

CHAPTER 8

In this chapter, we are summarising some of the important results and conclusions derived from them. We also briefly discuss the scope for further work. The work described in this thesis can be broadly classified as:

1. Studies on the barrier properties of alkanethiol Self-assembled monolayers (SAMs) in different non-aqueous electrolytic solvents.
2. Electrochemical studies on SAMs of some dithiols, hydroxy and carboxylic acid and amino thiols on gold.
3. Studies on the interfacial and barrier properties of the alkanethiol SAMs formed in different non-aqueous solvents and measured in aqueous and non-aqueous electrolytic solvents.
4. Studies on the barrier properties of alkanethiol coated gold microelectrodes.
5. Studies on the behaviour of SAM of thiocholesterol on gold as nanoporous assembly, array of microelectrodes and potential application as sensor of copper ions.

- 1. Studies on the barrier properties of alkanethiol Self-assembled monolayers (SAMs) in different non-aqueous electrolytic solvents.**

- a) We find that the alkanethiol monolayers are quite stable in solvents as electrolytic medium studied in this work, namely propylene carbonate, acetonitrile, formamide, acetic acid, DMF, DMSO and ethanol.

- b) However, solvents such as propylene carbonate and acetonitrile disorganise the monolayer due to their ability to solvate the methylene groups of alkanethiol. The ferrocene redox reaction in these solvents is unimpeded essentially due to the ability of the redox species to penetrate through the vacant spaces available in between randomly oriented thiol molecules.
- c) More ordered solvents such as formamide, acetic acid and water however, block the electron transfer reaction, a phenomenon that can be ascribed to their internal order due to hydrogen bonding that leads to strong solvophobic interaction among the terminal methyl groups of the alkanethiol.
- d) There is a clear correlation between the internal order of solvent molecules with the structural integrity and barrier properties of organic thiol monolayers.
- e) Neat alkanethiol SAMs exhibit excellent barrier properties in non-aqueous media compared to the monolayers formed in ethanol.

2. Electrochemical studies on SAMs of some dithiols, hydroxy and carboxylic acid and amino thiols on gold.

- a) From the measurements of interfacial capacitance values for dithiol coated gold surface, it can be inferred that the dithiol molecules are most likely to be adsorbed with only one sulphur atom bonded to gold resulting in a vertical orientation.
- b) From our cyclic voltammetry and impedance studies with ferrocene redox probe in acetonitrile, we conclude that (1,4-benzenedimethane thiol) BDMT molecules can form more organized monolayers on gold

than aliphatic octanedithiol SAMs due to extremely strong lateral van der Waals interaction among the phenyl rings.

- c) The barrier properties of the hydroxy and carboxylic acid thiol SAMs in different electrolytic non-aqueous solvents are related to both the structure of the thiol monolayers and solvents. Hence, in terms of the blocking behaviour of the hydroxy and carboxylic acid thiol monolayers to ferrocene redox reaction, the solvents can be arranged in the order, formamide \cong ethanol $>$ propylene carbonate \cong acetonitrile.
- d) Blocking behaviour of ionic SAMs towards ionic electroactive species depends on the pH of the electrolytic solution and applied potential.

3. Studies on the interfacial and barrier properties of the alkanethiol SAMs formed in different non-aqueous solvents and measured in aqueous and non-aqueous electrolytic solvents.

- a) 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.
- b) 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.

- c) 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.
- d) 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.

4. Studies on the barrier properties of alkanethiol coated gold microelectrodes.

- a) We have fabricated disk shaped gold and platinum microelectrodes with diameters of 10-50 μm by sealing sodalime glass with metal microwires and characterized by performing cyclic voltammetry in aqueous and acetonitrile solution. We have observed the characteristic sigmoidal voltammogram, from which we have calculated the electrode dimensions.

- b) We have studied the barrier properties of SAM modified ultramicroelectrodes using ferrocene/ferricenium redox couple in acetonitrile, ferrocyanide/ferricyanide redox couple in water, and ferrocyanide in ethanol+water mixture and also studied on the effect of solvents on the barrier properties of alkanethiol SAMs formed on microelectrodes.
- c) Our CV results of ferrocyanide redox reaction in ethanol+water mixture of different composition with alkanethiol coated Au microelectrodes suggest that increasing the water composition in ethanol+water mixture reduces the extent of disorganization (increase in barrier efficiency B.E. of ferrocyanide reaction) of alkanethiol coated Au surface.

5. Studies on the behaviour of SAM of thiocholesterol on gold as nanoporous assembly, array of microelectrodes and potential application as sensor of copper ions.

- a) TC SAM on gold acts as a nanoporous molecular assembly with large number of molecular defects with a size of about 5-8 Å. These defects arise due to the size and irregular shape of the molecule, which are periodic in nature rather than the random defects observed in ordinary alkanethiol SAMs.
- b) The TC SAM behaves as an array of microelectrodes and can be used a potential sensor for the detection of Cu^{+2} ions.

Scope for further studies :

In Chapter 5, we have formed some highly hydrophobic SAMs prepared by the method developed here. These highly hydrophobic SAMs exhibit the possible existence of “*hydrophobic interfacial gap*” between alkanethiol SAM-water interface, which incidentally supports the predictions of Lum, Chandler and Weeks (LCW) theory of length scale dependent hydrophobicity. We have come to the above conclusions from the abnormally low interfacial capacitance and high uncompensated solution resistance values obtained for highly hydrophobic alkanethiol SAMs in aqueous media. However, the interfacial capacitance data can only approximately predict the possible presence of a hydrophobic gap of about nanometer dimension at the interface. We are aware that further studies, possibly spectroscopic, need to be carried out to evaluate the exact nature and composition of this interfacial gap. Perhaps, highly sensitive interfacial techniques like Neutron Reflectivity, Grazing incidence X-ray Reflectivity and Surface Plasmon resonance spectroscopy may provide further insight into this intriguing phenomenon.

We have formed monolayer of SDS (Sodium dodecyl sulphate, an anionic surfactant) on neat HDT coated evaporated gold electrode and studied the adsorption isotherm by the measurement of interfacial capacitance in aqueous media. Monolayers of other surfactant molecules like CTAB (cationic surfactant) and Triton X-100 (nonionic surfactant) can also be formed on neat HDT coated gold surface. The effect of potential and pH of the electrolytic medium on the interfacial capacitance of both ionic and nonionic surfactant monolayers on neat HDT coated gold electrode in

aqueous medium can be studied. This may provide valuable information regarding the SAM-water and surfactant -water interfaces.