# Evidence for a 'Hydrophobic shield ' between the Alkanethiol SAM and aqueous electrolyte

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The suggestion that there can exist a hydrophobic shield between a hydrophobic organic adsorbed film on an electrode surface and an aqueous electrolyte stems from the fact that the water cannot extend the hydrogen bonding network around an extended hydrophobic surface (1). This phenomenon though suggested on theoretical grounds has not been experimentally proved so far though there have been suggestions in literature implying such a possibility (2). By the measurement of interfacial capacitance of a dielectric interface consisting of alkanethiol SAM on gold and an aqueous electrolyte, we show that there exists a thin nanometer size gap at the interface which can account for the observed results. We base our conclusions on the measurement of interfacial capacitance of three hydrophobic SAMs of Hexadecanethiol ,dodecanethiol ,decanethiol as well as a hydrophilic SAM of a hydroxy thiol adsorbed on a gold surface.

We have used evaporated gold (~100 nm thickness) on glass substrates for SAM formation. The samples were prepared by keeping the electrodes in the respective liquid for 1 hour and also in 1mM alkanethiols in several non-aqueous solvents for 24 hours. A hydrophilic monolayer was prepared from neat 11 mercapto 1-undecanol at $40^0$ C in a thermostat for 1 hour. The interfacial capacitance of SAM modified electrodes was determined both by cyclic voltammetry and impedance spectroscopy as described in literature. The potential was scanned between –0.10 to +0.20 V Vs SCE in 1M NaF. The Impedance measurements were carried out at a potential of 0.0 V Vs SCE in 1 M NaF in water .

From the impedance studies, the capacitance for neat HDT coated gold electrode is measured to be 0.23 $\mu$F $cm^{-2}$ . It can be seen from Table 1 that thia capacitance value for neat HDT is abnormally low compared to 1.42 $\mu$F $cm^{-2}$ obtained for the same thiol coated electrode prepared in 1 mM HDT in ethanol. It is worth noting that the value obtained for 1mM HDT is close to the theoretically expected value based on the chain length and orientation of HDT SAM .

It can also be seen from the Table I that the monolayers formed in solvents like acetonitrile, DMF, toluene, and cyclohexane exhibit lower impedance values than the one formed in ethanol showing a relatively higher permeability. Significantly, in the case of solvents like ethanol, DMF, hexadecane, toluene and cyclohexane, 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 1.1 - 1.4 $\mu$F $cm^{-2}$ assuming a Helmholtz parallel plate model for the double layer. The differences in the values among these solvents arises due to the varying levels of defects in the monolayer which is brought about among other factors by the intercalation of solvent molecules. This is especially true in the case of the electrode adsorbed in acetonitrile and hexadecane as solvents which are known to intercalate extensively within the monolayer thereby showing a larger capacitance . Surprisingly, we find that the capacitance values measured for monolayers formed in n-hexane, toluene and chloroform are quite low. Our results are also supported by the observation of unusually high resistance between the neat thiol SAM coated gold working electrode and reference electrodes compared to bare gold electrode. This phenomenon is again the direct consequence of the thin layer created at the interface which effectively increase the resistance ( $R_u$ ). This property is exhibited by SAMs formed in neat thiols as well as thiol adsorbed in certain solvents like hexane, chloroform and toluene.

**Table 1: Impedance and interfacial capacitance ( measured in 1 M NaF) of gold electrodes coated with hexadecanethiols adsorbed in different solvents**

| Solvents | $Z / \Omega\ cm^2$ @ 0.1 Hz | Capacitance ( $\mu Fcm^{-2}$ ) |
|---|---|---|
| Neat | $3.64 \times 10^6$ | 0.23 |
| Ethanol | $5.00 \times 10^5$ | 1.45 |
| n-Hexane | $7.5 \times 10^5$ | 0.54 |
| Chloroform | $8.00 \times 10^5$ | 0.86 |
| DMF | $3.50 \times 10^5$ | 1.42 |
| Toluene | $2.70 \times 10^5$ | 0.94 |
| Acetonitrile | $2.20 \times 10^5$ | 1.86 |
| Hexadecane | $1.68 \times 10^5$ | 2.50 |
| Cyclohexane | $1.00 \times 10^5$ | 1.28 |

The capacitance formed by 11-Mercapto - 1 – undecanol which has a hydrophilic hydroxy tail group shows the expected value of 2.10 $\mu Fcm^{-2}$ calculated on the basis of the chain length. This shows that this monolayer undergoes complete wetting. We explain this phenomenon using 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 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 effect" 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 close to it is geometrically unfavorable, it leads to a net depletion of water molecules at the vicinity leading to the creation of a thin water vapor layer at the interface. In our case, neat HDT coated Au electrode in water behaves as an extended hydrophobic surface which induces a so called drying transition. This thin vapor 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.

## References:

1. Lum, K.; Chandler, D.; Weeks, J.D. *J.Phys.Chem.B* **1999**, 103, 4570-4577
2. W.Plieth, W.Kozlowski and T.Twomey in *Adsorption of Molecules at Metal Electrodes* 269-270 Ed. Jacek Lipkowski and Philip N.Ross VCH Publishers Inc., **(1992)**
3. U.K.Sur and V.Lakshminarayanan *J.Colloid Interface Sci* **2002**, 254 , 410-413