

**STUDIES ON THE EFFECT OF SOME
SOLVENTS ON THE STRUCTURE,
INTEGRITY AND INTERFACIAL
PROPERTIES OF ORGANIC THIOL
MONOLAYERS**

by

Ujjal Kumar Sur

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Raman Research Institute

Bangalore-560080

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A list of abbreviations and symbols used in this thesis

1. SAMs	Self-Assembled Monolayers
2. CV	Cyclic Voltammetry or Cyclic Voltammogram
3. EIS	Electrochemical Impedance Spectroscopy
4. STM	Scanning Tunneling Microscope
5. FTIR	Fourier Transform Infrared Spectroscopy
6. UME	Ultramicroelectrode
7. DMF	Dimethyl Formamide
8. DMSO	Dimethyl sulphoxide
9. DDT	Dodecanethiol
10.HDT	Hexadecanethiol
11.TC	Thiocholesterol
12.Au	Gold
13.Ag	Silver
14.Pt	Platinum
15.SCE	Saturated Calomel Electrode
16.Q	Constant phase element
17. R_u	Uncompensated solution resistance
18. R_{ct}	Charge transfer resistance
19. C_{dl}	Double layer Capacitance
20.W	Warburg impedance
21. θ	Surface coverage
22.ATP	4-Amino Thiophenol
23.BDMT	1,4 Benzenedimethanethiol
24.ODT	1,8 Octanedithiol
25.SDS	Sodium dodecyl sulphate

Synopsis

Studies on the effect of some solvents on the structure, integrity and interfacial properties of organic thiol monolayers

This thesis deals with the electrochemical studies on the adsorption behaviour of some sulphur containing organic compounds mainly self-assembled monolayers (SAMs) of alkanethiol and alkanethiol derivatives on gold surfaces. More specifically, we focus on the effect of different solvents on the structure, integrity and interfacial properties of different organic thiol monolayers like alkanethiol, aliphatic and aromatic dithiol, hydroxy and carboxylic acid thiol and thiocholesterol.

We find from literature that relatively less attention has been paid to the study of blocking properties of alkanethiol SAMs in non-aqueous solvents primarily due to their perceived instability in these solvents. Cyclic voltammetric and electrochemical impedance spectroscopic studies were carried out to compare the barrier properties of monolayers on gold formed by alkanethiols of different chain lengths in solvents like acetonitrile, propylene carbonate, ethanol, formamide, di-methyl formamide, di-methyl sulphoxide and acetic acid. Our results show that the blocking behaviour of alkanethiol monolayer to the ferrocene electron transfer reaction varies in the order formamide \cong acetic acid $>$ ethanol \cong DMF \cong DMSO $>$ acetonitrile \cong propylene carbonate. The electron transfer through the monolayer is facilitated by the ability of the solvent molecules to interact with the thiol molecule and disorganize the monolayer. We have correlated the internal order of the solvent molecules with their ability to influence the structural integrity and barrier properties of the monolayer. The barrier properties of

hydroxy and carboxylic acid thiol SAMs in different non-aqueous solvents were also carried out. The effect of pH on the barrier properties of SAMs of 11-mercapto undecanoic acid and 4-amino thiophenol on gold have been studied using ferrocyanide and hexaammine ruthenium(III) chloride as redox probes.

We have studied the orientation and barrier properties of self-assembled monolayers of two alkanedithiols viz., hexanedithiol, octanedithiol, and an aromatic dithiol, 1,4 benzenedimethanethiol (BDMT) on gold in acetonitrile. From our studies, we conclude that BDMT molecules can form more organized monolayers on gold than aliphatic dithiol SAMs due to extremely strong lateral van der Waals interaction among the phenyl rings in the former. From the measurements of 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.

We have carried out comparative studies on SAMs formed in ethanolic solution of alkanethiol as well as from neat alkanethiol. The SAMs have been characterized using electrochemical techniques like cyclic voltammetry and electrochemical impedance spectroscopy as well as by non-electrochemical techniques like Scanning Tunneling Microscopy (STM) and Grazing Angle FT-IR Spectroscopy. Our experimental results prove that neat alkanethiol SAMs are more ordered and impermeable and exhibit excellent barrier properties in aqueous and non-aqueous media compared to the monolayers formed in ethanol. The lower permeability and better barrier property of neat alkanethiol SAM has been shown to be due to the formation of larger hydrophobic domains compared to 1 mM hexadecanethiol (HDT) coated surface. This was confirmed by our STM studies on the alkanethiol

coated Au surface. From the impedance results, we find that neat alkanethiol coated Au surface exhibits very low interfacial capacitance and large uncompensated solution resistance in aqueous media compared to normal values obtained in the case of ethanolic alkanethiol monolayer. From our results, we propose a model based on the possible existence of a “*hydrophobic gap*” between the alkanethiol SAM-water interface, which incidentally supports the predictions of Lum, Chandler and Weeks (LCW) theory of length scale dependent hydrophobicity. When the hydrophobic surface is small, hydrogen bonding of water still exists near the surface, although for an extended hydrophobic surface, the existence of hydrogen bonded water is geometrically impossible. As a result, it will produce a thin water vapour layer expelling the liquid water from the hydrophobic surface. This phenomenon is known as “Drying effect”. In our case, neat HDT coated Au electrode in water behaves as extended hydrophobic surface which may induce drying transition probably producing a thin water vapour layer adjacent to hydrophobic HDT surface. This thin vapour layer acts as series capacitor to the dielectric film of alkanethiol monolayer. This tends to lower the effective interfacial capacitance of the monolayer and also enhances the uncompensated solution resistance. 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 like formamide. This kind of “Drying effect” is not observed in case of neat 11- mercapto 1-undecanol coated Au surface in water, since the monolayer is now hydrophilic. Neat HDT coated SAM on evaporated Au has a highly impermeable ionic insulating property compare to monolayer formed from dilute HDT in ethanol and behaves as low leakage ideal capacitor (shows 90° phase angle over a wide frequency

range). This highly insulating monolayer of neat HDT coated gold acts as good receptor for surfactant like sodium dodecyl sulphate (SDS) for bilayer formation. We have measured the adsorption isotherm for the bilayer formation from interfacial capacitance studies and calculated the equilibrium constant and free energy change for the process.

We have evaluated the barrier properties of alkanethiol SAMs formed in different non-aqueous solvents using electrochemical impedance spectroscopy. Our impedance results show that the barrier properties of the SAMs 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 solvents like ethanol, acetonitrile, DMF, toluene, hexadecane. Interestingly, the monolayers formed in solvents like chloroform and hexane show very low interfacial capacitance and high uncompensated solution resistance values implying the possible existence of “hydrophobic gap” separating the alkanethiol SAM and the aqueous electrolyte. This gap acts as a series capacitor to the dielectric film of the alkanethiol monolayer.

We find in literature that the time duration of dipping the gold sample in 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. Our impedance measurements show that alkanethiol monolayer formed by adsorption in ethanol for a short time followed by dipping in water for much longer duration produces a more compact and highly impermeable monolayer. The formation of such high quality monolayer film is due to enhanced hydrophobic interaction among the alkanethiol molecules in water during the self -assembly process.

SAMs of alkanethiol were also formed on gold microelectrodes fabricated in our laboratory. The effect of different solvents on the structural integrity and barrier properties of SAMs were carried out using these SAM modified microelectrodes. The barrier property of alkanethiol SAM coated microelectrode was carried out in the mixed solvent of ethanol+water of different compositions.

We have investigated the structure of SAM of thiocholesterol (TC) on gold. Thiocholesterol is a cholesterol molecule possessing a thiol moiety in place of a hydroxyl group at the 3- β position. A large number of molecular defects with a size of about 5-8 Å are present in TC monolayer due to the size and irregular shape of the molecule, which are periodic in nature rather than the random defects present in ordinary alkanethiol SAMs. This TC monolayer on gold acts as a nanoporous molecular assembly, exhibits microelectrode arrays behaviour and can be used for electroanalytical and biosensors applications. This SAM has a surface coverage of only 65-70%. We have utilized this property of TC SAM to form mixed monolayer of HDT+TC. We have also used the TC SAM as sensors for detection of Cu⁺² ions.

From our studies we find :

1. There is a clear correlation between the internal order of solvent molecules with the structural integrity and barrier properties of organic thiol monolayers.
2. Neat alkanethiol SAMs are more ordered and impermeable and exhibit excellent barrier properties in aqueous and non-aqueous media compared to the monolayers formed in ethanol and other adsorption solvents.
3. Neat alkanethiol coated Au surface and alkanethiol monolayers formed in hexane and chloroform exhibit very low interfacial capacitance and large uncompensated solution resistance in aqueous media compared to normal values obtained in the case of ethanolic alkanethiol monolayer. Our results suggest a possible existence of a “*hydrophobic gap*” between the alkanethiol SAM-water interface, which incidentally supports the predictions of Lum, Chandler and Weeks theory of hydrophobic effect at small and large length scales. 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 like formamide. 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. The barrier properties of the SAMs 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.

5. We can conclude that alkanethiol monolayer formed by adsorption in ethanol for a short time followed by dipping in water for much longer duration produces a more compact and highly impermeable monolayer due to enhanced hydrophobic interaction among the alkanethiol molecules in water during the self-assembly process.
6. 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. The TC SAM behaves as an array of microelectrodes and can be used a potential sensor for the detection of Cu^{+2} ions.

Chapter 1 : Introduction In this chapter, we have discussed the formation and characterization of alkanethiol SAMs on gold (a brief review of different methods of characterization of alkanethiol SAMs), introduction to the field of microelectrodes and its utility on electrochemical studies and the aim and scope of our studies.

Chapter 2 : Experimental This chapter describes different experimental setups and also explains the working principles of different experimental techniques used in our studies in details.

Chapter 3 : Effect of bulk structure of some non-aqueous solvents on the barrier properties of alkanethiol monolayer

In this chapter, we have discussed the electron transfer barrier properties of alkanethiol monolayers of different chain lengths in seven different non-aqueous solvents (acetonitrile, propylene carbonate, ethanol, formamide, DMF, DMSO, acetic acid) by cyclic voltammetry and electrochemical impedance spectroscopy techniques.

Chapter 4 : Electrochemical studies on Self-Assembled Monolayers of some Dithiols, Hydroxy, Carboxylic acid and amino thiols on gold

In this chapter, we have discussed the structural integrity and barrier properties of different alkanethiol derivatives using electrochemical techniques like cyclic voltammetry and impedance spectroscopy. We have studied the effect of solvents on the stability and barrier properties of some organic dithiol molecules like 1,8 octanedithiol, 1,6 hexanedithiol and 1,4

benzenedimethanethiol. The barrier property of hydroxy and carboxylic acid thiols were also studied. This chapter also describes the effect of electrolytic pH on the barrier properties of charged SAMs (carboxylic acid and amino thiols) towards charged electroactive species.

Chapter 5 : Study on the barrier properties and interfacial properties of SAMs of alkanethiols formed in different non-aqueous solvents

We have discussed the barrier properties of alkanethiol SAMs formed in different non-aqueous solvents with and without redox species in aqueous media using electrochemical impedance spectroscopy in this chapter. The studies on the structure, hydrophobicity, permeability and other interfacial properties of alkanethiol SAMs formed in neat thiol and different solvents are discussed in this chapter.

Chapter 6 : Study on the effect of solvents on the barrier properties of alkanethiol SAMs formed on Au microelectrode

In this chapter, we have discussed the effect of solvents on the barrier properties of alkanethiol SAM coated disk shaped gold microelectrodes (of diameter 12.5 and 40 microns), which were fabricated and characterized in our laboratory. The method of fabrication of gold and platinum disk shaped microelectrodes were also discussed in this chapter in details.

Chapter 7: Self-Assembled Monolayers of Thiocholesterol on Gold: A potential application for electroanalytical sensors

In this chapter, we have discussed the structure, barrier property of thiocholesterol (TC) SAM on gold and its utility as microelectrode array and potential sensor for copper ion detection

Chapter 8: Conclusions and further scope of studies

In this chapter, we have discussed about the conclusions of the work done in this thesis and the scope for further studies.

The work done in this thesis has been published in the form of following papers :

1. Effect of bulk structure of some non aqueous solvents on the barrier properties of alkanethiol monolayer (*J. Electroanal. Chem.*, **516**, **2001**, p 31-38)
2. Existence of a Hydrophobic Gap at the Alkanethiol SAM-Water Interface: An Interfacial Capacitance Study (*J.Colloid. Interface. Sci.*, **254**, **2002**, p 410-413)
3. Cyclic voltammetric and electrochemical impedance studies on the structure, adsorption kinetics and barrier properties of some organic dithiol self –assembled monolayers on gold (submitted to *J.Colloid. Interface. Sci.*)
4. *Proc.of seventh International Symposium on Advances in Electrochemical Science and Technology*, SAEST, CECRI, INDIA, **27-29 November, Chennai, 2002, Volume 1, p B1-B4**, “Study of Electron transfer kinetics on SAM of Alkanethiol formed in non-aqueous solvents.”

5. **Proc.of seventh International Symposium on Advances in Electrochemical Science and Technology, SAEST, CECRI, INDIA, 27-29 November, Chennai, 2002, Volume 1, p B24-B27, “STM, FT-IR, and Electrochemical Impedance Spectroscopic studies on the Permeability of Alkanethiol SAMs.”**
6. Presence of a hydrophobic shield in Alkanethiol SAM–water interface: A study on monolayers prepared in different solvents (submitted to **J. Electroanal. Chem.**)
7. Hydrophobicity induced drying transition in alkanethiol Self-Assembled Monolayer-water interface (To be published in **Pramana**)
8. Study of Electron Transfer Kinetics on Self-Assembled Monolayers of Alkanethiols in Non-Aqueous Solvents (To be published in the **Proceedings of 203rd Meeting of The Electrochemical Society, Paris, France, April 27-May 2, 2003, AC2-2499**)
9. Evidence for a 'Hydrophobic Shield' between the Alkanethiol SAM and Aqueous Electrolyte (To be published in the **Proceedings of 203rd Meeting of The Electrochemical Society, Paris, France, April 27-May 2, 2003, AC2-2513**)