from 10^{-2} to 1mM. They suggested the existence of an adsorption/desorption equilibrium resulting in a submonolayer coverage at concentrations of 0.1mM and below. They verified that a monolayer of alkanethiol was formed using infrared reflection spectroscopy and showed that the kinetics were adequately described by the simple reversible Langmuir adsorption model. They report that the adsorption of 0.3mM Octadecanethiol in n-hexane on polycrystalline gold surface is quite rapid with the monolayer being formed typically in 3 - 4 seconds.

Schneider and Buttry et al. [13] also studied the adsorption kinetics of alkanethiol on gold in situ using a QCM but they did so under potential control in an electrochemical cell with a background of electrolyte. The work showed that the kinetics depend strongly on the solvent. They studied the adsorption of dodecanethiol from dimethyl formamide and acetonitrile at room temperature over a broad range of bulk concentrations (10µM to 10mM) with 0.1M tetrapropylammonium perchlorate electrolyte. In acetonitrile, a multilayer of up to 15 layers formed first followed by a relatively slow (-10hours) reorganisation which eventually lead to monolayer formation. When adsorbed from dimethyl formamide at under the same conditions, no initial multilayer formation was observed, and the adsorption was much more rapid resembling that seen by Shimazu et al. [8]. Using ex situ measurements of mass loading via a QCMB, Bard et al.[14] reported results very different from those of Bain et al.[4], Shimazu et al.[8], and Karpovich and Blanchard [12]. They studied the adsorption of 1mM octadecanethiol on gold from ethanol and reported that it took -100 minutes to form monolayer and prolonged contact led to the formation of multilayers. Hu and Bard [15] examined the adsorption of a charged thiol (HSC₁₀COO⁻) on gold formed in alkaline solution of mercaptoundecanoic acid at different concentrations using atomic force microscope. This was accomplished by measuring the interfacial forces between a modified tip of the atomic force microscope and the thiol adsorbed gold surface as a function of adsorption time. They observe a two step adsorption process with the first step where the surface coverage reaches 60% of the full monolayer coverage occuring within 15 min followed by a much slower process extending up to 2-3 hours. They report that the adsorption process can be described by Langmuir kinetics. These results are 2 orders of magnitude slower than the reported values of Karpovich and Blanchard for comparable concentration of thiol.

DeBono et al. [16] used surface plasmon resonance spectroscopy to study the self assembly of short chain hexanethiol and long chain dodecane and hexadecanethiols onto polycrystalline gold surfaces. The self assembly was followed based on the observed changes in reflectivity at a fixed angle of incidence as a function of time. They reported a two step mechanism at concentrations ranging from 10 μ M to 0.1 mM. Whereas the first step gave 50 – 80% of a monolayer, the second proceeded 100 fold more slowly and led to thicknesses exceeding one monolayer. Peterlinz and Georgiadis [17] followed the self assembly of $CH_3(CH_2)_{n-1}SH$ (n = 8,12,16 and 18) onto gold surface from ethanol and heptane solutions. They studied the chain length dependent and concentration dependent kinetics of film formation in ethanol and found that there are at least three distinct kinetic steps. The kinetics of the first most rapid step and the third slowest step is described well with Langmuir adsorption models. The kinetics of the second step are of zeroeth order and depend on the alkanethiol chain length, concentration and partial film thickness. The formation kinetics in heptane was described by a single step Langmuir adsorption model. They observe that their results are most consistent with a formation mechanism involving adsorption of both chemisorbed and physisorbed molecules during film formation in ethanol with the overall formation kinetics determined by the relative solubility of the alkanethiol in the solvent.

Bensebaa et al. [18] performed ex situ FT-IRRAS kinetics study on the adsorption of docosanethiol (5 μ M) onto polycrystalline gold from ethanol solution. They concluded that immersion times of 45 seconds are sufficient to form an ordered monolayer. Decreasing the immersion time below 45 seconds gradually increases the disorder. Dannenberger et al. [19] studied the adsorption of n-alkanethiols onto polycrystalline gold in situ and in real time under a variety of experimental conditions using second harmonic generation. The chain length of the thiols studied was varied from n = 4 to 22. The influence of the thiol concentration in different solvents (ethanol, hexane, dodecane and hexadecane) was examined in the range between 9.5 and 20 μ M. After fitting the data with different kinetic models they find that only Langmuir kinetics can explain the data

irrespective of the experimental conditions. They analyse the first fast step of the formation of thiol film at different concentrations and calculate the rate constant of adsorption. They also propose a kinetic model of thiolate formation which takes into account different adsorption sites.

As is obvious from this overview, numerous contradictory results have been reported. The discrepancies among these reports may reflect artifacts of the different experimental techniques used (e.g. differences in gold surface preparation or whether *in situ* or *ex situ* methods were applied to track the kinetics) or the inherent sensitivity of alkanethiol adsorption to solvent and external hydrodynamic conditions. It needs to be understood whether exposure of a clean gold surface to alkanethiol solutions at room temperature leads to the formation of multilayer. We also need to find out the time scale of the adsorption process and the rate law followed by the process.

In the present work we have attempted to study the adsorption kinetics using electrochemical impedance spectroscopy. One of the earliest methods used to study the adsorption processes in electrochemical systems is the measurement of capacitance of double layer. It is well known that the capacitance of the electrical double layer precisely describes the adsorption properties and it is being widely used in the study of self assembled monolayers. The impedance spectra of fully covered monolayers of adsorbed alkanethiols have been studied using electrochemical impedance spectroscopy by several workers. The measurement of capacitance is ideally suited for such studies as long chain alkanethiols are well known to form ordered monolayers on gold surfaces anchored by the gold – sulfur bond. The structure forms a dielectric barrier between the metal and the electrolyte. The interfacial capacity of a Metal-SAM-electrolyte interface consists of a series combination of the capacitance of SAM and the concentration dependent capacitance of the diffuse layer. The overall capacity is dominated by the smaller of the two, namely the capacitance of the SAM.

This technique can be used to measure the double layer capacitance C_{dl} of gold- solution interface as a function of time. Adsorption of alkanethiol on the gold surface leads to a reduction in the double layer capacitance. The variation of double layer capacitance C_{dl} as a function of time is a measure of the kinetics of the adsorption process.

5.1 Method:

The electrochemical cell can be modelled as an equivalent circuit consisting of a combination of resistors and capacitors. 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 solution resistance.



Randles equivalent circuit for an electrode reaction with double layer capacitance C_{dl} , charge transfer resistance R_{ct} and solution resistance R_s

The impedance of the Randles equivalent circuit can be expressed as follows,

$$Z = Z' - jZ'' \tag{1}$$

where,

$$Z' = R_s + \frac{R_{ct}}{1 + \omega^2 C_{dt}^2 R_{ct}^2}$$
(2)

and
$$Z'' = \frac{\omega C_{\mu} R^2}{1 + \omega^2 C_{dl}^2 R_{cl}^2}$$
(3)

where Z'and Z" are the real and imaginary components of the impedance, $R_{,n}$ and R are the charge transfer resistance and solution resistance respectively, $C_{,,n}$ is the interfacial double layer capacitance and $\omega = 2\pi f$ where f is the frequency of the applied a .c potential.

In a system where $\omega^2 C_{dl}^2 R_{cl}^2 >> 1$ the imaginary part of the impedance can be approximated as,

$$Z'' = \left(\frac{1}{C_{dl}\omega}\right) \tag{4}$$

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 the gold-SAM-electrolyte interface behaves as an ideally polarisable interface. Thus R_{ct} for this system is very large (>10⁶ Ω). By substituting these values in equation (3) we can see that by choosing an appropriate frequency of study the double layer capacitance C_{dt} can be directly obtained by measuring the imaginary component of the impedance [equation (4)]. As the alkanethiol adsorbs onto gold the capacitance of the interface starts decreasing. The change in the imaginary component of impedance and consequently of capacitance can thus be used to follow the kinetics of the adsorption process.

Measurement of the imaginary component of the impedance to characterise the defects in adsorbed alkanethiol monolayer on gold has been used by Nahir et al. [20]. Frubose and Doblhofer [21] measured the imaginary component as a function of time to compare the adsorption characteristics of octadecanethiol on gold with that of quartz crystal microbalance (QCMB). Bernabeu et al. [22,23] have studied the adsorption of different proteins on platinum disk electrodes by measurement of Z''. They showed that the method can be used to obtain the rate constant of adsorption of bovine serum albumin and fibrinogen on gold and platinum electrodes.

In our work, the evolution of the imaginary component of impedance was measured as a function of time at intervals of 160 ms to follow the adsorption process. The resolution so obtained is crucial for following the initial process of adsorption. The impedance is measured at a frequency corresponding to the value at the mid point of a "pseudo – plateau" of the capacitance – frequency curve obtained at a particular potential. The capacitance calculated at the chosen frequency is compared with the value calculated for full monolayer coverage for different alkanethiols reported in literature. We have followed the adsorption kinetics *in situ* for five different alkanethiols in ethanolic medium [24,25].

5.2 Experimental:

5.2.1 Preparation of Au (111) surface:

Au (111) surface was prepared by evaporation of gold onto Muscovite mica. The mica surface was cleaved just before mounting into the vacuum chamber (Hindhivac). The mica substrate after mounting into the vacuum chamber was cleaned by ion bombardment using oxygen gas. The substrate temperature was maintained at 350° C throughout. The pressure in the vacuum chamber was 2×10^{-5} mbar. Resistive evaporation of gold was carried out at a rate of 4-5 A⁰sec⁻¹. The substrate holder was rotated during evaporation in order to facilitate uniform deposition of gold over mica. The thickness of the gold film was monitored *in situ* using a quartz crystal microbalance. The final thickness of the gold film was 1020 A". X-ray diffraction studies of the gold film confirmed that the crystallographic

orientation is almost completely (111) in nature as can be seen from the diffraction pattern.

The gold samples were used as strips in the electrochemical cell with a well defined area exposed to the electrolyte, rest of the portion being insulated with parafilm and Teflon. The true surface area of the specimen remained constant even after dipping for 24 hours in the electrolyte. Prior to each experiment the gold sample was cleaned in piranha solution $(1:3 H_2O_2 \text{ and } H_2SO_4)$ for 30s, rinsed in Millipore water and then finally in ethanol before dipping into the cell.

5.2.2 Electrochemical cell:

The electrochemical cell is an all glass cell of about 18ml capacity with a provision for saturated calomel reference electrode in a separate compartment connected by a luggin capillary. This is done in order to prevent the mixing of water and ethanol. The cell has also a provision for inserting counter electrode of platinum foil and an inlet and outlet for nitrogen gas. The cell is cleaned thoroughly before each experiment and kept in a hot air oven at 100° C for at least about an hour before the start of the experiment.

5.2.3 Chemicals:

Ethanol 99.95% (EMerck), Lithium perchlorate (Fischer), Perchloric acid (Ranbaxy), Octanethiol, Octanedithiol, Decanethiol, Dodecanethiol, Hexadecanethiol,Octadecanethiol(Aldrich),Benzotriazole, Mercaptobenzothiazole, Benzimidazole, Mercaptobenzimidazole and Imidazole were used in this study.

5.2.4 Instrumentation:

The impedance studies have been performed using the PAR 263A potentiostat connected to SRS 830 two phase Lock-in amplifier. The amplitude of the input sinusoidal voltage is 4mV rms. The real and imaginary components of the current

response were acquired using Keithley HRES 16 bit data acquisition card and sampled at a rate of 160 ms per data point from which the imaginary component of impedance was calculated. The programme was written in Microsoft Quick Basic. The acquired data in ASCII were imported to Microcal Origin Software which was used for graphical analysis and curve fitting. All adsorption studies were carried out at a potential of 0.1V versus SCE (double layer region).

All adsorption measurement studies were carried out in absolute ethanol with 0.1M Lithium perchlorate (LiClO₄) as the supporting electrolyte. The electrolyte was bubbled with nitrogen prior to each measurement for about 15 minutes. The solution was not bubbled during measurement, though a blanket of nitrogen covered the electrolyte. The electrolyte was however not stirred. The gold electrode was dipped into the alkanethiol containing electrolyte even as the data acquisition was simultaneously carried out at a potential of 0.1V versus SCE.

5.3 Calculation of surface coverage:

Surface coverage θ was obtained using the formula [26]:

$$\theta = \left(\frac{C_0 - C_t}{C_0 - C_f}\right) \tag{5}$$

where C_0 is the bare electrode capacitance ,C, is the capacitance at any time *t* and C_f is the capacitance of the fully covered monolayer.

5.4 Results and Discussion:

The impedance spectrum of decanethiol adsorbed gold in ethanol + 0.1M LiClO₄ is shown in figure 1. We find that even at 0.1 Hz R_{ct} is not observed. This shows that the system behaves almost as an ideally polarised electrode. Figure 2 shows the capacitance - logarithm of frequency plot for 1mM decanethiol in ethanol + 0.1M LiClO₄. The capacitance is measured from the imaginary component of



Cole-Cole plot : Au(111) in 1mM Decanethiol + 0.1M LiClO₄ in ethanol







impedance. The pseudo plateau occurs above 1 Hz and there is very little change in capacitance from 30 Hz to more than about 3000 Hz. In practice one can choose any frequency within the region though it is preferable to select a mid point frequency for the study. We have carried out our measurements at 520 Hz. For the bare gold electrode also similar behaviour is exhibited as can be seen in figure 2 inset. We have also measured the capacitance at different potentials and we find the values are constant over a wide potential range from -1V to +0.4 V versus SCE.

The experiments to study adsorption kinetics has been performed in two different ways. The alkanethiol can be added to the solution in which the gold electrode is already immersed and the change in capacitance measured. Alternatively the gold electrode can be dipped into the solution already containing alkanethiol and capacitance variation measured.

In the first case the alkanethiol is added to the electrolyte using a pipette at high pressure close to the region of nitrogen bubbling. Fast mixing is ensured by bubbling nitrogen for about five seconds after the addition at a rate of 5 bubbles per second. The concentration of alkanethiol taken in the pipette is larger than that of the resulting solution. In particular for lower concentrations addition of alkanethiol solution may result in the concentration being greater than the desired value locally near the gold electrode before uniform mixing in the solution takes place. This will lead to errors in the measurement of kinetics at lower concentrations. Hence to eliminate this factor, for kinetic measurements we have chosen the method in which the gold electrode is dipped into the solution of the desired concentration. This method is free from the effects of unequal concentrations near the surface and bulk and hence is the preferred method for the study of adsorption kinetics.

When the gold electrode is dipped into the solution containing the alkanethiol the double layer gets formed. During the process of dipping the area of the electrode in contact with the solution increases. Since capacitance is directly

proportional to surface area C_{dl} also increases. Adsorption of alkanethiol onto the gold surface results in a decrease of capacitance. Thus at the instant of dipping there is a competition due to increase in capacitance due to increase in area and decrease in capacitance on account of alkanethiol adsorption. This results in a peak following which the capacitance decreases following alkanethiol adsorption. This phenomenon is seen only at higher concentrations where the rate of adsorption is very fast.

5.4.1 Chain length dependence of capacitance:

Figure 3 shows the capacitance versus time curves for gold electrode in ethanol + 0.1M LiClO₄ electrolyte for 1mM concentration of different alkanethiols at a potential of +0.1V versus SCE. In this case the alkanethiol is added to the solution in which the gold electrode is immersed since we are only interested in measuring the final capacitance of the monolayer. The capacitance values shown are per unit *true* area after taking into account the roughness factor of 1.15 determined from oxide stripping peak of the cyclic voltammogram in sulphuric acid. It can be seen that the capacitance falls rapidly to almost its final value within < 100 s in all the cases. There is little or no change in the measured capacitance at this concentration beyond the duration of the experiment (3200s). This has been verified by measuring the capacitance after dipping the electrode for 12 hours in the solution. The final capacitance is related to the dielectric constant and the thickness of the monolayer by the relationship based on Helmholtz model:

$$C = \frac{\varepsilon \varepsilon_0}{d} \tag{6}$$

where ε is the dielectric constant of the alkanethiol molecule, ε_0 is the permittivity of free space and *d* is thickness of the monolayer. For a fully covered monolayer, a plot of capacitance against inverse of monolayer thickness should



Figure 3: Capacitance versus time curves for evaporated gold in 1mM alkanethiols in ethanol + 0.1 M LiClO_4 at a potential of 0.1V versus SCE

yield a straight line from the slope of which the dielectric constant can be obtained.

Figure 4 shows an excellent linear fit when the final capacitance is plotted as a function of inverse of monolayer thickness for each alkanethiol. If the thickness increment per methylene group is assumed to be 1.1 A⁰ for a 30⁰ chain tilt, the dielectric constant calculated from the plot yields a value of 2.21 in agreement with the values reported in literature which also closely corresponds to the value for bulk polyethylene ($\varepsilon = 2.3$) which consists of *n* number of $-CH_2$ groups [3]. The excellent agreement suggests that the surface is fully covered with a closely packed monolayer of alkanethiol within the time of measurement and is also defect free. This also validates the correctness of the measurement of the impedance at the chosen frequency. We find that the final capacitance values for different alkanethiols are same if the experiment is also carried out by dipping the gold electrode into alkanethiol containing solution. These results show that there is no multilayer formation atleast during the time scale of measurement.

The plots also show that the full coverage is reached in all the cases within a minute and there is little or no change in the coverage after about 2 minutes in all cases. A closer inspection of the plots show that the 70% - 80% of adsorption takes place within the first five seconds followed by slower processes which in any case does not extend beyond about 20-30 minutes for all the alkanethiols studied in this work.

5.4.2 Study of adsorption kinetics:

We have studied the adsorption kinetics at three different concentrations namely, 1, 5 and 20 μ M and each of the measurements is carried out with three samples and the measured rate constants are the mean of these three measurements. We have also measured the standard deviation for the method. To measure the rate constants, the surface coverage of the adsorbed alkanethiol molecules on gold is



Figure 4 : Plot of final capacitance vs. inverse of monolayer thickness for different alkanethiols

plotted as a function of time of adsorption. This plot is fitted with the following three models:

1) Langmuir model:

In this model the surface coverage dependence on time of adsorption is expressed by the relation,

$$\theta(t) = \left[1 - \exp(-kt)\right] \tag{7}$$

where $\theta(t)$ is the coverage at any instant of time t and k is the rate constant of adsorption.

2) Diffusion controlled Langmuir model (DCL):

$$\theta(t) = \left[1 - \exp\left(-k\sqrt{t}\right)\right] \tag{8}$$

3) Purely diffusion controlled adsorption:

$$\theta(t) = k_d \sqrt{t} \tag{9}$$

where k, is the diffusion rate constant and is given by :

$$k_d = \left(\frac{2\,cD^{1/2}}{B\,\pi^{1/2}}\right) \tag{10}$$

where B is the number of molecules per unit area at fractional coverage (in this case at 100s), *c* is the concentration and D is the diffusion coefficient.

The raw data were fitted to the above models to see 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 and the second and third step extends for the rest of the coverage. Figure 5 shows the adsorption kinetics of decanethiol at different concentrations. The increase in the rate of adsorption with increase in concentration can be clearly seen. Besides this, it can also be seen that the full coverage is obtained only in the case of 1mM concentration within the duration of measurement. There is a distinct plateauing of the coverage at lower concentrations which asymptotically reaches the value for final coverage that is less than one. The first time constant corresponds to the adsorption of alkanethiol molecules onto the surface while the second time constants is due to the rearrangement of the alkyl chains to form an oriented closely packed monolayer. The third and final step which is the slowest relates to the reorientation of the terminal methyl end groups. The highest concentration studied. namely 1 mMshows capacitance of а 2.02 $\mu F cm^{-2}$ corresponds to a full monolayer coverage. However, the curve is so steep that it is difficult to locate the region of first time constant precisely. A typical capacitance-time curve for decanethiol at 1mM concentration is shown in figure 6. It can be seen from the graph inset that as soon as the electrode is dipped into the electrolyte, the capacitance rises and within about 480 ms the capacitance attains the maximum value of about $6 \,\mu F \, cm^{-2}$. The capacitance corresponding to the bare gold electrode is measured to be $9.52 \,\mu F \, cm^{-2}$ in the same electrolyte without alkanethiol being added. The difference of about $3.52 \,\mu F \, cm^{-2}$ is due to decanethiol adsorption which has taken place within the period 480 ms. The final capacitance attained is 2.02 $\mu F cm^{-2}$. This shows that a coverage of 40% is attained within the first 480 ms. In other words, the rate of formation of monolayer is so rapid at 1mM concentration that the rate constant cannot be measured until at



Figure 5 : Adsorption of decanethiol at different concentrations on gold in ethanol $+ 0.1M \text{ LiClO}_4$



Figure 6: Capacitance - time profile when the gold electrode is dipped in 1 mM decanethiol in ethanol + 0.1M LiClO₄ and measured at intervals of 160 ms. The inset is a magnified plot of the initial stages of adsorption showing the initial increase of capacitance during immersion of the electrode and the subsequent decay due to adsorption of decanethiol. The capacitance maximum corresponds to the surface already covered with about 40% of the monolayer

least 40% of the surface is covered. Hence the rest of the coverage – time plot in this case reflects the change beginning from this initial value of coverage.

Table 1

Initial coverage and initial and final capacitance values for different alkanethiols Capacitance of bare gold electrode: $9.52 \pm 0.45 \ \mu F \ cm^{-2}$

	Initial C	Final C	Initial
ALKANETHIOL	$(\mu F cm^{-2})$	$(\mu F cm^{-2})$	coverage (θ_i)
Octanethiol	6.40	2.45	0.420
Decanethiol	6.38	2.00	0.416
Dodecanethiol	6.07	1.75	0.442
Hexadecanethiol	6.25	1.40	0.401
Octadecanethiol	6.45	1.18	0.360

Table 1 shows the coverage (θ_i) within the first 480 ms in the case of different alkanethiols at 1mM concentration. The values of the capacitances are average of three measurements and the bare gold electrode value of 9.52 $\mu F cm^{-2}$ is a mean of 12 measurements with a standard deviation of 0.45 $\mu F cm^{-2}$. It can be seen that the initial coverage is almost the same (about 40%) in the case of all the alkanethiols studied showing that the rate of formation of monolayer does not change significantly with the chain length when the electrodes are dipped into the alkanethiol solution. This also shows that the measurement of rate constant cannot therefore be determined using ImM concentration of alkanethiol during the initial stages of adsorption. Kim et al. [11] find that for a concentration of 1mM dodecanethiol and hexadecanethiol the time required for initial coverage is of the order of minutes. Pan et al. [10] observe a two step process using QCMB for the adsorption of 5mM I-Dodecanethiol and Mercaptoundecanethiol onto gold from

ethanol. They find the first time constant of about 300 min^{-1} . We find that the time constant for 1mM obtained is about 4 - 5 orders of magnitude different from the results of the above workers.

Figure 7 shows the adsorption curve of decanethiol at the lowest concentration studied viz.1µM. The initial stages of adsorption during the first 100s follows purely diffusion controlled kinetics as can be seen by the linear relationship of from the θ versus $t^{1/2}$ plot in figure 7 (inset). About 40% of the coverage is completed during this time and the remaining curve fits to diffusion limited Langmuir equation. This shows that even at as low as concentration as 1 µM, the adsorption is not fully under diffusion control and the coverage does not follow the model represented by equation (9). We find however all the alkanethiols attain a coverage of 75% to 85% during the time of study (3200 s) at this concentration. This is unlike Karpovich et.al. [12] who find a fractional coverage of only 0.04% at a comparable concentration of 3 µM.

The slope of the θ versus $t^{1/2}$ plot during the period of pure diffusion control (0–100s) is the diffusion rate constant k, (Equation 9). The value of k, is found to be $0.041s^{-1/2}$. The diffusion coefficient *D* can thus be calculated from equation (10) which gives a value of $9 \times 10^{-5} cm^2 sec^{-1}$.

Figure 8 shows the decanethiol adsorption curve at 5μ M concentration. We find that there are two time constants corresponding to the range, 0-500s and 500s – 3200 s. This is in agreement with the results obtained by other workers. The second time constant is generally two orders of magnitude different, does not show any chain length dependence and generally occurs after 80% – 85% coverage is completed. Hence we are not considering the second time constant in our analysis of rate of adsorption .The curve corresponding to the first time constant is fitted with Langmuir and DCL models represented by equations (7) and (8). We find that while DCL model fits quite well from 0 –500 s, unlike the Langmuir model fits only after a few seconds of adsorption.



Figure 7: Coverage (θ) - Time plot for 1 μ M decanethiol in ethanol + 0.1M LiClO₄.The inset shows the θ vs t^{1/2}plot during the first 100 s after dipping. The linear plot shows that the coverage is under diffusion control during the initial stages of adsorption.



Figure 8: Adsorption of $5\mu M$ decanethiol in ethanol + 0.1M LiClO₄ during the entire duration of measurement

Figures 9(a-b) show the plots of 8 versus t and 8 versus $t^{1/2}$ at 5µM decanethiol concentration up to 500 s after immersion during which time about 80% coverage is completed. The insets of the figures represent the linear regression plots of Langmuir and Diffusion controlled Langmuir model (DCL) models to verify the extent of fitting. We find that at 5 µM the DCL model fits the data better than the Langmuir model. This can be seen clearly from the insets in figures 9(a-b). This indicates that the rate of coverage is governed by both diffusion of alkanethiols to the metal surface and the number of available vacant sites for adsorption.

Table 2

Rate constant of adsorption on gold in ethanol solution for different alkanethiols obtained using DCL and Langmuir models at 5 μ M and 20 μ M concentrations. The results are mean of three measurements

ALKANETHIOL	θ vs $t^{1/2}$ [5 μ M, 0 – 500 s]		θ vs t [20 μ M, 0 - 100 s]		
	$k \times 10^4 s^{-1/2}$	$k_c M^{-1} s^{-\frac{1}{2}}$	$k \times 10^4 s^{-1}$	$k_c M^{-1} s^{-1}$	
Octanethiol (C ₈ SH)	1380	27600	598	2992	
Decanethiol (C ₁₀ SH)	1377	27543	585	2925	
Dodecanethiol (C ₁₂ SH)	1307	26075	551	2756	
Hexadecanethiol (C ₁₆ SH)	1250	25060	554	2773	
Octadecanethiol (C ₁₈ SH)	1253	25097	507	2536	

In the case of 20μ M concentration from the plot of coverage – time we find that the curve can be fitted to three time constants corresponding to 0-100s for



Figure 9 (a): θ versus time plot for 5µM decanethiol in ethanol + 0.1M LiClO₄ for the first 500 s. The inset shows the linear regression plot to check the validity of Langmuir adsorption model.



Figure 9 (b): θ versus $t^{1/2}$ plot for 5µM decanethiol in ethanol + 0.1M LiClO₄. The inset shows the linear regression plot for the diffusion controlled Langmuir adsorption model.

the first and 100-3200s for the second and third respectively. The first time constant 0 - 100s is fitted with the Langmuir and DCL model to check their validity. Figures 10(a-b) show the plots of θ versus t and θ versus $t^{1/2}$ at 20 μ M concentration with the linear regression plots in the inset. It can be seen that in this case the θ versus t plot fits better than the θ versus $t^{1/2}$ curve (0-100s) showing that at this concentration diffusional effects are overcome and that the adsorption kinetics follow Langmuir model.

Table 2 lists the rate constants calculated for different alkanethiols using the DCL model (8 versus $t^{1/2}$) for 5 μ M and Langmuir model (θ versus t) for 20 μ M concentration. We have considered 0-500s for 5 μ M and 0-100s for 20 μ M concentrations for determination of rate constant as these time durations correspond to the first time constant in the θ versus t plot. The results presented are the average of three measurements. The concentration independent rate constants (k_c) is obtained using the relationship,

$$\mathbf{k} = k_c \, \mathbf{c} \tag{11}$$

It can be observed that the lower chain length alkanethiols (octane and decanethiol) have somewhat higher rate constants. However it can be seen that the chain length dependence is not quite systematic.

We find that our results at 20µM are comparable with that of Karpovich et al [12] and Dannenberger et al. [19] in similar systems. For example Karpovich et al. report a rate constant of 0.06 s⁻¹ for 10 µM octadecanethiol in cyclohexane which is close to our result of 0.05 s⁻¹ for 20µM octadecanethiol in ethanol. Again the concentration dependent rate constant of 2636 $M^{-1}s^{-1}$ for dodecanethiol adsorption in ethanol observed by Dannenberger et al. using second harmonic generation (SHG) technique compares well with our value of 2756 $M^{-1}s^{-1}$ in the same system. In both of the above works, the adsorption is shown to follow purely Langmuir kinetics.



Figure 10 (a): θ versus t plot for 20 μ M decanethiol in ethanol + 0.1M LiClO₄. The inset shows the linear regression plot for the Langmuir adsorption model.



Figure 10 (b): θ versus t^{1/2} plot for 20µM decanethiol in ethanol + 0.1M LiClO₄. The inset shows the linear regression plot for the diffusion controlled Langmuir adsorption model.

From the above results it is clear that the adsorption kinetics follows different mechanisms depending on the concentration of added alkanethiol. Thus the adsorption process is under purely diffusion control at 1 μ M in the initial stages following which it is under partly diffusion control (DCL), partial diffusion control (DCL) at lower concentration (5 μ M) and follows Langmuir adsorption kinetics at higher concentration (20 μ M). It is also clear that the rate of adsorption is extremely fast at highest concentration studied (viz 1mM) that the information on the initial stages of adsorption cannot be determined by this method (i.e., within a period of 480 ms) due to change in the area of the electrode occurring simultaneously. This is not a problem at lower concentrations as adsorption is slower and capacitance change due to alkanethiol adsorption is negligible compared to double layer charging and time required to dip the electrode into the solution.

In order to study the dependence of rate constant on concentration we studied the adsorption kinetics of decanethiol at three other concentrations namely 10μ M, 50μ M and 1mM respectively. The first time constants for 10μ M and 50μ M concentrations are found to be from 0-150s and 0-30s respectively. In the case of 1mM the rate of adsorption is extremely fast that the information on the initial stages of adsorption cannot be determined by this method (i.e., within a period of 480 ms) due to change in the area of the electrode occurring simultaneously. However a rough estimate can be made. 40% of coverage is completed in a duration of 480 ms (within 3 sampling points). For Langmuir kinetics this corresponds to a value of k of about 2.2 s⁻¹ and therefore to a value of k_c of $2315 M^{-1} s^{-1}$. We can see from Table 3 that this value is comparable with that of other concentrations studied. It also indicates that the adsorption process follows Langmuir kinetics at this concentration. **As** discussed earlier for 5μ M concentration the adsorption process follows diffusion controlled Langmuir (DCL) kinetics. For all the other four higher concentrations studied viz. 10μ M, 20μ M,

50µM and 1mM the adsorption follows Langmuir kinetics. Table 3 shows the rate constants calculated for different concentrations of decanethiol.

Table 3

Rate constants for adsorption of decanethiol on gold at different concentrations

Concentration	tı	θ vs t	
		$k \times 10^4 s^{-1}$	$k_c M^{-1} s^{-1}$
10μΜ	0-150 s	340	3415
20µM	0-100 s	585	2925
50μΜ	0-30 s	1470	2941
1 mM	0.48 s	22200	2315

We find that as the concentration of decanethiol increases the duration of the first time constant decreases. The rate constant k varies linearly as a function of concentration. Figures 11 and 12 show plots of rate constant k as a function of concentration without and with 1mM concentration. In figure 12 the k value for 1mM concentration is also included. The rate constant k_c which is obtained from equation (11) is concentration independent. From the slope of the curve we find that the value of k_c is 2980 M⁻¹ s⁻¹ for decanethiol.

5.4.3 Studies with Octanedithiol:

Octanedithiol is an alkanethiol with – SH group being present at both the ends. The structure of the molecule is.







During the self assembly process the alkanethiol can in principle adsorb with both the sulphur atoms bonded with gold or with only one sulphur atom chemisorbed onto gold as in the case of simple alkanethiols. Kobayashi et al. [27] have studied the structure of self assembled monolayers of octanedithiol molecule using an ultrahigh vacuum scanning tunneling microscope and by Fourier transform infrared reflection – absorption spectroscopy. Clearly resolved STM images of the octanedithiol SAM revealed striped structures as bright lines and the distance between the adjacent bright lines was about 1.5 nm which was in good agreement with the length of an octanedithiol molecule .The intensities of the CH₂ stretching band in FTIRRAS measurement of octanedithiol SAM were found to be stronger than those of alkanethiol SAMs. They showed that octanedithiol SAMs have structures where the molecules are aligned with their axes parallel to the Au (111) surface.

Scoles et al. [28] formed monolayers of 1,6 hexanedithiol on Au (111) from the gas phase. They characterised the monolayers by scanning tunneling microscopy, grazing incidence X-ray diffraction (GIXD) and low energy atom diffraction (LEAD). Molecular resolution STM images showed that the molecules lie in a striped arrangement with an inter row spacing of 5 A⁰. GIXD and LEAD also showed that the structure of the striped phase is consistent with the molecules being fully extended and flat on the surface with their molecular C-C-C plane parallel to the surface. Using different growth protocols for deposition including liquid phase deposition they found that the order of striped phases changed considerably. However no evidences of other ordered phases were found. They concluded that the results of both varied growth conditions and annealing experiments can be explained by the strong molecule/substrate interactions in the striped phases, which is a consequence of the strong interaction of both sulphur atoms with the gold surface.

Tour et.al. [29] using ellipsometry and X-ray photoelectron spectroscopy studied the solution grown monolayers and multilayers on gold films from a series

of conjugated organosulphur compounds including 1,4-phenyl dithiol and 4,4 biphenyldithiol. Because multilayer formation of conjugated dithiols on gold was observed, they inferred that one thiol end is adsorbed onto the surface while the other end is projected away from it.

Brust et al. [30] reported that multilayer structures of copper ions sandwiched between dithiol molecules can be formed using 1,6-hexanedithiol. Ellipsometry measurements suggested that the first monolayer of dithiols adsorb to the gold surface with only one of the thiol groups, resulting in layer by layer growth.

Riley et al. [31] used XPS to study monolayers of 1,8- octanedithiol onto gold. The data were found to be consistent with a structure with an upright configuration which was similar to that suggested by Brust et al. On the basis of STM observations, Nakamura et al. [32] have reported a similar upright configuration for 1,12-dodecanethiol and a thiophene containing dithiol monolayer on gold.

Cavallini et.al. [33] carried out an STM study on 1,8-octanedithiol electrochemically adsorbed on Ag (111) from aqueous solution. The adsorption of octanedithiol was found to give rise to close packed SAMs lying flat on the electrode surface.

We decided to investigate the structure of octanedithiol on gold by capacitance measurement. Measurement of capacitance can be used to find out the type of orientation of octanedithiol onto Au (111) surface as it is very sensitive to the thickness of the monolayer. The capacitance of the monolayer of SAM is given by equation (6). The SAM capacitance is inversely proportional to the thickness of the monolayer. If the octanedithiol molecule is aligned with its axis parallel to the Au (111) surface (both S atoms chemisorbed on gold) then its capacitance would be much lower than when it is adsorbed vertically with some tilt angle (only one S atom chemisorbed on gold) [3].

The impedance diagram of gold electrode covered with monolayer of octanedithiol in ethanol + 0.1M LiClO₄ is shown in figure 13.The double layer capacitance measured from the impedance plot is $2.86 \,\mu F \, cm^{-2}$. The coverage-time curves for octanedithiol at different concentrations are shown in figure 14. The capacitance at the highest concentration studied i.e. 5 mM corresponds to a value of $2.67 \,\mu F \, cm^{-2}$ which is in reasonable agreement with the impedance value. This capacitance corresponds to full monolayer coverage. The capacitance of octanethiol which is an alkanethiol of similar length is $2.2 \,\mu F \, cm^{-2}$ (Table 1). Since these two values are quite close we can conclude that octanedithiol adsorbs with only one S atom onto gold. If it were lying flat on the surface then it would have had a much larger capacitance corresponding to the small thickness of the SAM. This result contradicts the findings of Kobayashi et.al. but is very much in agreement with the results of Riley et.al. and Nakamura et.al.

5.4.4 Study with polycrystalline surfaces:

We have studied the effect of surface pretreatment on the adsorption kinetics of octadecanethiol on gold, silver and copper. The different pretreatments carried out are emerying (800grit emery) with 17μ m particle size, alumina polishing, electrochemical oxide formation, electropolishing, chemical etch and evaporation [for gold only]. Figures 15(a-b), 16(a-b), 17(a-b) show the plots of coverage – time for 1mM and 5 μ M concentrations for different surface pretreatments for gold, silver and copper respectively. In the case of gold we find that at both 1mM and 5 μ M the fastest coverage happens with the evaporated surface. In the case of electropolished surface we find that initially there is a very rapid surface coverage after which the rate of coverage decreases. The coverage for the alumina and emery treated surfaces with time are by and large similar. In chapter- 4 we find that the cyclic voltammetric behaviour of octadecanethiol modified gold pretreated by alumina and 800 grit emery in 0.1N NaOH show large variations. The gold





Figure - 13





Figure 15(a): Coverage (θ) vs. time plot for gold with different surface pretreatments in 1mM ODT + 0.1M LiClO₄ in ethanol



Figure 15(b): Coverage (θ) vs. time plot for gold with different surface pretreatments in 5µM ODT + 0.1M LiClO₄ in ethanol



Figure 16(a): Coverage (θ) vs. time plot for silver with different surface pretreatments in 1mM ODT + 0.1M LiClO₄ in ethanol



Figure 16(b): Coverage (θ) vs. time plot for silver with different surface pretreatments in 5µM ODT + 0.1M LiClO₄ in ethanol



Figure 17(a): Coverage (θ) vs. time plot for copper with different surface pretreatments in 1mM ODT + 0.1M LiClO₄ in ethanol



Figure 17(b): Coverage (θ) vs. time plot for copper with different surface pretreatments in 5µM ODT + 0.1M LiClO₄ in ethanol

electrode treated with 800 grit emery is found to be much more blocking to gold oxidation reaction than when pretreated with alumina. Thus the monolayer has more pinholes and defects on the alumina treated surface than on the 800 grit eniery treated surface. We can thus conclude that the rate of monolayer formation is not directly related to the nature of the final monolayer formed on the gold surface.

We observe that for 1mM concentration complete coverage is reached for all the different pretreated gold surfaces as was observed for evaporated gold surface [section 5.4.2]. On the other hand in the case of 5μ M we see that the niaximuni coverage is attained for the chemical etched surface (0.95). The alumina and 800 grit emery treated surfaces have the same final coverage (0.88) while the electropolished surface has the lowest coverage (0.81).

In the case of silver we find that the chemically etched surface has the fastest rate of coverage compared to 800 grit emery and alumina polished surfaces. As in the case of gold for 1mM concentration complete coverage is reached for all the different pretreated surfaces. We notice that in the case of silver even at 5μ M concentration a full coverage is reached for all the different pretreated surfaces (chemical etch, 800 grit emery and alumina). This may mean that a polycrystalline silver surface has more affinity towards alkanethiol molecules to form monolayer than a gold surface.

It is observed that at 5µM concentration for gold and silver the coverage – time plot fits well with Diffusion controlled Langrnuir model (DCL). The first time constant is observed in the range of (0-500s). The values of rate constants k calculated for different surface pretreatments in the case of gold and silver are given in Table 4 and 5 respectively. In the case of silver, for the chemically etched surface we find that the coverage – time plot fits the Langmuir equation better than the diffusion controlled Langmuir equation (DCL). The entire curve fits into a single exponential (0 – 3000s). The rate constant obtained is $k(s^{-1}) = 0.00346$.

Table 4

SURFACE	θ vs $t^{1/2}$ [5 μ M, 0 – 500 s]		
TREATMENT	$k \times 10^4 s^{-1/2}$	$k_{c} M^{-1} s^{-1/2}$	
Alumina (0.05µm)	728	14577.25	
Emery (17µm)	481	9638.55	
Chemical Etch	798	15961.69	
Electropolished	719	14398.84	
Electrochemical oxide	771	15420.2	
Evaporated	1253	25097	

Rate constant of adsorption of octadecanethiol on gold in ethanol solution obtained using DCL model at 5µM concentrations for different surface pretreatments

Table 5

Rate constant of adsorption of octadecanethiol on silver in ethanol solution obtained using DCL model at $5\mu M$ concentrations for different surface pretreatments

SURFACE	θ vs t ^{1/2} [5 μ M, 0 – 500 s]		
TREATMENT	$k \times 10^4 \ s^{-1/2}$	$k_c M^{-1} s^{-1/2}$	
Alumina (0.05µm)	854	17094.01	
Emery (17µm)	260	5208.33	

From Table 4 we find that the evaporated surface gives the fastest coverage. The rate of coverage for different pretreatments in the case of gold is,

Evaporated surface > Chemical Etching > Electrochemical oxide formation

> Alumina treatment > Electropolishing > Emery treatment
In the case of electropolished surface initially there is a sharp increase in coverage
followed by slower rate of coverage. Figures 18 (a-b) shows the coverage - time



Figure 18(a): Coverage (θ) vs. time plot for oxidised gold in 1mM ODT + 0.1M LiClO₄ in ethanol for the initial period



Figure 18(b): Coverage (θ) vs. time plot for oxidised gold in 1mM ODT + 0.1M LiClO₄ in ethanol for the entire duration of measurement

plot of octadecanethiol adsorption onto oxide treated gold surface at different times. The coverage-time curve of the oxide treated surface shows an irregular variation in the plot in the initial stages of adsorption. It shows that the capacitance is oscillating with time. This could be because of the rupture of oxide film due to the adsorption of alkanethiol. The increase in capacitance could be due to removal of oxide layer and decrease due to subsequent adsorption of alkanethiol.

Since copper is always covered with an oxide surface in ambient conditions we can make only a qualitative comparison about the effect of surface pretreatments on the rate of adsorption. We find as in the case of silver that the rate of adsorption is the fastest on the chemically etched copper surface. For 1mM concentration complete coverage is attained for all the different pretreated surfaces. In the case of 5μ M concentration we find that in all the cases the coverage is much less than unity. They are 0.84,0.6,0.6 and 0.5 for chemically etched, alumina treated, electropolished and 800 grit emery treated respectively. A concentration of 5μ M is not enough to form a complete monolayer on the surface of copper. We also find that the coverage-time curve is not smooth. There are certain times at which the rate of surface coverage changes abruptly.

The final capacitance values after adsorption of octadecanethiol from 1mM solution on gold, silver and copper is shown in Table 6. We find that the final capacitance of surface treated with emery to be the highest compared to other surface treatments for ail the three metals. Since capacitance is directly proportional to the real surface area, the real surface area should be the greatest for an emery treated surface. For gold the surface roughness follows the order,

Emery treatment $(17\mu m)$ > Alumina polishing $(0.05\mu m)$ > Chemical Etching > Evaporated surface > Electropolishing

Table 6

SURFACE	Final Capacitance $C_{dl} \mu F cm^{-2}$		
TREATMENT	GOLD	SILVER	COPPER
Alumina (0.05µm)	2.45	2.2	1.49
Emery (17µm)	2.68	2.45	2.17
Chemical Etch	2.08	1.4	0.98
Electropolished	1.15		1.12
Evaporated	1.18		

Final capacitance values after adsorption from 1mM octadecanethiol for different surface pretreatments

For all the three metals the chemically etched surface is found to have a smaller real surface area than the mechanically treated surfaces (emery and alumina). This could be because of preferential dissolution of certain crystal facets during the etching process resulting in the creation of a surface with lower capacitance.

In the case of electropolished surface, we find that for gold the capacitance is almost the same as that of an evaporated gold on mica [Au (111)] surface. A similar result is found for copper also. This indicates that the roughness factor of an electropolished surface is quite low i.e. real area being very close to the geometric area.

5.4.5 Study of the second and third time constants:

We find that the entire surface coverage – time curve can be fitted to a sum of two exponentials in the case of 5 μ M concentration and to a sum of three exponentials for higher concentrations as follows.

For 5
$$\mu$$
M
 $\theta(t) = A_1 \left[1 - \exp(-k_1 \sqrt{t_1}) \right] + A_2 \left[1 - \exp(-k_2 t_2) \right]$
(12)

At higher concentrations

$$\theta(t) = A_{1}[1 - \exp(-k_{1}t_{1})] + A_{1}[1 - \exp(-k_{2}t_{2})] + A_{1}[1 - \exp(-k_{3}t_{3})]$$
(13)

where $A_{1,1}A_{2,2}A_{3,3}A_{3,4}$ are coefficients, $k_{1,2}a_{2,3}a_{3,4}a_{3,3}a_{3,4}a_{3,4}a_{3,5}a_{3,4}a_{3,5}a_{3,4}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a_{3,5}a$

ALKANETHIOL	Conc.	First time	$k, x 10^4$	$k_2 x 10^4$	$k_3 \times 10^4$
		constant			
		duration <i>t</i> ,			
OCTANETHIOL	5μΜ	0 - 500 s	1380	12.65	
	20μΜ	0 – 100 s	598	80.64	4.545
DECANETHIOL	5μΜ	0 – 500 s	1377	13.17	
	10μΜ	0 – 150 s	340	84.74	13.64
	20µM	0 – 100 s	585	108.29	11.58
	50μΜ	0 – 30 s	1470	117.6	8.326
DODECANETHIOL	5μΜ	0 - 500 s	1307	9.285	
	20µM	0 – 100 s	551	87.7	10.952
HEXADECANETHIOL	5μΜ	0 - 500 s	1250	14.577	
	20µM	0 – 100 s	554	78.125	8.583
OCTADECANETHIOL	5μΜ	0 - 500 s	1253	7.843	
	20μΜ	0 – 100 s	507	99.09	10.964

Table 7

Rate constants of alkanethiols with different concentrations

(For 5µM k, is in $s^{-\frac{1}{2}}$. For all other concentrations and 5µM(k₂) the unit of k_2, k_3 is s^{-1}).

We find that for $5\mu M$ the entire coverage- time curve can be fitted to an equation having only two time constants. The first exponential follows diffusion

controlled Langmuir model. For higher concentrations the coverage- time curve can be fitted to a three exponential curve. We find that for concentrations above 5μ M, for all the alkanethiols the second rate constant k_2 is smaller by 4-5 times from the first rate constant k,. The third rate constant is smaller by an order of magnitude from the second rate constant. The second rate constant is found to have some dependence on the concentration. On the other hand the third rate constant is independent of concentration as can be seen from the values of decanethiol.

The first step in the adsorption process is identified with Au-S bond formation. The second step can be linked to the straightening of the alkyl chains. The third and final step which is the slowest relates to the reorientation of the terminal methyl end groups [34]. In the case of 5μ M concentration the second and third step are contained in a single rate constant. In all the cases at the end of the first time constant the coverage reaches a value of around 75 – 80 %.

In the case of Octanedithiol we find that at the lowest concentration studied viz. 1 μ M in the initial 40 s the adsorption is under pure diffusion control. This corresponds to 27% of the surface coverage. The diffusion controlled rate constant k, is 0.0405 $s^{-\frac{1}{2}}$. The rate constant values obtained for different concentrations of octanedithiol as shown in Table 8.

Como	Einst time	1 104	1 104		Ein al
Conc.	riist time	$k_1 \times 10^{\circ}$	$k_2 \times 10^{7}$	$k_{3} \times 10^{4}$	Final
	constant				coverage
	duration t_1				
1μ Μ	0 – 500 s	1009	452		0.61
5μΜ	0 – 500 s	2188	400		0.76
20μΜ	0 - 20s	1748	158.7	8.389	0.80

Table 8

Rate constants of octanedithiol at different concentrations

 k_1 for 1µM and 5µM is in $s^{-\frac{1}{2}}$. k, for 20µM and k_2, k_3 is in s^{-1} .

We find that the first rate constant can be calculated by DCL model for $1\mu M$ and $5\mu M$ repectively. For $20\mu M$ the rate process is described by the Langmuir model. In the case of octanedithiol also for $5\mu M$ the third rate constant is absent. The final coverage of the monolayer increases as the concentration is increased.

We find from the coverage – time plots of octanedithiol that the rate of adsorption is faster than that of other alkanethiols studied.

5.4.6 Adsorption kinetics of azoles:

We have studied the adsorption kinetics of azoles on copper in a similar manner as for alkanethiols. In this case the frequency used for study is 1000 Hz. This value is obtained from the capacitance – frequency plot of the Cu-BTA system which is taken to be a representative for studying the adsorption of azoles. The capacitance-frequency plot shows a pseudo plateau from which the value of 1000 Hz is fixed as the frequency of study [fig 19]. At this frequency the capacitance can be directly obtained by measuring the imaginary component of the impedance. All the studies are carried out at the rest potential. The electrolyte used is 0.1N NaOH. We have carried out studies at 1mM and 5 mM concentrations of the azoles. The copper electrode was dipped into the solution containing the azole even as the data acquisition was simultaneously carried out at the rest potential. Figure 20 shows plots of the capacitance – time curve at 5 mM concentration for different azoles studied. We find that the final capacitance measured at 5mM concentration varies depending on the nature of adsorption of the azole. The final capacitance values for different azoles at the end of 3200 s for 5 mM is shown in Table 9.





Figure 20: Plot of capacitance vs. time for copper adsorbed with different azoles in 0.1 N NaOH at 5mM concentration

Table 9

Azole	$C_{dl} \mu F cm^{-2}$
BTA	4.31
MBT	2.2
BIMD	0.94
MBIMD	1.65
IMD	3.00

Double layer capacitance of copper adsorbed with different azoles (5 mM concentration)

The capacitance values measured are very close to the capacitance values obtained by impedance spectroscopy. This also validates the method and the frequency of study for the copper-azole system.

Capacitance can be used as an estimate of the thickness of film formed due to adsorption of the azole. We find the capacitance of the Benzimidazole covered copper surface to be the least and that of BTA to be the highest. This indicates that the BIMD-Cu film is thicker and also less permeable to the solvent. The film formed by BTA might not be as thick as that of BIMD .It is also possible that the Cu-BTA complex formed is permeable to solvent molecules resulting in a net higher capacitance value for the surface film. The capacitance values for the different azoles obtained are of the order,

BIMD < MBIMD < MBT < IMD < BTA

In the case of 1mM concentration also the same trend is followed. Other analytical techniques are required to conclusively find out the nature of the film.

Figure 21 shows the coverage - time plots for all the azoles at 5mM concentration. We find that at about 800 s more than 95% of the coverage is complete in all the cases.



Figure 21: Plot of coverage (θ) vs. time for copper adsorbed with different azoles in 0.1 N NaOH at 5mM concentration

5.5 Conclusion:

Measurement of electrical double layer capacitance from the imaginary component of impedance provides a simple and effective in situ method of following the adsorption kinetics of alkanethiol molecules on gold surface. The advantage of this method lies in the fact that it is possible to follow the kinetics during the initial stages of adsorption by measuring the capacitance changes at short intervals of time (160 ms). 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. Any meaningful measurement of adsorption kinetics can only be carried out at lower concentrations (< 1 mM). A study of the surface coverage as a function of time at three different concentrations shows that the adsorption follows diffusion controlled Langmuir kinetics at low concentrations (5µM) and Langmuir kinetics at higher concentrations. This behaviour is true of all the five alkanethiols studied in this work. In the case of $1\mu M$ concentration we find that the adsorption is purely diffusion controlled in the initial stages following which it follows diffusion controlled Langmuir kinetics. The variation of capacitance with the inverse of the monolayer thickness is found to be linear. The dielectric constant calculated from the slope is 2.21 which is similar to that of bulk polyethylene indicating the formation of a compact monolayer. 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.

In the case of polycrystalline surfaces we find that the chemically etched surface shows the fastest adsorption kinetics compared to other kinds of surface pretreatments. For gold at 5μ 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. The surface treated with 800 grit emery is found to have the largest capacitance among the different pretreated surfaces.

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 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 reveals that within 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 results indicate that the thickness of the film is highest for Benzimidazole (BIMD) and least for Benzotriazole (BTA).

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