CHAPTER 5

Study on the barrier properties and interfacial properties of SAMs of alkanethiol formed in different non-aqueous solvents

5.0 Introduction :

Ever since the discovery of Self-assembled monolayers (SAMs) of alkanethiol molecules in early eighties [1,2], various non-aqueous solvents have been used to form the monolayers without consideration to the effect that these solvents will have on the barrier properties. There has been voluminous amount of work carried out on the alkanethiol self-assembled monolayers prepared in ethanol, which due to its low toxicity, low cost, and high purity, has been a preferred solvent for the formation of alkanethiol monolayers [1-3] on gold. Several other solvents like hexane, hexadecane, chloroform and acetonitrile have been also used though much less frequently. Bain et al. [4] used contact angle measurements to study the effects of the solvents on the monolayer formation. However, from literature we find that there has not been any detailed electrochemical studies aimed at evaluating the barrier properties of the alkanethiol monolayers formed in different solvents. We show in this chapter that contrary to the general assumption, the effect of adsorbing solvent medium is not trivial to the formation of an effective monolayer, but in fact has a profound bearing on

the nature of the SAM such as its permeability, hydrophobicity and other interfacial properties.

We find in literature that the time duration of dipping the sample in the adsorbing medium often vary from a few hours to several days. It is not clear whether dipping in the adsorbing medium for longer duration actually helps in the formation of better monolayer. This question has been addressed in this chapter.

We have discussed the barrier properties of alkanethiol SAMs formed in different non-aqueous solvents with and without redox species in aqueous media [5] using electrochemical impedance spectroscopy. Recently, Boubour et al. [6] have used electrochemical impedance spectroscopy to measure impedance of thiol adsorbed gold in aqueous electrolyte without any redox species in order to evaluate the ionic insulating property of the monolayer. They have shown that this measurement provides a quick and non damaging method of assessing the SAM quality. We have used similar method to study the barrier properties alkanethiol monolayers prepared in different solvents and assess their quality. Alkanethiol and related SAMs are normally formed in dilute ethanolic solution of the respective thiol usually in millimolar concentration. We have already established that the neat alkanethiol coated Au surface exhibit better property in non-aqueous solvents compared to dilute ethanolic alkanethiol coated Au surface [7]. However, we find from literature that there has been no comparative studies on the permeability of SAMs formed in neat and dilute ethanolic alkanethiol solution. In this chapter, we have characterized and evaluated the barrier properties of the SAMs using electrochemical techniques like cyclic voltammetry and electrochemical impedance spectroscopy as well as non-

electrochemical techniques like Scanning Tunneling Microscopy and Grazing angle FT-IR spectroscopy [8].

The thermodynamic origin of hydrophobic effect is usually attributed to unfavourable free energy of solvation of small non-polar solute molecules such as, for example, hydrocarbons in water. This positive free energy of solvation is due to ordering of water molecules surrounding a hydrocarbon species that results in a decrease of entropy of solvation. This rather significant lowering of entropy of the system dominates over the favourable energy change ($\Delta H < 0$) associated with the hydrogen bond formation. A study of hydrophobic effect is central to many of the biological, chemical and physiological processes like protein folding, coagulation, conformational changes in bio-polymers, micellization, adhesion, nonwetting, froth floatation etc. Recent work on the molecular dynamics simulation studies of water conduction through hydrophobic channel of a carbon nanotube suggests that the behaviour of water at molecular level is quite different from macroscopic regimes [9]. Therefore, a detailed study of hydrophobic interactions at different length scales is desirable in understanding several important chemical and biological processes such as protein folding and water conduction through biological pores of nanometer dimensions [10]. We find that alkanethiol SAMs on gold provide a highly hydrophobic non-polar surface ideal for such a study. In this chapter, we show from our measurements of interfacial capacitance and uncompensated solution resistance in aqueous media that the behaviour of neat alkanethiol SAMs and SAMs formed in hexane and chloroform [11-14] support the predictions of Lum, Chandler and Weeks theory of hydrophobic effect at small and large length scales [15-17].

We have studied the monolayer formation by an anionic surfactant namely sodium dodecyl sulphate (SDS) on the neat alkanethiol coated Au surface. We have followed the rate of coverage of this surfactant monolayer and calculated the equilibrium constant and free energy of adsorption from the adsorption isotherm [13].

5.1 Experimental :

5.1.1 Electrodes and cells

A gold disk electrode of geometric area of 0.002 cm^2 was used as the working electrode for measurement of uncompensated solution resistance from electrochemical impedance spectroscopy in presence of redox species in water. Evaporated gold (~100 nm thickness) on glass with chromium underlayers (2-5 nm thickness) were used as substrates for SAM formation for the impedance study and also for grazing angle FT-Infrared spectroscopy. The substrate was heated to 350 ^{0}C during gold evaporation, a process which normally yields a substrate with predominantly Au (111) orientation. For STM studies, the substrates were prepared using replica technique from the evaporated gold on mica [18]. This is accomplished by electroplating about 200 μm thick copper on the evaporated face of the gold surface and peeling off the plated layer from mica to get a much smoother surface. A conventional three electrode electrochemical cell was used in this study. A platinum foil of large surface area was used as counter electrode. A saturated calomel electrode (SCE) was used as reference electrode in aqueous medium, whereas a silver rod was used as a quasi-reference electrode in formamide. For experiment in ethanol, an electrochemical cell with a provision for SCE in a separate compartment connected by a Luggin capillary was used. Before each experiment, the electrolyte was completely

deaerated by passing oxygen free nitrogen gas. During the experiment, a blanket of nitrogen gas was maintained on top of the solution. The cell was cleaned thoroughly before each experiment and kept in a hot air oven at 100^0C for at least one hour before the start of the experiment.

5.1.2 Electrode pretreatment and thiol adsorption

For uncompensated solution resistance measurement, a gold disk electrode of geometric area 0.002 cm^2 sealed in a glass of compatible thermal expansion coefficient was used. This electrode was polished using aqueous slurries of progressively finer alumina (1.0, 0.3 and 0.05 μm sizes), sonicated to remove alumina particle and finally etched using dilute aqua regia (3:1:4 ratio of concentrated HCl, concentrated HNO_3 and water) for one minute. Evaporated Au substrate was cleaned with piranha solution (1:3 H_2O_2 and conc H_2SO_4), rinsed in millipore water before SAM formation. The SAMs were formed in neat hexadecanethiol (HDT), dodecanethiol (DDT) and decanethiol (DT) by keeping the electrode in the respective liquid for 1 hour, rinsing it in ethanol and finally in Millipore water. The monolayer was also prepared by keeping the substrate in 1 mM alkanethiol in different solvents for 24 hours. The monolayer was also prepared by keeping the gold substrate in 1 mM alkanethiol in ethanol for 1 hour and then kept in water for 6 hours. A hydrophilic monolayer was prepared from neat 11- mercapto 1-undecanol at 40^0 C in a thermostat for 1 hour as it is a solid at room temperature.

5.1.3 Instrumentation

Cyclic voltammetry was carried out using an EG&G potentiostat (Model 263A) interfaced to a PC through a GPIB card (National Instruments). The potential ranges and scan rates used are shown in the respective figures.

The interfacial capacitance of SAM modified electrodes was determined by cyclic voltammetry as described in literature [2,19]. These values are also validated by impedance spectroscopy. The impedance data were also analyzed using the Boukamp's impedance software [20] by fitting to an appropriate equivalent circuit. The capacitance values presented here are for true area after accounting for the roughness factor of 1.5 for the substrate. The true area was determined from the measurement of charge of the oxide stripping peak by potential cycling in 0.1 M perchloric acid. CV measurements were carried out at a scan rate of 1V/s using EG&G 263A potentiostat and Power CV software. The potential was scanned between – 0.10 to +0.20 V vs SCE in 1 M NaF which corresponds to the double layer charging region for this system. The impedance measurements were carried out at a potential of 0.0 V vs SCE in 1 M NaF in water using EG&G 263A potentiostat and SRS 830 Lock-in-amplifier. A pure sine wave of 10 mV amplitude was applied to the cell. Impedance studies in presence of redox species were carried out at the respective formal potential of the redox systems as derived from cyclic voltammetry. The uncompensated solution resistance (R_u) between the working electrode and reference electrode was determined from the high frequency intercept of the Nyquist plot.

STM studies have been carried out using a home built instrument [21] which was calibrated using atomic resolution images of ZYA grade HOPG. An electrochemically etched tungsten tip was used for imaging. The images shown here are raw data images except for plane correction using Scanning probe image processor software (Image Metrology, Denmark). Several images were obtained at different regions of the surface under study in order to confirm the representative character of the images presented in this chapter.

The IR spectra were obtained using FT-IR 8400 model (SHIMADZU) with a fixed 85^0 grazing angle attachment (FT–85; Thermo Spectra-Tech).

Measurement of capacitance from impedance spectroscopy data :

It is well known that interfacial capacitance is extremely sensitive to monolayer thickness and in aqueous medium, a well ordered alkanethiol monolayer on gold has an interfacial capacitance value of the order of 1-2 $\mu F\ cm^{-2}$ depending on the chain lengths.

The electrochemical cell can be modeled as a Randle's equivalent circuit with a parallel combination of double layer capacitance and charge transfer resistance in series with the solution resistance. The impedance of the Randle's equivalent circuit can be expressed as, $Z = Z' - jZ''$ where

$$Z' = R_s + \frac{R_{ct}}{1+\omega^2 C_{dl}^2 R_{ct}^2} \quad \text{and} \quad Z'' = \frac{\omega C_{dl} R_{ct}^2}{1+\omega^2 C_{dl}^2 R_{ct}^2}$$ being the real and imaginary

components of the impedance, R_{ct} and R_s are the charge transfer resistance and solution resistance respectively, C_{dl} 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 $\omega^2 C_{dl}^2 R_{ct}^2 \gg 1$ the imaginary part of the impedance can be approximated as, $Z'' = 1/C_{dl}\omega$. 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 (>10^6 Ω). Thus, 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 [22]. Measurement of the imaginary component of impedance to study the adsorption of alkanethiols has been used by different groups [22-25]. The plot of measured capacitance as a function of frequency exhibits a pseudo-plateau at higher frequencies (>100 Hz) where the measured capacitance

values remain constant. In our analysis, we have measured the capacitance at this region which is more accurate than the single frequency measurement. Using this method, we had earlier shown from the linear plot of capacitance vs chain length of different alkanethiols, [22] the measured capacitance is extremely sensitive to the dielectric thickness of the monolayer.

5.1.4 Chemicals

All the chemicals used in our study are analytical-grade reagents. Ethanol 99.95% (Emerck), lithium perchlorate (Acros Organics), ferrocene (Acros Organics), potassium ferrocyanide (Loba), potassium ferricyanide (Qualigens), sodium fluoride (Qualigens), decanethiol, dodecanethiol, hexadecanethiol, 11-mercapto 1-undecanol (Aldrich), perchloric acid (Qualigens), acetonitrile (Ranbaxy), formamide (SRL), hexane (Emerck), chloroform (Spectrochem), toluene (Ranbaxy), DMF (Spectrochem), hexadecane (Lancaster) were used in our study. Millipore water was used in our study for making aqueous solution.

5.2 Results and discussion :

5.2.1 Evaluation of barrier properties of alkanethiol SAMs formed in different solvents

Fig. 1 shows the Nyquist plot of 1 mM HDT coated evaporated Au electrodes prepared in different solvents for 10 mM ferrocyanide+10 mM ferricyanide in 1M NaF in water measured at 0.240 V vs SCE from impedance spectroscopy. The alkanethiol adsorbed gold electrode dipped in an electrolyte constitutes a metal – dielectric – electrolyte interface. In the absence of any redox species, this interface presents an impedance to the ionic permeation [6]. To evaluate this impedance, we have performed impedance measurements in 1M NaF at a potential of 0.0 V vs SCE. Figure

2 shows the Bode impedance plot of 1 mM HDT coated evaporated Au electrodes prepared in various solvents and measured in 1 M NaF in water. Table 1 shows the impedance values at 0.1 Hz and 1 Hz measured from Bode impedance plots for 1 mM HDT coated evaporated Au electrodes prepared in various solvents at a potential of 0.0 V vs SCE in 1 M NaF. It can be seen from the Nyquist plot that the blocking behaviour of alkanethiol monolayer to ferrocyanide redox reaction varies in the order of hexane>ethanol>acetonitrile>hexadecane in terms of adsorbing medium. This behaviour is also reflected from the impedance values shown in Table 1 for 1 M NaF in water.

Table 1

Impedance values for HDT coated evaporated Au electrode adsorbed in different solvents and measured in 1M NaF in water at 0.0 V vs SCE

SOLVENTS	$Z / \Omega\,cm^2$ @ 0.1 Hz	$Z / \Omega\,cm^2$ @ 1.0 Hz
Neat solventfree thiol	3.6×10^6	4.0×10^5
Ethanol (24 hours)	5.0×10^5	5.7×10^4
Ethanol (1 hour + 6 hours in water)	1.5×10^6	1.6×10^5
n-Hexane	7.5×10^5	1.4×10^5
Chloroform	8.0×10^5	1.3×10^5
Dimethyl Formamide	3.5×10^5	4.9×10^4
Acetonitrile	2.2×10^5	2.9×10^4
Hexadecane	2.0×10^5	2.1×10^4

The monolayers formed in solvents like acetonitrile, DMF, toluene, and hexadecane exhibit lower impedance values than the one formed in ethanol. The monolayer formation is quite often influenced by the intercalation of solvent molecules during adsorption process. This is shown by the low impedance value obtained for SAM formed in large hexadecane molecules, which intercalate into the monolayer during adsorption. In some case, the solvent molecules effectively solvate the alkyl chain of the alkanethiol monolayer and prevent them from forming a compact monolayer as in the case of acetonitrile [26,27]. Ethanol, however, solvates the alkyl chain of alkanethiol monolayer to a lesser extent than acetonitrile. Hence, monolayer formed in ethanol is less permeable and more compact than monolayer formed in acetonitrile, which is highly disorganizing solvent. On the other hand, nonpolar solvents like hexane and chloroform which can neither intercalate nor disorganize by solvation during adsorption, provide ideal environment for highly impermeable monolayer formation.

5.2.2 **Comparative studies on the barrier property and permeability of alkanethiol SAMs formed in neat and dilute ethanolic thiol solution**

Cyclic voltammetric studies

We have evaluated the barrier property of the monolayers by using ferrocyanide as the redox probe in cyclic voltammetry. Figure 3 shows the cyclic voltammogram of 10 mM ferrocyanide in 1M NaF. It can be seen that both neat and 1 mM hexadecanethiol coated gold electrodes block the ferrocyanide redox reaction almost to the same extent. Obviously, the large sized ferrocyanide ions are not so sensitive to the presence of the pinholes and defects possibly present in the monolayer. We therefore, determined the blocking nature of the SAM coated gold electrode by carrying out cyclic voltammetry of Au oxidation and reduction reactions in 0.1 M $HClO_4$. It is

well known that the oxide stripping current provides a quick assessment of the extent of pinholes and defect sites in monolayer, since smaller sized hydroxyl ion should actually come into direct access to the electrode surface through pinholes [2] for the reaction to take place.

Figure 4a (Inset) shows the CV of bare gold electrode in 0.1 M $HClO_4$ with the characteristic features. Figures 4b, 4c and 4d are the 5th scan CVs of gold electrode with monolayers formed by dipping in neat HDT, 1 mM HDT (adsorption in ethanol for 1 hour and kept in water for 6 hours) and 1 mM HDT (adsorption in ethanol for 24 hours) respectively. It can be seen that the measured charges from the oxide stripping peaks (a measure of permeability) are in the order bare gold > 1 mM HDT coated gold > neat HDT coated Au. It can be seen from the figures that the monolayer formed from neat thiol (Figure 4b) shows much better blocking than the one formed in 1 mM HDT in ethanol (Figure 4d). It is also interesting to note from the CV (Figure 4c) that the monolayer formed by just one hour of adsorption in 1mM HDT in ethanol followed by dipping the electrode in water for 6 hours exhibits better barrier property than the monolayer formed by keeping for 24 hours in ethanol. This will be explained in the following section.

Impedance spectroscopic studies

Figures 5A, B and C show the Bode impedance and phase-angle plots for neat HDT, 1 mM HDT (adsorption in ethanol for 24 hours), and 1 mM HDT (adsorption in ethanol for 1 hour and kept in water for 6 hours) respectively. It can be seen from the plot that neat HDT coated Au shows higher impedance (Figure 5A) than the one formed in ethanol for 24 hours (Figure 5B). On the other hand, it can also seen that the monolayer formed by adsorption in ethanolic solution for 1 hour and keeping in water for 6 hours shows (Figure 5C) about three times higher impedance than the one formed

by keeping in ethanolic solution continuously for 24 hours (Figure 5B). It can be also seen from the Bode phase angle plot that both neat HDT coated Au (Figure 5A) and monolayer formed by adsorption in ethanolic solution for 1 hour and keeping in water for 6 hours (Figure 5C) exhibit a 90^0 phase angle over a large frequency range (from 3 Hz to 1 kHz) indicating ideal low leakage capacitive behaviour. On the other hand, ethanolic alkanethiol coated Au exhibits a lower value of phase angle (85^0) implying the capacitor is leaky. All these results clearly prove that neat HDT coated Au is extremely impermeable to ions in aqueous medium compared to dilute ethanolic HDT coated SAM. Evidently, keeping the gold electrode for adsorption in ethanol for a longer time does not help much in the formation of an impermeable monolayer. However, keeping in 1 mM ethanolic solution for a short time (1 hour) ensures adsorption of enough molecules for a complete monolayer coverage and when it is dipped in water for 6 hours, the rearrangement of the adsorbed molecules leads to the formation of a compact monolayer. This happens because, the hydrophobic environment provided by water molecules actually induces the adsorbed thiol molecules to come together. It is well known that the alkanethiol adsorption on gold proceeds in more than one step [4,28,29]. The first step of alkanethiol self assembly, which takes place in a few seconds, is the formation of Au-S bond. The second step has been linked to the strengthening of the alkyl chain. The third and final step which is the slowest, relates to the reorientation of the terminal methyl groups. Our results point to the conclusion that the second and third steps are facilitated by the presence of water molecules.

Grazing Incidence FT-IR Studies

We have carried out grazing angle FT-IR spectroscopy on alkanethiol SAM [8]. Figure 6 shows the C-H region in the IR spectrum of neat and 1 mM HDT coated Au surface. Porter et al. [19] have characterized the alkanethiol monolayers on gold formed in dilute ethanolic medium by grazing angle FTIR. They have carried out a very detailed study of the structure as a function of the chain length. From Figure 6, we can suggest that formation of SAM of alkanethiol does not alter the peak positions compared to the bulk structure. The bands at 2917 and 2850 cm^{-1} are the asymmetric and symmetric C-H stretching modes of CH_2 group, whereas the bands at 2878 and 2964 cm^{-1} correspond to symmetric and asymmetric C-H stretching modes of CH_3 group. It can be also seen that there is almost no change in the peak positions for C-H stretching modes in case of both neat HDT and 1 mM HDT coated Au. However, there is 1 cm^{-1} shift in the peak position of asymmetric C-H stretching mode of CH_2 group (2916 cm^{-1}) for neat HDT coated Au electrode. 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. In particular, the asymmetric CH_2 stretching vibration (d-) at ~2918 cm^{-1} is a useful indicator; its position varies from 2916 or 2917 cm^{-1} for SAMs of exceptional quality. Hence, our IR results indicate the formation of high quality ordered SAM in both neat and 1 mM HDT.

STM Studies on the Permeability of Alkanethiol SAM

Figures 7 A & B illustrate the STM images of 1 mM HDT (adsorbed in ethanol) and neat HDT coated Au surface respectively. It can be seen from the images that the monolayer formed in 1 mM HDT in ethanol exhibits several small sized domains with numerous grain boundary regions (Figure

7 A), whereas neat HDT coated gold surface shows much larger sized domains (Figure 7 B), with less number of grain boundaries. This explains the higher permeability of 1 mM HDT coated surface to ions in aqueous electrolyte compared to neat HDT coated Au surface. These results are in conformity with that of Sun and Crooks [30] who have imaged and characterized a large number of nanometer sized pinholes in their STM studies of alkanethiol monolayers formed in ethanol. We have observed characteristic depressions on the alkanethiol coated Au surface, which are not observed on bare gold. Such depressions were also observed by other research groups [31-33]. The formation of depressions on alkanethiol coated Au surface is due to etching of Au surfaces by alkanethiol during self-assembly process, just like the chemical etching of gold by aqua-regia. Gold surfaces are slowly etched during prolonged deposition; evidence of the etching process has been obtained by analyzing the thiol deposition solutions. Edinger et al. [31] found enough gold in an ethanolic $HSC_{21}CH_3$ deposition solution after 24 hours immersion of a gold substrate correspond to the loss of 3% of a monolayer of gold atoms. Sondag-Huethorst et al. [32] systematically studied the erosive behaviour of thiol deposition solutions. The amount of gold in a 3.5 mM $HSC_{11}CH_3$ methanolic solution increases with deposition time until about 10 min, after which no further increase in gold content is observed. The 10 min deposition time coincides approximately with complete deposition of SAM as observed by STM images and contact-angle measurements. From the correlation between the amount of gold measured in the thiol solution by atomic absorption spectroscopy, the amount of gold corresponds to the total area of the holes in STM images. They concluded that the depressions observed in the STM images are neither pinholes nor defects in the thiol layer, but holes in

outermost layer of the underlying gold substrate. The atomic resolution STM images also showed that the holes are filled with thiol. Although, we have not observed atomic resolution STM images of alkanethiol coated Au surfaces, we have observed similar depressions on thiol coated gold. Thus, our result supports the observation of Sondag-Huethorst et al [32].

5.2.3 Existence of a hydrophobic gap at the Alkanethiol SAM-water interface

Interfacial Capacitance Study

Figure 8 illustrates the Bode phase angle plot of neat HDT coated gold electrode in 1M NaF showing 90° phase angle over a wide frequency range, a behaviour indicative of a low leakage ideal capacitor. Figure 9 shows the plot of capacitance as a function of frequency for neat HDT coated Au, which exhibits no dispersion with frequency (Capacitance remains more or less constant throughout the whole frequency range). From the impedance studies, the capacitance for neat HDT coated gold electrode is measured to be $0.31 \, \mu F \, cm^{-2}$ (with a S.D. of $0.04 \, \mu F \, cm^{-2}$ for 6 samples). It can be seen from Table 2 that there is a good correspondence in capacitance values as measured by cyclic voltammetry and impedance spectroscopy for different systems. However, the capacitance value of $0.31 \, \mu F \, cm^{-2}$ (from impedance) obtained for neat HDT is abnormally low compared to $1.45 \, \mu F \, cm^{-2}$ obtained for the same thiol coated electrode prepared in 1 mM ethanolic HDT. It is worth noting that the value obtained for 1 mM HDT is close to the theoretically expected value based on the chain length and orientation of HDT SAM. A capacitance lowering of this large magnitude in the case of neat HDT SAM may be intuitively attributed to multilayer formation during adsorption.

Table 2

Capacitance of different thiol coated gold electrodes using Cyclic voltammetry (CV) and Impedance spectroscopy

System	$C / \mu F \, cm^{-2}$ (from CV)	$C / \mu F \, cm^{-2}$ (from Z)
Neat HDT in 1M NaF in water	0.29	0.31
Neat HDT in 0.1M LiClO$_4$ + ethanol	1.50	1.55
Neat HDT in 1M NaF +3 mM SDS + water	1.10	1.04
1 mM (in ethanol) HDT coated in 1M NaF + water	1.42	1.45
Neat Decanethiol in 1M NaF +water	0.55	0.51
Neat Dodecanethiol in 1M NaF +water	0.35	0.34
Neat 11-Mercapto 1–undecanol in 1M NaF + water	2.10	2.00
Neat HDT in 0.1 M LiClO$_4$ + formamide	0.59	0.55
1 mM (in ethanol) HDT coated in 0.1 M LiClO$_4$ + formamide	1.35	1.32
1 mM (in hexadecane) HDT coated in 1 M NaF+water	2.54	2.50

However, the expected capacitance of 1.55 $\mu F \, cm^{-2}$ measured for neat HDT coated electrode in 0.1M LiClO$_4$ in a non-aqueous medium of *ethanol*

rules out such a possibility. It is therefore felt that some hitherto unknown factor is affecting the measured capacitance of neat thiol coated electrode in aqueous media. This result can not be explained by a simple parallel plate model of double layer with the alkanethiol monolayer as the sole dielectric separator.

In order to explain this phenomenon, we propose a model for the SAM – electrolyte interface in which the extremely hydrophobic alkanethiol film repels water molecules adjacent to it and in the process creating a gap between the monolayer film and water. This effectively increases the overall thickness of the dielectric layer that is manifested as an abnormally low value of interfacial capacitance. Although, there are several theoretical models [34,35] and experimental studies [36-42] on hydrophobicity and water structure near hydrophobic surfaces, we believe that this behaviour can be satisfactorily explained by Lum, Chandler and Weeks theory of length scale dependent hydrophobicity [15-17]. According to Lum, Chandler, Weeks theory (LCW Theory), '*hydrophobicity*' is length scale dependent. When hydrophobic surfaces are too small (or the concentration of hydrophobic species too low), the energetic cost is insufficient to cause segregation. Instead, a different hydrophobic interaction occurs, which acts only weakly and only on small length scales. Weak short-ranged hydrophobic effects have been understood on the basis of a theory developed by Pratt and Chandler [34]. The theory tells that the mutual attractions between water are so favourable that hydrogen bonded water structure still persists in presence of a small hydrophobic species. This is true in case of aqueous solvation of small hydrophobic molecule like butane or butanol. However, the nature of hydrophobicity changes for an extended hydrophobic surface, leading to the depletion of hydrogen bonds. It is this energetic

effect, the loss of hydrogen bonding, that leads to the segregation of oil from water. This is relevant to the solvation of macromolecules like protein. This kind of depletion effect was anticipated long ago by Stillinger [35].

For small hydrophobic units consisting of apolar solutes, the water molecules can reorganise around them without sacrificing their hydrogen bonds. In the close vicinity of small hydrophobic units, the possible configurations of hydrogen bonding may be restricted, but the overall amount of hydrogen bonding remains relatively unchanged. So the solvation free energy of the system is largely entropic and not enthalpic and solvation free energy is proportional to the volume of hydrophobic unit. However, for an extended hydrophobic unit, the existence of hydrogen bonded water close to it is geometrically unfavourable. Hence, the energetic cost of assembling hydrophobic units is significantly more favourable than the entropic cost of keeping them separate. In this case, the solvation free energy of the hydrophobic unit is largely enthalpic and is proportional to the surface area of the interface between the unit and water. The most important implications of the LCW theory is the predictions for the solvation free energy (also known as excess chemical potential) of a hard sphere. This free energy is shown by the plot of excess chemical potential per unit surface area exposed to water as a function of hard sphere radius R (Figure 10). For a value of R beyond 2 nm, this quantity is roughly constant, slightly higher than the free water-vapour interfacial free energy (Surface tension). For large radii, a thin water vapour layer exists between the boundary of sphere and surrounding liquid. Thus, for extended hydrophobic surfaces, there is a net depletion of water molecules at the vicinity leading to the creation of a thin water vapour layer at the interface. The process is called *'drying transition'* and the phenomenon *'drying effect'*.
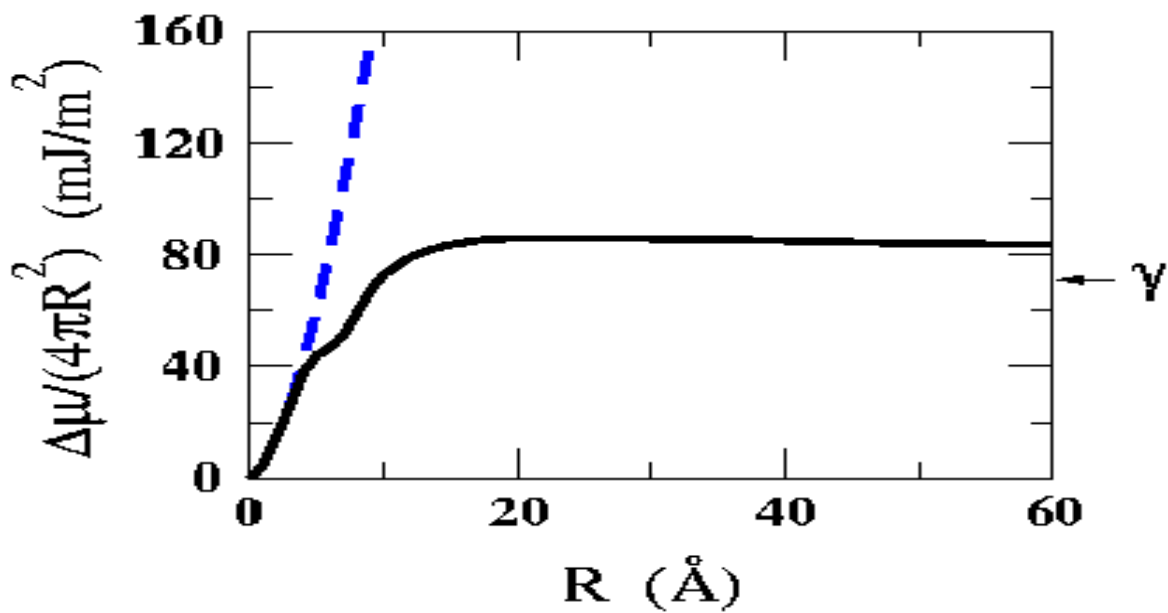
Figure 10

Drying transition;Plot of Excess chemical potential as a function of hard sphere radius

In our case, neat HDT coated Au electrode in water behaves as an extended hydrophobic surface which may induce a *Drying transition*, creating a thin water vapour gap at the interface. The thin vapour layer acts as an additional dielectric separator that is in series with the dielectric film formed by alkanethiol molecules. Such a series combination, effectively increases dielectric separation and lowers the interfacial capacitance of the monolayer in an aqueous medium.

However, it can be seen from Table 2 that the SAM formed in 1 mM HDT in ethanol has a capacitance value that corresponds to a wetting monolayer calculated on the basis of its chain length and orientation. This can be attributed to the large number of pinholes and grain boundaries present in the SAM formed in ethanol. This conclusion is confirmed by our STM studies as discussed previously.

The above conclusion is also corroborated by our impedance studies based on the equivalent circuit model described by Protsailo and Fawcett

[43]. The equivalent circuit consists of the resistance of the monolayer expressed as R_{SAM} in parallel with a constant phase element CPE usually represented as Q. This combination is in series with uncompensated solution resistance R_u. The values of different components of the above mentioned equivalent circuit are shown in Table 3. We have obtained a very high value of R_{SAM} for neat HDT SAM, namely, 24.7 $M\Omega$ cm^2 (Table 3), while 1 mM HDT SAM shows a R_{SAM} value of 2.9 $M\Omega$ cm^2, which is almost an order of magnitude less than the value obtained for neat HDT SAM. This is obviously due to the leakage of capacitive charge through the pinholes and defects in 1 mM HDT SAM (which is represented by lower value of R_{SAM}).

Table 3

Values of different components of the equivalent circuit R(QR) obtained from the fitting of impedance data for HDT coated evaporated gold electrode measured in 1 M NaF in water at 0.0 V vs SCE
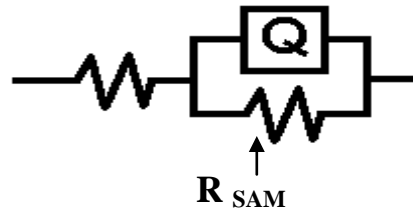
System	R_u /Ω cm^2	Q/Ω^{-1} cm^{-2} s^n	n	R_{SAM} /$M\Omega$ cm^2
Neat HDT coated Au	2.14	0.27	0.98	24.7
1 mM HDT coated Au (in ethanol)	3.37	2.09	0.94	2.9

Q values shown here are after consideration of roughness factor

We conclude from the capacitance values obtained using CV and impedance experiments and also from the STM images that the dilute ethanolic HDT coated gold *does not* form an extended hydrophobic unit essential to induce drying effect. Instead, this SAM surface consists of a large number of tiny hydrophobic domains around which the hydrogen bonded liquid water structure can continue to coexist, a process in conformity with LCW theory of hydrophobicity at small length scales. It is possible to estimate the capacitance of the thin water vapour layer due to this drying effect. If we model the neat HDT capacitance, (C_{neat}= 0.31 μF cm^{-2}) as an effective capacitance due to a series combination of wetting SAM (C_{film} of 1 mM HDT = 1.45 μF cm^{-2}) and that of the thin water vapour layer (C_{vap}) or (C_{gap}) then, since

$$(C_{neat})^{-1} = (C_{film})^{-1} + (C_{vap})^{-1}$$

the capacitance C_{vap} of the thin water vapour layer can be calculated to be 0.39 μF cm^{-2}. Figure 11 A shows the schematic representation of the presence of hydrophobic gap between the alkanethiol SAM-water interface. We have calculated the possible dimension of this interfacial gap. Since, the capacitance of a dielectric film is given by the expression C = ε ε_0 / d, where ε_0 the permittivity in free space which is 8.854× 10^{-12} farad/ m and assuming a value of ε =1 for the hydrophobic gap (assuming air is present in the gap), we obtain the width of the gap d to be about 2.2 nm. The actual dimension of this gap is possibly much larger than this, as ε of any water vapour present within this gap will be much higher. Further experimental work is required to determine the exact dimension and composition of this interfacial gap. However, it is worth pointing out that such a hydrophobic gap is absent when the SAM is hydrophilic, formed

using a neat hydroxy terminated thiol. This is schematically shown in Figure 11B. In this case, the measured interfacial capacitance corresponds to almost the exact chain length of the thiol.

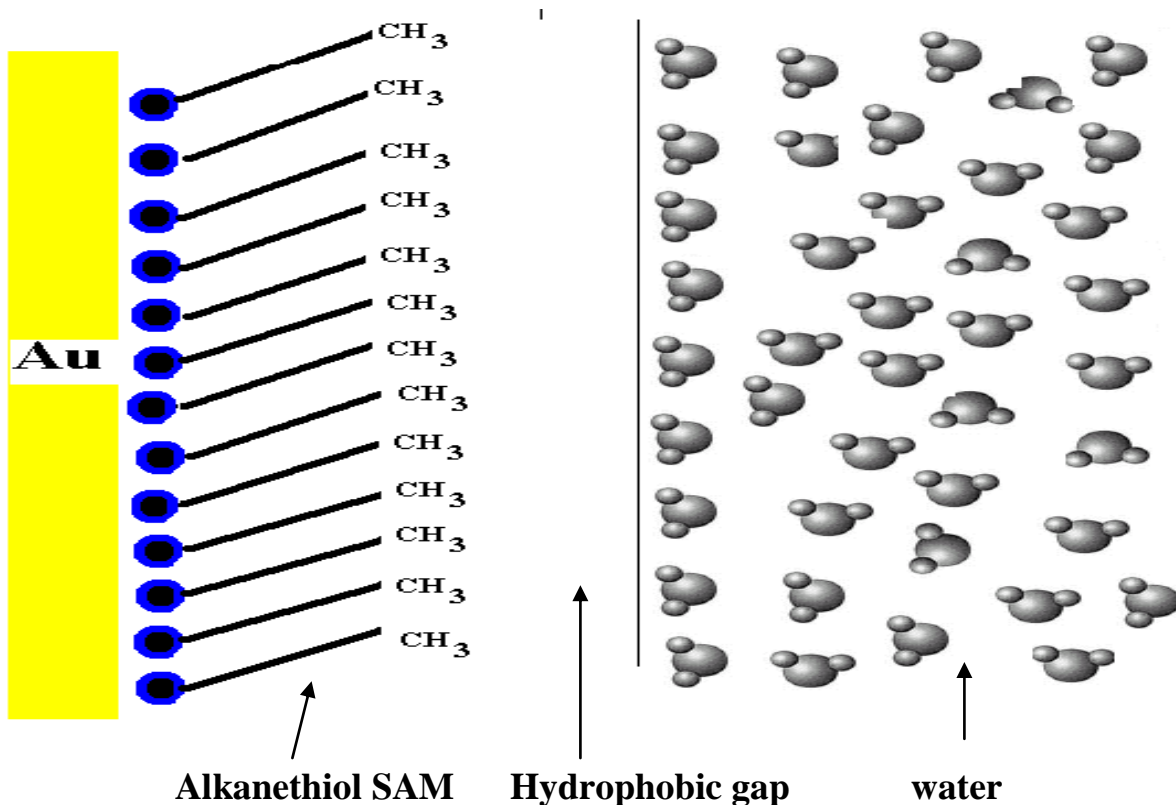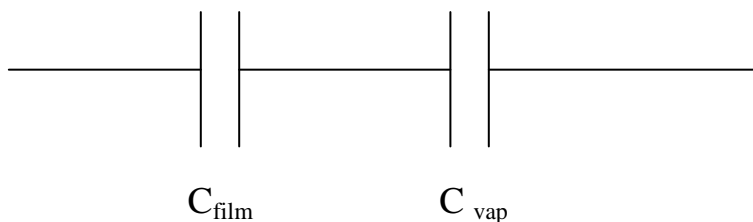**Alkanethiol SAM   Hydrophobic gap   water**

Figure 11 A

Neat HDT Coated Au surface in aqueous media acts as extended hydrophobic surface creating a hydrophobic gap at the interface due to drying transition

C_{film} C_{vap}

$$(C_{neat})^{-1} = (C_{film})^{-1} + (C_{vap})^{-1}$$

Table 2 also shows the capacitance values for the SAMs formed in three neat alkanethiols and a neat hydroxy terminated thiol. The low capacitance

values measured for the three alkanethiols are consistent with our earlier discussions.
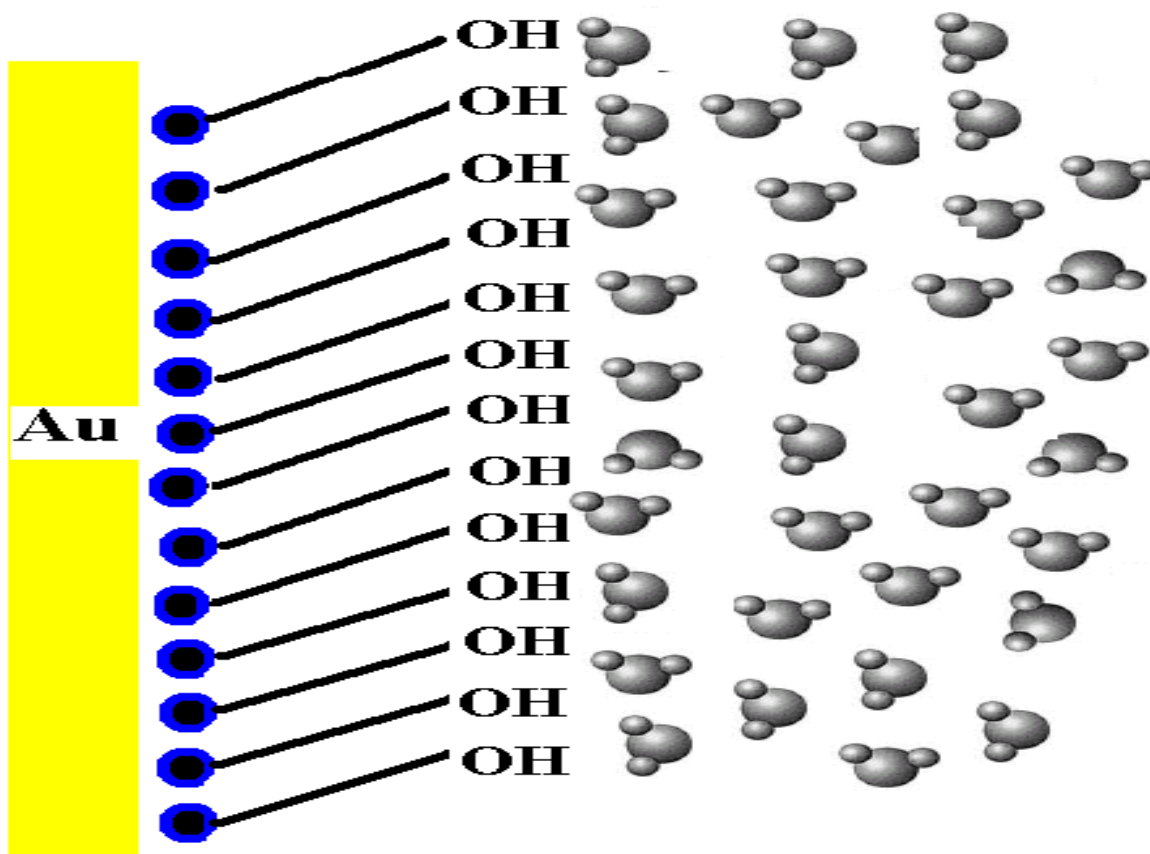

Figure 11 B

Hydrophilic hydroxy thiol SAM, showing absence of hydrophobic gap

We have carried out CV and impedance studies of neat 11− mercapto 1−undecanol coated and neat dodecanethiol coated electrodes in 1M NaF. These two thiols have almost the same chain lengths but different terminal functional groups. From the CVs shown in Figure 8, we obtain for the neat dodecanethiol coated electrode a capacitance of 0.35 μF cm^{-2} and for the hydroxy terminated 11−mercapto 1−undecanol, a much higher value of 2.1 μF cm^{-2} which is in agreement with that obtained by Chidsey and Loiacono [44]. Unlike the alkanethiol SAM, the monolayer formed from hydroxy thiol is hydrophilic which means that there is no hydrophobic gap to decrease the

measured capacitance. Interestingly, in a solvophilic medium like ethanol, which can solvate the alkyl tail of alkanethiol monolayer, such hydrophobic forces do not exist even for neat HDT coated electrode [7]. This explains the normal capacitance value that corresponds closely to the theoretically expected value based on the chain length and orientation of HDT monolayer in ethanol as electrolytic medium as can be seen from Table 2.

We find from our studies that the phenomenon of "Drying Effect" is not unique to water alone but is generally true for other non aqueous solvents with extensive hydrogen bonded network. For example, in the case
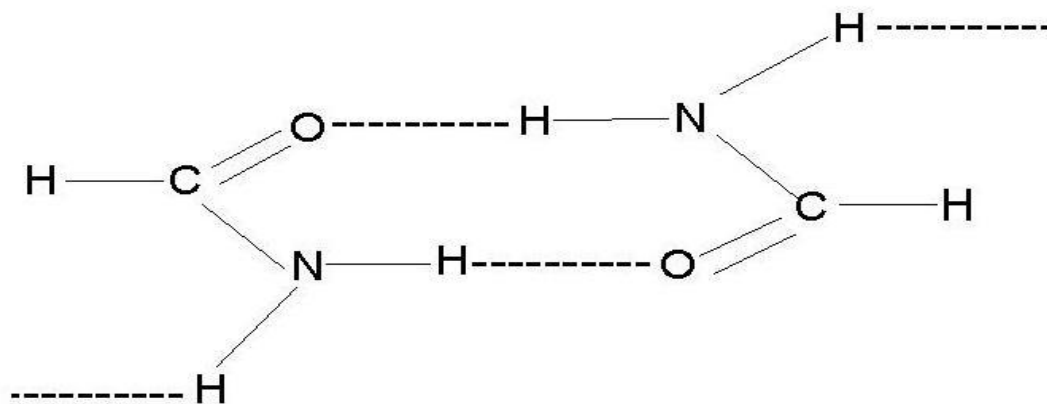
Two- dimensional (layered) structure of formamide

of formamide which has a two dimensional network of hydrogen bonded molecules [45,46], the capacitance of neat hexadecanethiol coated gold electrode is quite low as can be seen from Table 2. It is worth mentioning that such a capacitance lowering is not observed in the case of many non-hydrogen bonded non-aqueous solvents such as acetonitrile and propylene carbonate. These results suggest that there is a clear correlation between hydrophobicity and strong hydrogen bonding within the solvent medium.

In literature, we find that Plieth et al. [47] have suggested the possible existence of extended double layer structures in case of highly hydrophobic organic adsorbates coated electrode-aqueous electrolyte interface in general terms. Our results based on the interfacial capacitance data show the experimental realisation of this possibility in a simple hydrophobic system of alkanethiol SAM on gold in water.

Since, there is a strong evidence for the existence of *nanometer size gap* at the interface, we explored the possibility of filling this gap with a long chain amphiphilic species which can act as a bridge. We have therefore, formed an additional monolayer of SDS (Sodium dodecyl sulphate, an anionic surfactant) on neat HDT coated gold surface. Usually, such a bilayer formation (SDS+HDT on gold) should decrease the capacitance provided the dielectric constant of the interface does not change significantly. Surprisingly, the interfacial capacitance value increases instead of decreasing as is to be normally expected for any bilayer formation (addition of 3 mM SDS to neat HDT coated electrode actually increases the capacitance of the interface from the initial value of 0.31 μF cm^{-2} to 1.04 μF cm^{-2}). This seemingly anomalous behaviour fits in very well with our model of a hydrophobic gap between the neat alkanethiol coated SAM-water interface prior to SDS addition. Being amphiphilic, the added SDS molecules can now occupy this gap, bridging the polar water molecules and hydrophobic methyl group of alkanethiol as shown schematically in the Figure 12. The increase in the measured capacitance of the interface upon the addition of SDS implies either a *decrease* in the thickness of the dielectric interface or an *increase* in its dielectric constant or possibly both. At this juncture, it is difficult to speculate which of these factors is actually responsible for this increase of the capacitance value.
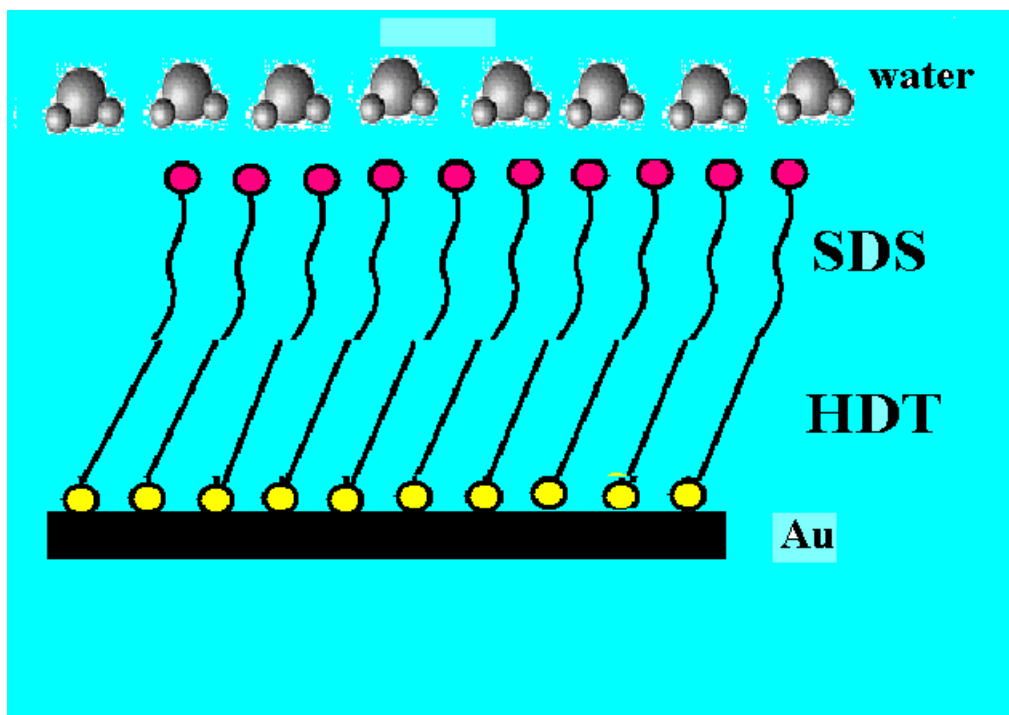
Figure 12

Schematic representation of the bridging of the hydrophobic gap between alkanethiol SAM -water interface due to the formation of monolayer of anionic surfactant SDS on neat HDT coated evaporated gold electrode.

Measurement of adsorption isotherm of SDS on neat HDT coated Au

The adsorption of the SDS molecules on neat HDT coated surface can be followed by measuring the capacitance of the interface at different concentrations of SDS. The coverage θ is calculated using the formula [48] $\theta = (C_0 - C_t) / (C_0 - C_f)$ where C_0 is the capacitance of the thiol adsorbed gold electrode, C_f the capacitance of the SDS bilayer at limiting coverage and C_t is the capacitance at any concentration of SDS.

Figure 13 shows the adsorption isotherm, where θ is plotted against the concentration of SDS. The shape of the curve shows that the adsorption may follow the Langmuir adsorption isotherm. The Langmuir adsorption isotherm can be expressed as [48],

$$Bc = \frac{\theta}{1-\theta}$$

where c is the concentration of inhibitor, θ is the fractional surface coverage, B is the modified adsorption equilibrium constant [49,50] related to the molar free energy of adsorption ΔG as,

$$B = \frac{1}{c_{solvent}} \exp\left(\frac{-\Delta G}{RT}\right)$$

where $c_{solvent}$ is the molar concentration of the solvent which in the case of water is 55.5 M^{-1}. The constant B determines the equilibrium constant governing the partition of the solute, in this case surfactant, between the surface layer and the bulk phase.

The Langmuir adsorption isotherm can be rearranged to obtain the following expression:

$$\frac{c}{\theta} = \frac{1}{B} + c$$

Hence, a plot of $\frac{c}{\theta}$ versus c should yield a straight line with intercept of $\frac{1}{B}$ if the adsorption is Langmuirian. Figure 13 shows such a plot for SDS adsorption on HDT. The almost perfect straight line confirms that the adsorption follows Langmuir isotherm. From the plot, we obtain an equilibrium constant B and free energy of adsorption ΔG as 9807 M^{-1} and - 32.7 kJ mol $^{-1}$ respectively. The rather high value of free energy of adsorption suggests that the process is driven by strong hydrophobic interaction between terminal hydrophobic groups of alkanethiol and SDS.
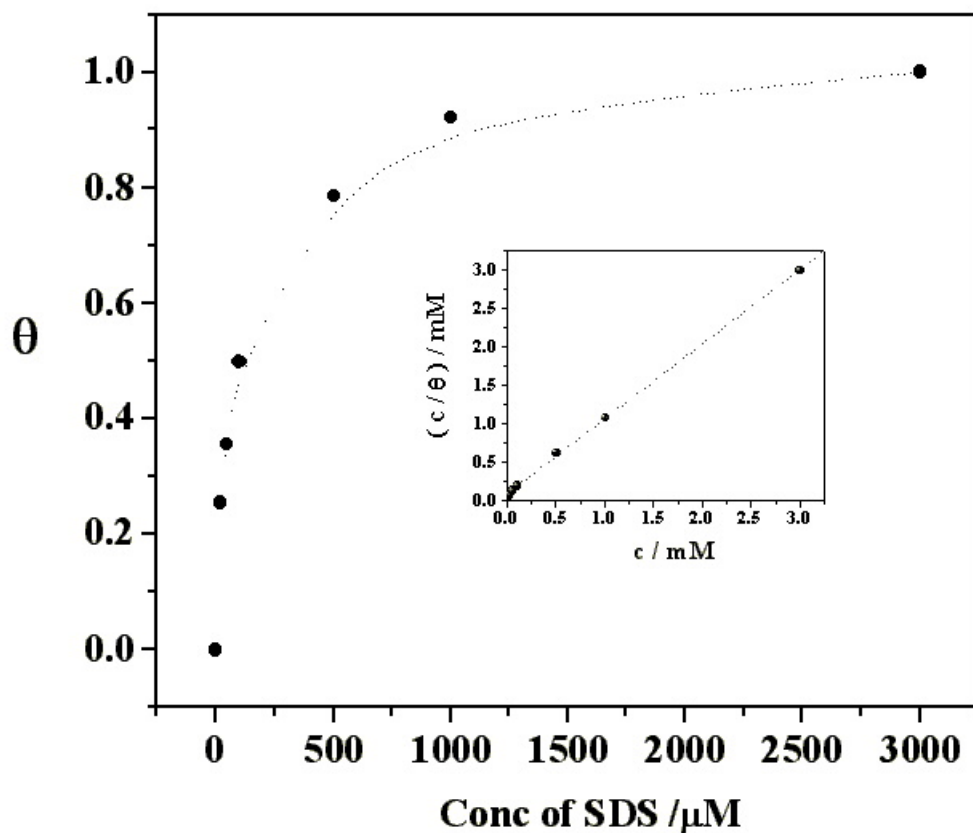
Figure 13

*Plot of coverage of SDS over neat HDT coated monolayer on evaporated gold electrode as a function of concentration of SDS. **Inset :** Fit of the coverage vs concentration data with Langmuir isotherm.*

5.2.4 <u>Effect of solvents as adsorption media on the interfacial capacitance of alkanethiol SAM measured in aqueous media</u>

Capacitance studies provide important information on the nature of the interface and helps to model it in terms of equivalent circuit. The capacitance values obtained from the imaginary component of the measured

impedance are shown in Table 4. Capacitance values were also determined by cyclic voltammetry. It can be seen from Table 4 that there is a good correspondence in capacitance values as measured by cyclic voltammetry and impedance spectroscopy for different systems. In the case of solvents

Table 4

Capacitance values for HDT coated evaporated Au electrode adsorbed in different solvents and measured in 1M NaF in water at 0.0 V vs SCE by cyclic voltammetry and impedance spectroscopy

Solvents	$C/\ \mu F\ cm^{-2}$ from CV	$C/\ \mu F\ cm^{-2}$ from Impedance
Ethanol(24 hours)	1.42	1.45
Ethanol (1 hour+ 6 hours in water)	0.90	0.92
n-Hexane	0.58	0.54
Chloroform	0.87	0.86
Toluene	0.96	0.94
Dimethyl formamide	1.44	1.42
Acetonitrile	1.90	1.86
Hexadecane	2.54	2.50

like ethanol and DMF, we find that the measured capacitance values of 1 mM HDT coated gold electrodes in 1 M NaF is close to the expected value of 1.4 μF cm^{-2} assuming a Helmholtz parallel plate model for the double layer. However, in case of solvents like acetonitrile and hexadecane, measured capacitance values of 1 mM HDT coated gold electrodes in 1 M NaF were found to be very high (Table 4). The differences in the capacitance values among these adsorbing solvents may be due to the varying levels of defects and pinholes in the monolayer which is brought about by various factors like intercalation or solvation of solvent molecules. This is especially true in the case of the electrode adsorbed in acetonitrile medium which is known to solvate the monolayer extensively, thereby showing a larger capacitance [26,27]. It can be seen from Table 4 that the capacitance obtained for the SAM formed in hexadecane is much larger than the SAM adsorbed in other solvents. This result can be explained as being due to the intercalation of large hexadecane molecules into the monolayer during the adsorption, a process already reported by Bain et al. [4]. The intercalated solvent molecules prevent the effective packing of the thiol molecules, resulting in an imperfect monolayer. This is manifested in the increased capacitance as now the ions of the electrolyte have closer access to the electrode. The capacitance obtained in the case of SAM adsorbed in DMF shows the expected value implying that there is little or no intercalation or solvation of solvent molecules in this case. Surprisingly, however, the capacitance values measured for monolayers formed in hexane and to some extent in chloroform and toluene are unusually low.

A lower value of measured capacitance than calculated on the basis of the parallel plate model is usually attributed to a multilayer film formation. However, the expected capacitance value measured for thiol coated

electrode in an electrolytic solvent like ethanol rules out any such possibility. For example, 1 mM HDT monolayer formed in hexane has a capacitance value of 0.54 μF cm^{-2} in aqueous medium, whereas the same monolayer shows 1.43 μF cm^{-2} in 0.1 M LiClO$_4$ + ethanol. Similar behaviour was observed in case of neat alkanethiol coated Au surface measured in water and formamide [11]. This behaviour can be satisfactorily explained by Lum, Chandler, and Weeks theory of hydrophobicity [15-17], where hydrophobicity is length scale dependent as mentioned previously.

In our case, monolayers formed in solvents like hexane, chloroform, and toluene behave as extended hydrophobic units as observed from their unusually low capacitance values measured in aqueous electrolyte. These systems may induce drying transition, which possibly produces hydrophobic gap in the form of thin water vapour layer adjacent to alkanethiol coated surfaces. This water vapour layer acts as a hydrophobic shield to the ions of aqueous electrolyte. As a result, an extended double layer structure is formed which is different from normal parallel plate model. This thin water vapour layer acts as a capacitor in series with the dielectric film formed by alkanethiol molecule. This tends to lower the effective interfacial capacitance of the monolayer. Thus, the unusual low capacitance value for HDT coated surface formed in hexane and chloroform actually manifests such powerful hydrophobic forces causing drying transition. We have calculated the capacitance of thin water vapour layer due to drying transition in HDT SAMs adsorbed in solvents like hexane, chloroform and toluene. Table 5 shows the value of capacitance of hydrophobic shield in the form of thin water vapour layer. If we model the net HDT capacitance (C_{net}= 0.54 μF cm^{-2} for the SAM formed in hexane) as an effective capacitance due to a

series combination of wetting SAM (C_{film} of 1 mM HDT = 1.45 μF cm^{-2}) and that of the thin water vapour layer (C_{vap}) or (C_{gap}) then, since

$$(C_{net})^{-1} = (C_{film})^{-1} + (C_{vap})^{-1}$$

the capacitance C_{vap} of the thin water vapour layer can be calculated to be 0.86 μF cm^{-2}.

Table 5

Capacitance values of the "*Hydrophobic gap*" due to "*Drying Transition*" in different systems measured by impedance spectroscopy

$$(C_{net})^{-1} = (C_{film})^{-1} + (C_{vap})^{-1}$$

System	C_{net} /μF cm^{-2}	C_{film}/μF cm^{-2}	C_{vap}/μF cm^{-2}
Neat HDT coated Au	0.31	1.45	0.39
1 mM HDT coated Au (1 hour in ethanol+6 hours in water)	0.92	1.45	2.52
1 mM HDT coated Au (adsorbed in hexane)	0.54	1.45	0.86
1 mM HDT coated Au (adsorbed in chloroform)	0.86	1.45	2.11
1 mM HDT coated Au (adsorbed in toluene)	0.94	1.45	2.67

It is also significant that the SAM which was adsorbed in ethanol for a short time (1 hour) and dipped in water for 6 hours shows not only very high impedance, but also relatively lower capacitance than the electrode which was dipped in ethanol for 24 hours (Table 4). This again points to the formation of more hydrophobic SAM in the former just like alkanethiol SAMs formed in neat thiol and solvents like hexane, chloroform, toluene. Our results clearly show that the interfacial property like interfacial capacitance of a hydrophobic surface is dependent on the nature of hydrophobicity which is also dependent on the nature of adsorption medium.

Uncompensated Solution Resistance Measurements

We also show here from the unusual high values of uncompensated solution resistance measured in aqueous electrolyte, the possible existence of an interfacial gap for the HDT monolayer prepared in hexane and neat liquid thiol. For example, we have obtained a resistance of 200 Ω in our cell for the bare gold disk electrode in 10 mM ferrocyanide + 10 mM ferricyanide in 1 M NaF in water at +0.240 V vs SCE. However, in the case of HDT coated SAMs prepared in hexane and neat liquid thiol, the measured resistance values are 936 Ω and 836 Ω respectively. Since, the electrolyte NaF has a very high conductivity and the conductivity of this electrolyte is same in both bare and alkanethiol coated gold electrode, the large increase in the uncompensated solution resistance can be attributed to the possible existence of the hydrophobic gap at the interface of the SAMs prepared in hexane and neat liquid thiol. It is interesting to note that the alkanethiol SAM prepared in ethanol as adsorbing medium does not show any increase in the

resistance value (198 Ω) pointing to the absence of any hydrophobic gap in this case. Similarly, we have observed high resistance value for neat HDT coated SAM for 1 mM ferrocene + 1 mM ferricenium in 0.1 M LiClO$_4$ in formamide (Table 6).

Table 6

Uncompensated solution resistance (R$_u$) of alkanethiol coated gold electrodes measured from the impedance spectroscopy for 1 mM ferrocene + 1 mM ferricenium in 0.1 M LiClO$_4$ in formamide at 0.0 V vs SCE

System	R$_u$/ Ω
Bare gold	1063
Neat HDT coated Au	4540
1mM HDT coated Au (adsorbed in ethanol)	1065

This result is also in conformity with the results of capacitance studies we discussed earlier.

5.3 Conclusions :

The following conclusions can be inferred from our studies :

1. Our impedance and cyclic voltammetry results show that the permeability and the barrier properties of alkanethiol SAM in aqueous medium depend to a large extent on the solvent used as adsorption medium. Highly impermeable monolayers of alkanethiol are formed in

solvents like hexane and chloroform compared to the monolayers formed in solvents like ethanol, DMF, acetonitrile, hexadecane and toluene.

2. We find that neat alkanethiol coated Au surface is more impermeable and exhibits better barrier properties in aqueous medium compared to dilute ethanolic alkanethiol coated surface. Our impedance results prove this for the first time and these results were supported by our STM observations. The better barrier properties of neat alkanethiol SAMs compared to 1 mM alkanethiol monolayer in ethanol is due to the formation of larger hydrophobic domains by neat HDT coated Au surface.

3. Our results show that when the adsorption of thiol is carried out in ethanol for a short time of 1 hour and the specimen is later kept in water for 6 hours, there is a large increase in impedance of the film showing an excellent barrier properties. This can be explained as arising out of the strong hydrophobic interaction among the alkanethiol molecules in water which helps to bring together the alkyl chains more tightly to form a compact monolayer.

4. We also find that alkanethiol SAMs formed in neat thiol and solvents like hexane and chloroform exhibit abnormally low interfacial capacitance and high uncompensated solution resistance values, which suggests the possible existence of a "hydrophobic gap" between the alkanethiol SAM-water interface.While our results support the predictions of Lum, Chandler and Weeks theory of length scale dependent hydrophobicity, we are aware that further studies, possibly spectroscopic, need to be carried out to evaluate the exact nature and composition of the interfacial gap.

REFERENCES

1. R.G.Nuzzo, D.L.Allara, *J.Am.Chem.Soc.*, 105 (1983) 4481

2. H.O. Finklea, *Electrochemistry of Organized Monolayers of Thiols and Related Molecules on Electrodes*, A.J.Bard and I.Rubinstein (Eds.), Marcel Dekker, New York, 1996

3. A. Ulman, *An introduction to ultrathin organic films*, Academic Press: San Diego, 1991, 286

4. C.D.Bain,E.B.Troughton, Y.Tao, J.Evall, G.M.Whitesides, R.G.Nuzzo, *J.Am.Chem.Soc.,* 111 (1989) 321

5. U.K.Sur, V.Lakshminarayanan, *Proc.of seventh International Symposium on Advances in Electrochemical Science and Technology*, SAEST, CECRI, INDIA, 27-29 November, Chennai, 2002, p B1-B4

6. E.Boubour, R.B.Lennox, *Langmuir*, 16 (2000) 4222

7. U.K.Sur, V.Lakshminarayanan, *J. Electroanal. Chem.*, 516 (2001) 31

8. U.K.Sur, V.Lakshminarayanan, *Proc.of seventh International Symposium on Advances in Electrochemical Science and Technology*, SAEST, CECRI, INDIA, 27-29 November, Chennai, 2002, p B24-B27

9. G.Hummer, J.C. Rasaiah, J.P. Noworyta, *Nature,* 414 (2001) 188

10. O.Beckstein, P.C. Biggin, M.S.P. Sansom, *J.Phys.Chem.B,* 105 (2001) 12902

11. U.K.Sur, V.Lakshminarayanan, *J. Colloid.Interface. Sci.*, 254 (2002) 410

12. U.K.Sur, V.Lakshminarayanan,(communicated to *J. Electroanal. Chem.)*

13. U.K.Sur, V.Lakshminarayanan, (To be published in *Pramana*)

14. U.K.Sur, V.Lakshminarayanan, (To be published in *Proceedings of 203rd Meeting of The Electrochemical Society,* Paris, France, April 27-May 2, 2003, AC2-2513)

15. K. Lum, D. Chandler, J.D.Weeks, *J.Phys.Chem.B,*103 (1999) 4570

16. D.Chandler, *Nature,* 417 (2002) 491

17. P.Ball, *H$_2$O: A Biography of Water*, Phoenix, London, 1999

18. J.Diebel, H.Lowe, P.Samori, J.P.Rabe, *Appl.Phys.A*, 73 (2001) 273

19. M.D.Porter, T.B.Bright, D.L.Allara, C.E.D.Chidsey, *J.Am.Chem.Soc.*, 109 (1987) 3559

20. B.A.Boukamp, *Equivalent Circuit Software*, Perkin Elmer, 2nd Edition

21. V.Lakshminarayanan, *Curr.Sci.*, 74 (1998) 413

22. R.Subramanian, V.Lakshminarayanan, *Electrochim. Acta.,* 45 (2000)501

23. T.M.Nahir, E.F.Bowden, *Electrochim. Acta.,* 39 (1994) 2347

24. C.Frubose, K.Doblhofer, *J.Chem. Soc. Faraday Trans.,* 91 (1995) 1949

25. D.Yan, J.A.Saunders, G.K.Jennings, *Langmuir* 18 (2002) 10202

26. M.R.Anderson, M.N.Evaniak, M.Zhang, *Langmuir*, 12(1996) 2327

27. A.Kudelski, P. Krysinski, *J. Electroanal. Chem.,* 443 (1998) 5

28. R.F.De Bono, G.D. Loucks, D.D. Manna, U.J.Krull, *Can.J.Chem.,* 74 (1996) 677

29. M.Himmelhaus, F.Eisert, M.Buck, M.Grunze, *J.Phys.Chem.* B., 104 (2000) 576

30. L.Sun, R.M.Crooks, *J.Electrochem.Soc.*, 138 (1991) L23

31. K.Edinger, A.Golzhauser, K.Demota, Ch. Woll, M.Grunze, *Langmuir*, 9 (1993) 4

32. J.A.M. Sondag-Huethorst, C.Schonenberger, L.G.J.Fonnink, *J.Phys. Chem.*, 98 (1994) 6826

33. C.Schonenberger, J.A.M. Sondag-Huethorst, J.Jorritsma, L.G.J.Fonnink, *Langmuir*, 10 (1994) 611

34. L. R. Pratt, D. Chandler, *J. Chem. Phys.,* 67 (1977) 3683

35. F. H. Stillinger, *J. Solution Chem.,* 2 (1973) 141

36. H.K.Christenson, P.M.Claesson, *Science,* 239 (1988) 390

37. W.A.Ducker, Z.Xu, J.N.Israelachvili, *Langmuir,* 10 (1994) 3279

38. J.L.Parker, P.M.Claesson, P.J.Attard, *J.Phys.Chem.,* 98 (1994) 8468

39. R.M.Pashley, P.M.McGuiggan, B.W.Ninham, D.F.Evans, *Science,* 229 (1985) 1088

40. H.K.Christenson, P.M.Claesson, *Adv. Colloid Interface. Sci.,* 91 (2001) 391

41. L.F.Scatena, M.G.Brown, G.L.Richmond, *Science,* 292 (2001) 908

42. X. Zhang, Y. Zhu, S. Granick, *Science,* 295 (2002), 663

43. L. V. Protsailo, W.R.Fawcett, *Electrochim. Acta.*, 45 (2000) 3497

44. C.E.D.Chidsey, D.N.Loiacono, *Langmuir*, 6 (1990) 682

45. J.Israelachvili, *Intermolecular and Surface Forces*, 2nd edition, Academic Press , London ,1997, p 122

46. C.Reichardt, *Solvents and Solvent effects in Organic chemistry*, 2nd edition, VCH, New York,1990, p14

47. W.Plieth, W.Kozlowski, T. Twomey, *"Adsorption of Molecules at Metal Electrodes"* Chapter 5, p 269 (VCH, New York, 1992) J.Lipkowski, P.N.Ross (Eds.)

48. J.Lipkowski, P.N.Ross (Eds.), *Adsorption of Molecules at Metal Electrodes,* VCH, New York, 1992, p 91,186

49. B.B.Damaskin, O.A.Petrii, V.V. Batrakov, in *Adsorption of Organic Compounds on Electrodes,* Plenum Press, New York,1971

50. B. Kronberg, *J.Colloid.Interface. Sci.,* 96 (1983) 55