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Hydrophobicity-induced drying transition in alkanethiol self-assembled monolayer–water interface

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Abstract. During the course of our investigation of the electron transfer properties of some redox species through highly hydrophobic long chain alkanethiol molecules on gold in aqueous and non-aqueous solvents, we obtained some intriguing results such as unusually low interfacial capacitance, very high values of impedance and film resistance, all of which pointed to the possible existence of a nanometer size interfacial gap between the hydrophobic monolayer and aqueous electrolyte. We explain this phenomenon by a model for the alkanethiol monolayer–aqueous electrolyte interface, in which the extremely hydrophobic alkanethiol film repels water molecules adjacent to it and in the process creates a shield 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. This behaviour is very much akin to the 'drying transition' proposed by Lum, Chandler and Weeks in their theory of length scale dependent hydrophobicity. For small hydrophobic units consisting of apolar solutes, the water molecules can reorganize around them without sacrificing their hydrogen bonds. Since for an extended hydrophobic unit, the existence of hydrogen bonded water structure close to it is geometrically unfavourable, there is a net depletion of water molecules in the vicinity leading to the possible creation of a hydrophobic interfacial gap.

Keywords. Hydrophobicity; hydrophobic gap; self-assembled monolayer; length scale dependent hydrophobicity; interfacial capacitance; uncompensated solution resistance.

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1. Introduction

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 the 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, non-wetting, froth floatation etc. In 1959, Kauzmann identified hydrophobic interactions as a primary source of protein stability [1] which was later confirmed by X-ray crystallography. 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 [2]. 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 [3]. We find that alkanethiol self-assembled monolayers (SAMs) on gold provide a highly hydrophobic non-polar surface ideal for such a study [4,5].

The process of the formation of SAMs of alkanethiol on gold is very simple. A clean, fresh gold substrate is immersed into a dilute solution of alkanethiol in an organic solvent. The time of immersion varies from a few minutes to several hours. The concentration of the thiol molecules and the immersion time of the substrate in the adsorption solvents play a very important role in the self-assembly process. Typically, the concentration of the thiol is at millimolar levels, although concentration from micromolar to neat liquid thiols have been reported in literature. Ethanol has been the most common solvent for the formation of alkanethiol monolayers on gold, although several other solvents like tetrahydrofuran, acetonitrile, hexane etc. have been used by different groups. In addition to simple alkanethiol SAMs, monolayers with different terminal functional groups, aromatic thiols, thiol with attached polymers, lipids, proteins, peptides and redox centers have been studied. In 1983, Nuzzo and Allara [6] published the first paper that deals with the formation of organized self-assembled monolayer of dialkyl sulphide on gold. Since the discovery of SAMs of alkanethiol, there has been several reports in literature describing the methods of obtaining the most blocking and highly oriented monolayers on gold. Most of these efforts focus on varying different parameters of self-assembly process like substrate morphology, substrate cleanliness, substrate pre-treatment, alkanethiol concentration, adsorption time, adsorption solvent, alkanethiol purity etc. [4,5].

The process of self-assembly of alkanethiol on the surface of gold is known to occur in three steps. The first step is the chemisorption of the head group onto the substrate. In a molecular self-assembly process, the bonding can be covalent as in the case of alkyltrichlorosilanes on hydroxylated surfaces or covalent but slightly polar as in alkanethiol monolayers on gold. The energies associated with such chemisorption process are of the order of tens of kJ mol^{-1} (in the case of thiolate on gold it is about 200 kJ mol^{-1}). The next step is the inter-chain van der Waals interactions among the alkyl groups, where the energy associated with it is a few kJ mol^{-1}. The third and the final step is the reorientation of the terminal groups.

Self-assembled monolayers of alkanethiols form a $(\sqrt{3} \times \sqrt{3})\mathrm{R}30^\circ$ overlayer structure on Au (111) surfaces as observed from the electron diffraction and scanning tunneling microscopic (STM) studies [7,8]. This means that the vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ which define the adsorbate unit cell is longer than $\mathbf{b}_1$ and $\mathbf{b}_2$ of the Au (111) substrate unit cell by a factor of $\sqrt{3}$ and the angle between $\mathbf{b}_1$ and $\mathbf{a}_1$ vectors (also $\mathbf{b}_2$ and $\mathbf{a}_2$ vectors) is 30°. The spacing between the adjacent sulphur atoms in this structure (4.99 Å) is about three times larger than the van der Waals diameter of sulphur atom (1.85 Å). This distance is also greater than the distance of closest approach of the alkyl chains (4.24 Å). Therefore, the chains tilt by an angle 30° with respect to surface normal to maximize their van der Waals interactions [9]. Depending on the chain length and the terminal group, various superlattice structures are superimposed on the $(\sqrt{3} \times \sqrt{3})\mathrm{R}30^\circ$ overlayer structure. The most common superlattice is the $c(4 \times 2)$ reconstruction.

Such organized SAMs of alkanethiol molecules exhibit several interesting properties and have several potential applications like corrosion inhibitions, lubrications, wetting, sensors, molecular electronics etc. The monolayers provide an ideal model systems for studying the role of different molecules in biological membranes and have contributed to a large extent in the field of long range electron transfer, wetting, protein adsorption, and molecular recognition [10–12].

Recently, using the interfacial capacitance data, we have demonstrated the possible existence of a thin hydrophobic gap between alkanethiol SAM–1 M NaF aqueous electrolyte interface, when the monolayer is prepared in neat alkanethiol on gold [13]. In a normal metal–aqueous electrolyte interface, the measured differential capacitance is considered to be a series combination of parallel plate Helmholtz capacitance C_{H} and Gouy–Chapman diffuse layer capacitance C_{GC}. For a sufficiently concentrated electrolyte, $C_{\mathrm{GC}} \gg C_{\mathrm{H}}$ especially for an electrode covered by a thin organic film such as a long chain self-assembled monolayer of alkanethiol. If a well-ordered alkanethiol monolayer alone is a sole dielectric film, the interfacial capacitance value is of the order of 1–2 μF cm^{-2} depending on its chain length. From our work, we find that when the alkanethiol SAM is prepared from a neat liquid thiol instead of the usual solvent-based thiol, the measured interfacial capacitance is unusually low. This phenomenon cannot be explained by a simple parallel plate model normally invoked to describe the structure of alkanethiol SAM-coated Au electrode–electrolyte interface. In this paper, we show that the enhancement of the neat alkanethiol SAM-coated gold–electrolyte interfacial film resistance measured in aqueous media very much supports our earlier conclusions. Moreover, our studies lead us to believe that such a hydrophobic gap is also created at the alkanethiol SAM–water interface, when the monolayers are formed in solvents like hexane and chloroform. Interestingly enough, addition of a surfactant like sodium dodecyl sulphate (SDS) results in the formation of an additional monolayer on neat HDT (hexadecanethiol)-coated gold 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.

2. Experimental

The evaporated gold (∼100 nm thickness) on glass with chromium underlayers (2–5 nm thickness) were used as substrates for SAM formation for the impedance studies. The substrate was heated to 350°C during gold evaporation, a process which normally yields a substrate with predominantly Au (111) orientation. For the measurement of monolayer film resistance, a gold disk electrode with a geometric area of 0.002 cm^2 sealed in soda lime glass of compatible thermal expansion coefficient was used. For STM studies, the substrates were prepared using replica technique from the evaporated gold on mica [14]. 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. 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 monolayers were prepared by keeping the gold substrates in 1 mM alkanethiol in hexane and chloroform as adsorption media for 24 h. Final rinsing of the SAM-coated substrate was carried out in respective pure solvent and finally in millipore water. Monolayer was also prepared in neat alkanethiol, which is liquid at room temperature.

It is well-known that interfacial capacitance is extremely sensitive to monolayer thickness. In the absence of redox species, the gold–SAM–electrolyte interface behaves as an ideally polarizable interface. Thus R_{ct} for this system is very large $(>10^6\ \Omega)$ and we can show [15,16] that in this case, by choosing appropriately large enough frequency, the imaginary component of impedance is directly related to the double layer capacitance as $Z'' = 1/C_{\text{dl}}\omega$. Measurement of the imaginary component of impedance to study the adsorption of alkanethiols has also been used by different groups [15–18]. Using this method, we had earlier shown from the linear plot of capacitance vs. chain length of different alkanethiols, that the measured capacitance is extremely sensitive to the dielectric thickness of the monolayer [15]. The plot of the measured capacitance of the SAM 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 normally employed. The capacitance values presented here are for true area after accounting for the roughness factor of 1.5 for the substrate after potential cycling in 0.1 M perchloric acid. 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 the 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 [19], 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.

All the chemicals used in our study are analytical-grade reagents. Millipore water was used in our study for making aqueous solutions.

3. Results and discussion

Table 1 shows the interfacial capacitance values of neat and 1 mM HDT (hexadecanethiol)-coated (adsorbed in ethanol, hexane, and chloroform) evaporated gold electrodes measured from the impedance spectroscopy at 0.0 V vs. SCE in 1 M NaF in water. It can be seen

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

Solvents	C/μF cm^{-2}
Ethanol	1.45
Hexane	0.54
Chloroform	0.86
Neat liquid thiol	0.31

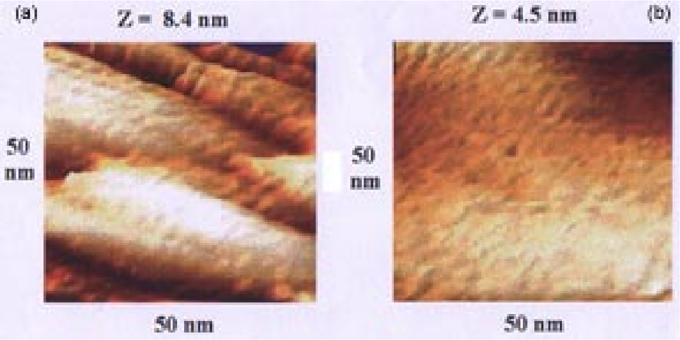

Figure 1. Constant current STM images. Tunneling current: 0.5 nA, bias voltage: sample +100 mV, scan range: 50 nm × 50 nm. (**a**) 1 mM HDT-coated gold (24 h in ethanolic solution) shows numerous domains acting as small hydrophobic units. (**b**) Neat HDT-coated gold with larger domains acts as an extended hydrophobic surface.

that the capacitance values measured for monolayers formed in neat thiol and solvents like hexane and chloroform are unusually low, compared to the capacitance values for monolayer formed in ethanol.

A lower value of measured capacitance than the one calculated on the basis of the parallel plate model can be 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 $0.54\,\mu\mathrm{F\,cm}^{-2}$ in aqueous medium, whereas the same monolayer shows a capacitance value of $1.43\,\mu\mathrm{F\,cm}^{-2}$ in 0.1 M $\mathrm{LiClO_4}$ + ethanol. Similar behaviour was observed in the case of neat alkanethiol-coated Au surface measured in water and formamide [13]. Although, there are various theoretical models [20,21] and experimental studies [22–28] on hydrophobicity and water structure near hydrophobic surfaces in literature, we believe that this unusual behaviour can be satisfactorily explained only by Lum, Chandler and Weeks (LCW) theory of length scale dependent hydrophobicity [29,30]. According to this theory, for small hydrophobic units consisting of apolar solutes, the water molecules will be able to reorganize around them without sacrificing their hydrogen bonds. For this case, the solvation free energy is largely entropic and is proportional to the volume of hydrophobic unit. This model explains the case of a monolayer that is formed in ethanol producing a SAM with several defects and pin holes that act as numerous small hydrophobic units around which hydrogen bonded liquid water structure can continue to coexist [13].

Figures 1a and 1b show STM images of 1 mM HDT (ethanolic) 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 1a), whereas neat HDT-coated gold surface shows much larger sized domains (figure 1b), with less number of grain boundaries. These results are in conformity with that of Sun and Crooks [31] who have imaged and characterized a large number of nanometer-sized pinholes in their STM studies of alkanethiol monolayers formed in ethanol. This explains the higher permeability of the 1 mM HDT-coated surface (formed in ethanol) to ions in aqueous electrolyte compared to that of neat HDT surface. This conclusion is confirmed by our impedance studies on neat and ethanolic HDT SAMs as discussed below.

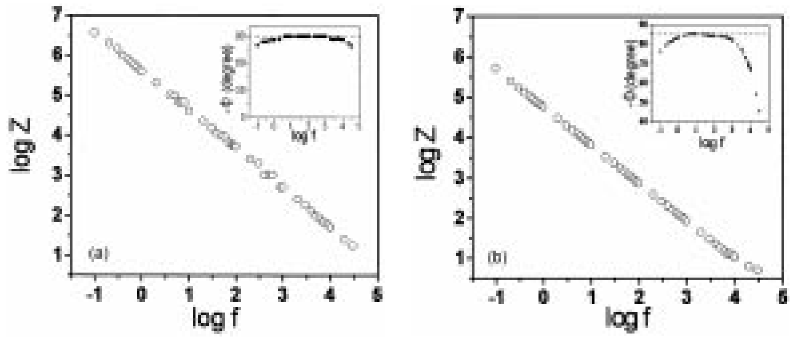

Figure 2. Bode impedance and phase-angle (inset) plots for (**a**) neat HDT and (**b**) 1 mM HDT (adsorbed in ethanol) coated Au in 1 M NaF in water at 0.0 V vs. SCE.

Figures 2a and 2b show the Bode impedance and phase-angle plots for neat HDT and 1 mM HDT-coated Au in 1 M NaF in water respectively. It can be seen from the plot that neat HDT-coated Au shows higher impedance compared to 1 mM HDT-(adsorbed in ethanol) coated surface in water. It can also be seen from Bode phase-angle plot that neat HDT-coated Au exhibits 90° phase angle over a large frequency range, indicating ideal capacitive behaviour. On the other hand, ethanolic alkanethiol-coated Au exhibits a lower value of phase angle (85°) implying that the capacitor is somewhat leaky.

From the above results it can be inferred that the neat HDT-coated Au is extremely impermeable to ions in aqueous medium compared to dilute ethanolic HDT-coated SAM and acts as a hydrophobic wall or a so-called extended hydrophobic unit. For such a surface, the previously described model breaks down, as existence of hydrogen bonded water around it is now geometrically unfavourable. This leads to a net depletion of water molecules at the vicinity leading to the creation of a thin water vapour layer at the interface, a process known as 'drying transition'. The cause for such a transition has been attributed to an increase in the solvation-free energy for a large non-polar surface in proportion to its surface area which eventually approaches the value close to liquid water–vapour surface tension. This results in the creation of a thin water vapour gap at the interface.

It is not just the monolayer formed in neat alkanethiol which exhibits this drying transition. Such a phenomenon is also found in the case of monolayers formed in solvents like hexane and chloroform which behave as extended hydrophobic units as observed from their unusually low capacitance values measured in aqueous electrolyte. The SAMs prepared in these solvents may induce drying transition in an aqueous electrolyte, possibly producing 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, a 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 molecules which tends to lower the effective interfacial capacitance of the monolayer from its normal values observed in ethanolic alkanethiol SAM.

We conclude from the capacitance values obtained using 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

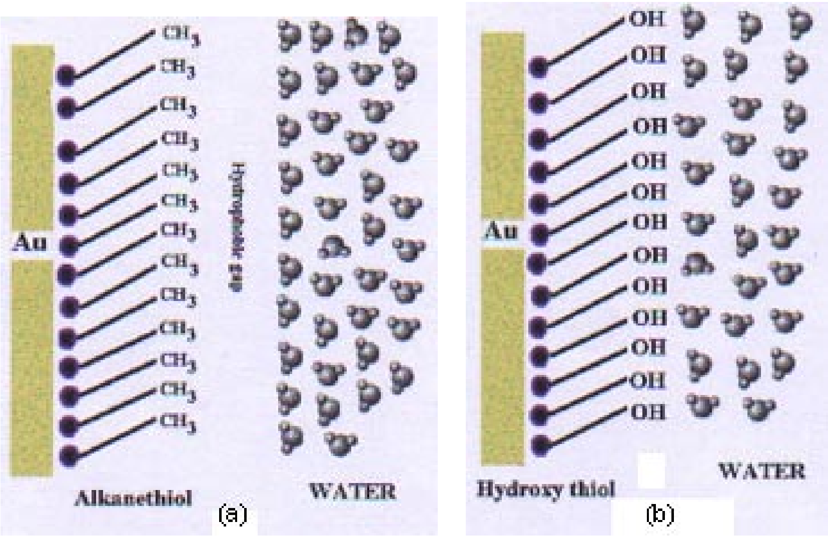

Figure 3. (**a**) Schematic representation of the hydrophobic gap between alkanethiol–SAM water interface when the SAM is formed from hydrophobic alkanethiol. (**b**) Schematic representation of the interface between hydrophilic hydroxythiol and water.

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 ($C_{\text{neat}} = 0.31\ \mu\text{F cm}^{-2}$) as an effective capacitance due to a series combination of wetting SAM (C_{film} of HDT SAM $= 1.25\ \mu\text{F cm}^{-2}$) and that of the thin water vapour layer (C_{vap}) then, since

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

the capacitance C_{vap} of the thin water vapour layer can be calculated to be 0.39 $\mu\text{F cm}^{-2}$. Figure 3a 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. As the capacitance of a dielectric film is given by the expression $C = \varepsilon\varepsilon_0/d$ where ε_0 is the permittivity in free space which is 8.854×10^{-12} F m^{-1} and assuming a value of $\varepsilon = 1$ for the hydrophobic gap (assuming air is present in the gap), we obtain the width of the gap d to be about 2.1 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 3b. In this case, the measured interfacial capacitance corresponds to almost the exact chain length of the thiol.

In literature, we find that Plieth *et al* [32] have suggested the possible existence of extended double layer structures in the 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 realization of this possibility in a simple hydrophobic system of alkanethiol SAM on gold in water.

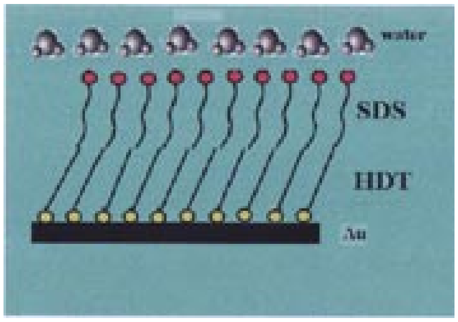

Figure 4. Schematic representation of the bridging of the hydrophobic gap between alkanethiol–SAM water interface due to the formation of monolayer of anionic surfactant SDS on neat HDT-coated evaporated gold electrode.

We also show here, from the unusual high values of alkanethiol film 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 film 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. As the electrolyte NaF has a very high conductivity and the conductivity of this electrolyte is the 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. This result is also in conformity with the results of capacitance studies we discussed earlier.

As 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 an anionic surfactant sodium dodecyl sulphate (SDS) on neat HDT-coated gold surface. Usually, such a bilayer formation (SDS + HDT on gold) should decrease the interfacial 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. 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 figure 4. 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.

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

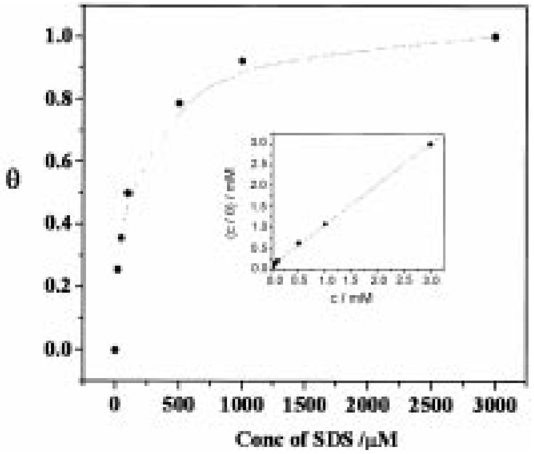

Figure 5. Plot of coverage of SDS over neat HDT-coated monolayer on evaporated gold electrode as a function of concentration of SDS. Inset: Fit of the coverage vs. concentration data with Langmuir isotherm.

θ is calculated using the formula [33] $\theta = (C_0 - C_t)/(C_0 - C_f)$ 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 the capacitance at any concentration of SDS.

Figure 5 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 [33],

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

where c is the concentration of the inhibitor and θ the fractional surface coverage. B is the modified adsorption equilibrium constant [34,35] related to the molar free energy of adsorption ΔG as,

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

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 c/θ vs. c should yield a straight line with intercept of $1/B$ if the adsorption is Langmuirian. Figure 5 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.

4. Conclusions

We find that alkanethiol SAMs formed in solvents like hexane and chloroform and neat liquid thiol exhibit abnormally low interfacial capacitance and high film resistance values, which suggests the existence of a 'hydrophobic gap' between the alkanethiol SAM–water interface due to 'drying transition'. While these studies 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. From our interfacial capacitance studies, we find that an anionic surfactant such as sodium dodecyl sulphate adsorbs on neat HDT-coated gold surface and occupies the hydrophobic gap. We have followed the variation of surface coverage with concentration of SDS from capacitance data and show that the process can be described by the Langmuir adsorption isotherm.

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