CHAPTER 3

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

3.0 Introduction :

Ever since the discovery of the self -assembled monolayers (SAMs) of long chain alkanethiols [1,2], there have been intense efforts to achieve the most blocking and defect free films by controlling various factors, such as substrate morphology, alkanethiol purity, deposition solvent, deposition time, alkanethiol concentration etc. However, 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 owing to their perceived instability in these solvents. However, non-aqueous solvents provide a wide range of unique properties which can be usefully exploited for various applications involving SAMs. In addition to this, the electrochemistry involved in non-aqueous solvents is novel from the point of view of solubility, chemical stability of redox probe molecules over wide potential ranges which is not possible in aqueous media to investigate the stability and structural integrity of alkanethiol SAMs. Finklea et al. [3] have carried out pioneering studies of electron transfer kinetics in alkanethiol monolayers with attached pentammine (pyridine) ruthenium redox centers

in several non aqueous solvents. The kinetics of electron transfer in the electroactive monolayer were examined using cyclic voltammetry and chronoamperometry. Their studies clearly establish 'through bond tunneling mechanism' for electron transfer. Finklea has earlier found that in acetonitrile, electron transfer of ferrocene/ferricenium redox couple is either unimpeded or only slightly reduced from that of an uncoated gold electrode [4]. This was explained as arising from the ability of the acetonitrile to solvate the alkane chain of alkanethiol monolayer allowing the ferrocene or ferricenium molecule to penetrate through the monolayer.

We find that there exists some controversy in literature concerning the role of propylene carbonate as an electrolytic medium for the redox reaction. Creager and Groat have studied the barrier properties of alkanethiol coated monolayer on gold in propylene carbonate [5]. They have concluded that monolayers with excellent barrier properties can be formed and maintained in propylene carbonate only when a small amount alkanethiol is present in the contacting solution and within a specific potential range. They also state that alkanethiol monolayer is normally quite unstable in propylene carbonate and desorbs upon potential cycling. This is in conflict with that of Finklea et al. [3] who reported that a redox terminated alkanethiol is quite intact, albeit in a disorganised form in propylene carbonate.

In our work, we attempt to resolve this question, as this has an important bearing in understanding the stability and barrier properties of the alkanethiol monolayers not just in propylene carbonate but also in other non-aqueous solvents in general [6]. We examine the stability and structural integrity of the alkanethiol monolayer and correlate with the bulk structure of some non-aqueous solvents [6]. Such a study will lead us to categorise the solvents in terms of their ability to influence the properties of the monolayer

in any specific pre-defined manner. For example, one can then choose the solvent medium to modify and control the interface structure of the electrode with the aim of tailoring the interfacial film with a specific ion and molecular transport properties. This will also provide us novel electrochemical systems with unique characteristics to study the mechanism of heterogeneous electron transfer reactions in the presence of insulating films. With this in view, we have studied the electron transfer barrier properties of the monolayers formed by both neat and dilute ethanolic alkanethiols of different chain lengths (dodecane and hexadecanethiols) in seven non-aqueous solvents viz., propylene carbonate, acetonitrile, ethanol, formamide, acetic acid, dimethyl formamide (DMF), and dimethyl sulphoxide (DMSO) using cyclic voltammetry and electrochemical impedance spectroscopy. In this context, we also have suggested a probable mechanism of ferrocene electron transfer reaction in the presence of highly insulating alkanethiol monolayer on gold in these non-aqueous solvents [7].

3.1 Experimental :

3.1.1Electrodes and cells

Gold working electrode was constructed (as described in details in Chapter 2) by proper sealing of 99.99% pure gold wire (Arora Mathey) of 0.5 mm diameter with soda lime glass having thermal expansion coefficient close to that of gold. The electrode has a geometric area of 0.002 cm^2. This small area working electrode has highly reproducible true surface area (as measured by potential cycling in 0.1M perchloric acid) even after repeated usage.

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 ethanol medium, whereas a silver rod was used as a quasi-reference electrode in acetonitrile, propylene carbonate, formamide and other non-aqueous solvents as suggested in literature [8,9]. The silver quasi-reference electrode has a potential of –0.2 V with respect to saturated calomel electrode (SCE) [10] in acetonitrile. This electrode has almost a stable potential in non-aqueous solvents and also is free of any liquid junction potential. However, in few voltammograms, we find a small shift in E^0 values for alkanethiol coated gold electrode for ferrocene redox reaction compare to bare gold. This can be attributed to the use of Ag rod as quasi-reference electrode. 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.

3.1.2 Electrode pretreatment and thiol adsorption

Immediately before use, the gold 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 . This procedure had been shown to yield a substrate with the best blocking properties for supporting self-assembled monolayer of alkanethiols [11,12]. The electrode was thoroughly rinsed with millipore water and was dipped in *neat* alkanethiol without any solvent medium for 1 hour. This is to exclude the possibility of the interference from ethanol

molecules (the usual solvent medium for adsorption) which might get trapped during the formation stage and carried over to the cell containing a different solvent. After the adsorption of alkanethiols, the electrode is rinsed with the respective solvent used for the study. We have also conducted experiments where the monolayer is formed by dipping the electrode in either a 20 mM solution of thiol in ethanol for 8 hours or 1 mM solution for 24 hours.

3.1.3 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.Electrochemical impedance studies were performed using an EG&G potentiostat (Model 263A) along with a two phase lock-in amplifier (Stanford Research Systems Model SR830). A pure sine wave of 10 mV amplitude was derived from the lock- in amplifier for application to the cell. Impedance studies were carried out at formal potential of the respective systems as measured from the cyclic voltammograms. The impedance data were analyzed using the Boukamp's impedance software [13] by fitting to an appropriate equivalent circuit.

3.1.4 Chemicals

Ethanol 99.95% (Emerck), tetrabutylammonium tetrafluroborate (Aldrich), lithium perchlorate (Fischer), ferrocene (Acros Organics), dodecanethiol (DDT) and hexadecanethiol (HDT) (Aldrich), perchloric acid (Qualigens), acetonitrile (Ranbaxy), propylene carbonate (Spectrochem), formamide (SRL), DMF, DMSO (Spectrochem), acetic acid (SD fine chemicals),

sodium acetate (Qualigens), potassium ferrocyanide (Loba) were used in this study. Millipore water was used for making aqueous solution.

3.2 Results and discussion :

3.2.1 Propylene carbonate

Figure 1 A shows the cyclic voltammograms of ferrocene redox reaction. The CVs were carried out on a bare gold electrode and also in 20 mM DDT (dodecanethiol) coated electrode with 1 mM ferrocene in propylene carbonate containing 0.1 M tetrabutylammonium tetrafluroborate as supporting electrolyte. It can be seen that the CV of bare uncoated gold electrode shows the expected behaviour of reversible peaks, while that of the first cycle CV of the 20 mM dodecanethiol coated electrode exhibits irreversible broadened peaks with a positive shift in anodic peak potential. After a few scans (about 20), a normal voltammogram with a small shift in the peak potentials possessing the characteristics quite similar to bare gold electrode appears. This type of voltammetric behaviour may at the outset suggest removal of dodecanethiol molecules during potential scanning in propylene carbonate. In fact, a detailed study of the behaviour of alkanethiol monolayer in propylene carbonate had been carried out earlier by Creager and Groat [5]. They also found that blocking character of an alkanethiol monolayer decreases rapidly on continuous potential scanning which was attributed to desorption of thiol molecules from the gold electrode in propylene carbonate.

In order to check whether there is indeed a desorption of thiol during potential cycling in propylene carbonate as suggested by Creager et al. [5],

we have carried out the following studies on the electrode immediately, after potential scanning in propylene carbonate.

(1) CV of $Fe(CN)_6{}^{3-} | Fe(CN)_6{}^{4-}$ in 1M KCl in water.

(2) Electrochemical desorption of alkanethiol monolayer by cycling to very negative potential (below -1.0 V vs SCE) in propylene carbonate followed by CV of $Fe(CN)_6{}^{3-} | Fe(CN)_6{}^{4-}$ in 1M KCl.

In the above study, we have used $Fe(CN)_6{}^{3-}$ as a redox probe to evaluate the integrity of SAM.

Figure 1B shows the CV of ferrocyanide redox reaction on bare gold electrode in 1M KCl in water which has the usual characteristics of a reversible redox reaction and that of dodecanethiol coated electrode for the same system which was subjected to potential scanning in propylene carbonate. It can be seen that this electrode exhibits very good blocking to ferrocyanide redox reaction, which is a clear indication that dodecanethiol molecules have not desorbed during the potential scanning in propylene carbonate.

This is further proved by another experiment; We have found that alkanethiol SAM can be desorbed by cycling to very negative potential (below -1.0 V vs SCE) in propylene carbonate (Figure 1C). It can be seen from the desorption peak that the alkanethiol monolayer was very much intact during the earlier potential scanning in propylene carbonate. After desorption of alkanethiol monolayer, again a CV of ferrocyanide redox reaction was carried out on the electrode. Figure 1B shows that the CV so obtained has features very much similar to that of bare gold electrode. This proves that alkanethiol monolayer has not disintegrated but somehow allows the ferrocene electron transfer.

The above results clearly prove that the alkanethiol monolayer is stable in propylene carbonate contrary to the interpretation of the result by Creager et al [5]. The ferrocene redox reaction in propylene carbonate must then be occurring probably by "through space tunneling" process mediated by the thiol film when the redox species approaches close enough for the electron transfer to occur. Finklea et al.[4] observed similar phenomenon in acetonitrile and hypothesizes that there is a strong interaction between the nonpolar hydrocarbon tail of alkanethiol monolayer and acetonitrile. This loosens the tight packing of monolayer and allows the redox reaction to occur [4]. Our results confirm this observation with regard to propylene carbonate also, where the dodecanethiol monolayer undergoes some kind disorganization which results in significant faradaic current during ferrocene redox reaction. It is also worth noting that the disorganised monolayer present while in propylene carbonate again becomes compact once it is dipped in aqueous medium as evidenced by the blocking of the $Fe(CN)_6^{3-}$ redox reaction. This goes to prove that propylene carbonate does not in any way damage the monolayer other than disturbing the ordered arrangement of molecules on the surface.

Figures 2A shows the CVs of bare gold and neat DDT modified gold electrode respectively for the ferrocene redox reaction in propylene carbonate. We studied neat thiol coated electrode as we wanted to exclude the possibility of the solvent molecules getting trapped within the monolayer interior and influencing its blocking properties. This is especially important as the solvent used during adsorption (ethanol) is different from the solvent used for the redox studies. The first cycle CV of neat DDT coated gold electrode exhibits a good blocking behaviour which however, on repeated scanning after a few cycles exhibits a quasi-reversible voltammetric wave

with a large peak separation. This suggests that the monolayer obtained by adsorption in neat DDT is more difficult to disorganise than the one adsorbed in 20 mM DDT. It can be seen from Figure 2B that neat HDT (hexadecanethiol) exhibits better barrier property towards ferrocene redox reaction in propylene carbonate which is maintained even after several cycles of potential scanning (Figure 2B).   Evidently, the longer chain length hexadecanethiol is more difficult to disorganise than DDT.

Figure 2B also shows the CVs for ferrocene redox reaction in propylene carbonate on HDT coated gold electrode prepared by dipping in 1 mM solution of thiol in ethanol for 24 hours. It is clearly seen that the monolayer formed in 1 mM HDT does not show any significant blocking to the ferrocene reaction in contrast to that of neat HDT.

3.2.2 Acetonitrile

While propylene carbonate is a polar, high conductivity solvent with dielectric constant close to that of water, acetonitrile is a solvent having relatively low dielectric constant. Figure 3A shows the cyclic voltammograms of ferrocene reaction on bare gold electrode and 1 mM dodecanethiol coated electrode in acetonitrile containing 0.1M tetrabutylammonium tetrafluroborate. The first cycle CV of 1 mM dodecanethiol coated electrode exhibits a partial blocking behaviour. As scanning continues however, we get voltammogram with peak current similar to bare gold electrode. These results show that the disorganization of alkanethiol monolayer in acetonitrile is very much similar to that of propylene carbonate. Figure 3B shows the voltammogram of the same electrode undergoing complete reductive desorption of dodecanethiol

monolayer in acetonitrile when cycled to very negative potential (below - 1V vs SCE).

Figure 4A illustrates CVs obtained with neat dodecanethiol coated electrode for the ferrocene redox reaction in acetonitrle. It can be seen that the reaction is blocked initially during the first cycle. However, this current increase with scanning and the CV appears similar to that of bare gold electrode after about 20 scans. However, the peak separation (100 mV) now is larger than that shown in Figure 3A which means that the reaction is not fully reversible as when the thiol monolayer is formed with 1mM dodecanethiol. In contrast to this, it can be seen from Figure 4B that longer chain neat hexadecanethiol coated electrode exhibits excellent barrier for electron transfer even after continued potential scanning in acetonitrile.

3.2.3 Impedance studies

Figure 5A shows the Nyquist plot of bare gold disk electrode for 1 mM ferrocene + 1 mM ferricenium in acetonitrile containing 0.1M tetrabutyl ammonium tetrafluroborate as supporting electrolyte carried out at a potential of +0.30 V vs SCE. It can be seen that the reaction is diffusion controlled for almost the whole frequency range of 0.1 Hz to 30 kHz showing a fast charge transfer reaction. The equivalent circuit can be represented by the simple Randle's circuit with the Warburg impedance Z_f due to mass transfer in parallel with the CPE, which is approximated to double layer capacitance C_{dl} along with the series uncompensated solution resistance R_u.

Figure 5 B shows the the impedance plot for the same electrode after adsorption in 1 mM dodecanethiol in ethanol for 24 hours. It is evident from the plot that the reaction is still under mass transfer control over the wide

frequency range, very similar to that of bare gold. Obviously, the presence of thiol monolayer has not altered the charge transfer process significantly and the thiol monolayer is not blocking the electron transfer process, as in this case the result from impedance is in agreement with our CV results. However, when the impedance studies were conducted with neat dodecanthiol adsorbed electrode, the plot in Figure 5 C is obtained which shows a very clear semi circle at high frequencies corresponding to charge transfer controlled process. At low frequencies however, the effect of diffusion is dominating. This supports the CV results (Figure 4A) which shows a peak separation of 100 mV corresponding to a quasi-reversible electron transfer process. These results also reinforce our argument that the monolayer formed in neat dodecanethiol has a much better barrier property than the one formed in 1mM thiol in ethanol towards the ferrocene redox reaction in acetonitrile.

Figure 6A shows that impedance plot for the gold disk electrode after adsorbing in 1 mM hexadecanethiol. The small semicircle at high frequencies reveals a charge transfer process which become diffusion controlled again at mid frequency regions. However, when the adsorption is carried out in neat hexadecanethiol the reaction is under charge transfer control almost throughout the entire frequency range studied (Figure 6B). This result is very much consistent with the CV of Figure 4B which shows that the monolayer formed with neat hexadecanethiol has a better blocking characteristics in acetonitrile.

The charge transfer resistance (R_{ct}) values for the ferrocene reaction in   acetonitrile are calculated for neat DDT and HDT adsorbed electrodes by the extrapolation of the semicircles shown in Figures 5C and 6B respectively from which R_{ct} values of 113 Ω cm^2 and 2650 Ω cm^2 are obtained. These

values correspond to apparent rate constants (k_{app}) of 2.35×10^{-3} cm s^{-1} and 1.0×10^{-4} cm s^{-1} respectively which means that the rate constant has decreased by a factor of 23 times when the chain length of the thiol has increased by four methylene groups.

It is well established in literature that if the tunneling is the process through which the electron transfer takes place, then the rate constant should depend exponentially on the monolayer thickness, according to the expression $k^0_{app} = k^0 \exp(-\beta d)$ where β is the tunneling parameter, d is the monolayer thickness and k^0_{app} and k^0 are the the apparent rate constant on thiol coated electrode and rate constant on bare gold electrode respectively. Normally, β values are measured using the heterogeneous rate constants obtained by systematically varying the chain length of the adsorbed alkanethiols. A value of 0.9 per methylene group was reported for $Fe(CN)_6^{3-|4-}$ reaction through hydroxythiol monolayer by Miller et al. [14] and 0.83 for the $[Ru(NH_3)_6]^{3+|2+}$ couple by Protsailo et al [15]. If we use the above expression for the apparent rate constant calculation and substitute a k^0 value of $1-10$ cm s^{-1}, β of 0.83 and k^0_{app} value of 1.0×10^{-4} cm s^{-1} for HDT coated electrode from the impedance results, we get the distance d in the exponent to be in the range of 11 to 14 Å. This turns out to be smaller than the monolayer thickness of 18 Å expected for a compact HDT coated electrode with 30^0 chain tilt. Similarly, for DDT coated electrode with an expected monolayer thickness of 13 Å, the distance d obtained is 7-10 Å. This may mean that the redox species penetrates the monolayer partially upto a certain distance and then the electron transfer occurs by tunneling. Such a scenario is very much possible due to the ability of acetonitrile to slightly disorganise the monolayer even when it is formed in neat thiol.

The double layer capacitance obtained from the maximum of the cole–cole plot yields a value of 3.71 $\mu F\,cm^{-2}$ (geometric area) for HDT coated monolayer. This corresponds to a capacitance of 1.48 $\mu F\,cm^{-2}$ (real area) with a roughness factor of 2.5, which is in quite a good agreement with the literature value. However, the double layer capacitance measured for dodecanethiol is 6.71 $\mu F\,cm^{-2}$ of the geometric area which yields a capacitance value of 2.68 $\mu F\,cm^{-2}$ of the true area. This is rather high compared to the value of 1.75 $\mu F\,cm^{-2}$ reported for dodecanethiol. This rather large value may be ascribed to the disorganised monolayer through which the acetonitrile molecules penetrate and change the nature of the dielectric film on the electrode. This is also supported by observations by other workers [16,17].

Our impedance results are quite consistent with the conclusions arrived at after CV measurements. The reversible CV of Figure 3A for the electrode adsorbed in 1 mM DDT can be compared with the impedance plot of the same system in Figure 5B where the reaction appears to be diffusion controlled almost throughout the entire range of frequencies. On the other hand, the electrode prepared by adsorption in neat DDT exhibits a clear semicircle at high frequencies, signifying a charge transfer process. The impedance plot of Figure 6B shows a semicircle with a large value of R_{ct} for neat HDT coated electrode in acetonitrile, confirming the fully blocking behaviour exhibited by the same system in the CV of Figure 4B.

The above results in acetonitrile or propylene carbonate show that these solvents have a tendency to disorganise the monolayer and allow a closer access of the redox species to the electrode surface for the electron transfer to take place easily. If the disorganisation of the monolayer is

effected by these solvents due to their interaction with the terminal methylene chains, then it follows that organic solvents which cannot show such a behaviour should be more blocking to ferrocene reaction. In order to check this possibility, we have conducted CV studies of thiol adsorbed electrodes using formamide as electrolytic solvent, since its solvent structure differs significantly from those of acetonitrile and propylene carbonate.

3.2.4 Equivalent circuit analysis of impedance data

There has been no report in literature of the equivalent circuit modeling of impedance data of alkanethiol SAMs in non-aqueous medium in the presence of some redox species. Here, we model the interface of 1 mM and neat DDT and HDT coated Au electrodes for ferrocene redox reaction in acetonitrile to a Randle's type equivalent circuit. Table 1 shows the values of different components, viz., R_u, R_{ct}, C_{dl}, Q, and W obtained by fitting the impedance data to the equivalent circuit R(Q(RW))(The equivalent circuit is shown at the top of the Table 1, Q is the constant phase element). As the impedance of the CPE is given by $Z_{CPE} = 1/Q(j\omega)^n$, when $n = 1$, a purely capacitive behaviour is expected (i.e. $Q = C_{dl}$). The values of n in the case of neat DDT and HDT are 0.94 and 0.98 respectively, which indicates that there is very little deviation from purely capacitive behaviour. However, the n values in the case of 1 mM DDT and HDT coated Au surfaces are 0.60 and 0.67 respectively, indicating much larger deviation from purely capacitive behaviour. The CPE has no definite physical significance and does not represent any specific interfacial process [18,19]. However, it is helpful in the analysis of impedance data affected by frequency dispersion. For instance, the perturbation to purely charge transfer process caused by deep pores or rough surfaces can be represented in terms of CPE. In our impedance analysis, the deviation from the capacitive behaviour as

represented by constant phase element Q is brought about by the disorganisation introduced by the acetonitrile molecules on the organic thiol monolayer.

<div align="center">Table 1</div>

Values of different components of the equivalent circuit R(Q(RW)) obtained from the fitting of impedance data for ferrocene redox reaction in acetonitrile
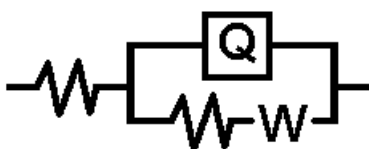
System	R_u /Ω cm^2	Q/Ω^{-1} cm^{-2} s^n	n	R_{ct} / Ω cm^2	W/Ω cm^2
1 mM DDT coated Au	2.85	6.28×10^{-3}	0.60	3.785	6.33×10^{-3}
1 mM HDT coated Au	1.83	1.64×10^{-4}	0.67	50.27	2.31×10^{-3}
Neat DDT coated Au	2.76	9.8×10^{-6}	0.94	111.92	4.18×10^{-3}
Neat HDT coated Au	3.06	4.65×10^{-6}	0.98	2379	2.22×10^{-3}

3.2.5 Formamide

The barrier property of alkanethiol monolayer in formamide has not been studied so far. Formamide is a highly polar, hydrogen bonded solvent having dielectric constant greater than water (ε for formamide is 109.5). Formamide has a two dimensional layered structure as shown in Figure 7.
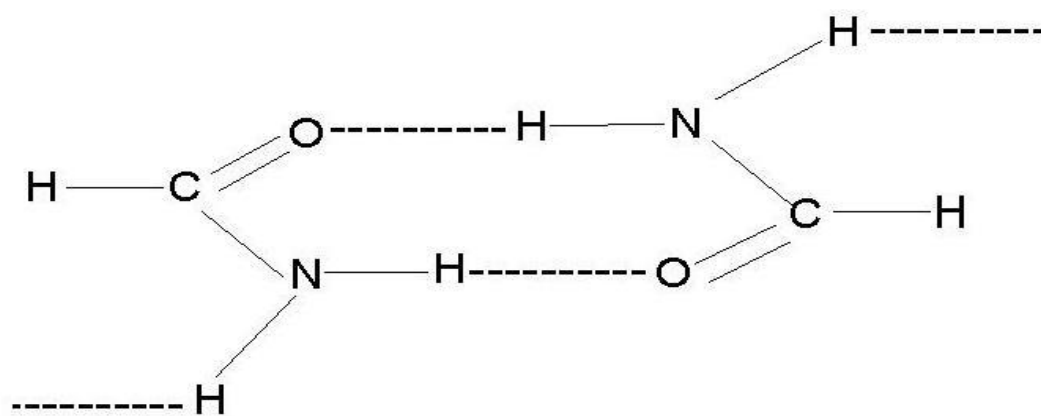
Two- dimensional (layered) structure of formamide

Figure 7

Figure 8 shows the cyclic voltammograms of bare gold and alkanethiol coated electrode with 1 mM ferrocene in formamide containing 0.1 M LiClO$_4$. It illustrates the voltammogram of electrode adsorbed in 1 mM dodecanethiol and that of the electrode dipped in neat dodecanethiol. While both the electrodes block ferrocene redox reaction even after continued potential scanning in formamide, the one adsorbed in neat thiol has much better barrier property as can be seen from the figure. This excellent blocking property of alkanethiol monolayer to ferrocene redox reaction in

formamide can be attributed to the two-dimensional (layered) hydrogen bonded structure of formamide molecules [20,21]. Due to the association of formamide molecules by strong hydrogen bonding, formamide cannot solvate the alkyl tails of alkanethiol molecules and consequently, no disorganisation of the monolayer takes place to permit entry of ferrocene molecules. Such a behaviour is in direct contrast to that of the monolayer in propylene carbonate and acetonitrile.

It is therefore clear that the disorganisation of the monolayer is directly related to the organisation within the solvent molecules. Solvents like acetonitrile and propylene carbonate which lack significant ordering or aggregation, are free to solvate the alkyl tail groups of thiol molecules and thereby screen the attractive interaction between them. If the solvent molecules are bound to each other, for example, by hydrogen bonding or strong dipolar interaction, they do not disturb the orderly arrangement of thiol monolayer. This is also the reason for excellent barrier properties of thiol monolayers in water as evidenced by large number of results available in literature [2]. Water has a unique structure of tetrahedral network with three dimensional H-bonding and therefore has a much higher order than many other solvents. The alkyl tails of alkanethiol monolayer repel water molecules and come closer to one another, thereby forming a more impermeable and compact monolayer. This is the case with formamide too.

3.2.6 Ethanol

The barrier property of alkanethiol in ethanol is of interest because of its widespread use as a solvent medium for the formation of well ordered compact monolayer of alkanethiol on gold. It is worthwhile, examining the

effect of ethanol as the electrolytic solvent on the monolayer integrity as this ultimately determines the barrier property.

Figure 9 shows the CV of bare gold electrode and alkanethiol coated electrode with 1 mM ferrocene in ethanol containing 0.1 M $LiClO_4$. The gold electrode was dipped in 1 mM DDT in ethanol for 24 hours and the CV was carried out in 1 mM ferrocene in ethanol containing 0.1 M $LiClO_4$. Figure 9 shows the CV with 1 mM dodecanethiol coated electrode after a few cycles (around 20) and it is evident that the monolayer is fully disorganised. This shows that the monolayer formed by keeping the electrode in ethanol is fully disorganised by interaction of alkyl tails of DDT with the solvent molecules. Figure 9 also shows the CV of the electrode after 100 cycles with a monolayer formed in pure DDT without any ethanol in the adsorbing medium. It can be seen that the blocking of the redox reaction is better in this case compared to the monolayer formed in 1 mM DDT. These results show that monolayer formed from 1 mM DDT permits ferrocene electron transfer reaction, whereas adsorption in neat DDT produces a film with excellent blocking properties in ethanol.

The above results with ethanol shows that its behaviour is quite different from the other three solvents studied in this work. We find that while, propylene carbonate and acetonitrile can penetrate the barrier and solvate the thiol molecules of the monolayer formed in pure DDT, ethanol is unable to break the barrier and enter into the film. On the other hand, ethanol is able to solvate the monolayer formed in 1 mM DDT in ethanol and allows the redox reaction to take place. This behaviour is also in marked contrast to that of formamide which cannot penetrate the monolayer and loosen the thiol monolayer formed from 1 mM DDT in ethanol .

Unlike propylene carbonate and acetonitrile, both of which lack long range order in bulk, ethanol can form ring like one dimensional H-bonding with the nearest neighbours and as such it does have some long range order [20,21]. However, it lacks the compact two dimensional layered structure of formamide. Hence, the solvent order that exists in ethanol is intermediate between that of acetonitrile and propylene carbonate on the one hand and formamide on the other. This is reflected in its behaviour *vis-a-vis* the thiol monolayer.

3.2.7 Dimethyl formamide

The barrier property of alkanethiol monolayer in dimethyl formamide has not been studied so far. Dimethyl formamide (DMF) is a dipolar aprotic solvent, which is associated by dipole-dipole interactions [20,22].

Figure 10 shows the CV of bare gold electrode and alkanethiol coated electrode with 1 mM ferrocene in DMF containing 0.1 M $LiClO_4$. The gold electrode was dipped in 1 mM DDT in ethanol for 24 hours and the CV was carried out in 1 mM ferrocene in DMF containing 0.1 M $LiClO_4$. Figure 10 shows the CV with 1 mM dodecanethiol coated electrode after a few cycles (around 20) and it is evident that the monolayer is fully disorganised. This shows that the monolayer formed by keeping the electrode in ethanol is fully disorganised by interaction of alkyl tails of DDT with the solvent molecules. Figure 10 also shows the CV of the electrode after 100 cycles with a monolayer formed in pure DDT without any ethanol in the adsorbing medium. It can be seen that the blocking of the redox reaction is better in this case compared to the monolayer formed in 1 mM DDT. These results show that monolayer formed from 1 mM DDT permits ferrocene electron

transfer reaction, whereas adsorption in neat DDT produces a film with excellent blocking properties in DMF.The above results with DMF shows that its behaviour is quite similar to that of ethanol. This is due to the weak dipole-dipole interaction between DMF molecules which is quite similar to the one dimensional hydrogen bonding present in ethanol molecules. However, it is weaker than the two-dimensional hydrogen bonding present in formamide.

3.2.8 Dimethyl sulphoxide

The barrier property of alkanethiol monolayer in dimethyl sulphoxide has not been studied so far. Dimethyl sulphoxide (DMSO) is a dipolar aprotic solvent, which is associated by dipole-dipole interactions just like DMF [20,22].

Figure 11 shows the CV of bare gold electrode and alkanethiol coated electrode with 1 mM ferrocene in DMSO containing 0.1 M LiClO$_4$. The ferrocene redox reaction in DMSO has been well studied [23,24]. The gold electrode was dipped in 1 mM DDT in ethanol for 24 hours and the CV was carried out in 1 mM ferrocene in DMSO containing 0.1 M LiClO$_4$. Figure 11 shows the CV with 1 mM dodecanethiol coated electrode after a few cycles (around 20) and it is evident that the monolayer is fully disorganised. This shows that the monolayer formed by keeping the electrode in ethanol is fully disorganised by interaction of alkyl tails of DDT with the solvent molecules. Figure 11 also shows the CV of the electrode after 100 cycles with a monolayer formed in pure DDT without any ethanol in the adsorbing medium. It can be seen that the blocking of the redox reaction is better in this case compared to the monolayer formed in 1 mM DDT. These results show that monolayer formed from 1 mM DDT permits

ferrocene electron transfer reaction, whereas adsorption in neat DDT produces a film with excellent blocking properties in DMSO.The above results with DMSO shows that its behaviour is quite similar to that of ethanol and DMF.

3.2.9 Acetic acid

Acetic acid is a weak organic acid, where two molecules are associated by homo-intermolecular hydrogen bonding forming a dimer [20,21]. This kind of hydrogen bonding is much stronger than the one dimensional H bonding present in ethanol or the dipole-dipole interaction in DMF and DMSO. The barrier property of alkanethiol monolayer in acetic acid has not been studied so far. Figure 12 shows the cyclic voltammograms of bare gold and alkanethiol coated electrode with 1 mM ferrocene in acetic acid containing 0.5 M NaOAc. It illustrates the voltammogram of electrode adsorbed in 1 mM dodecanethiol and that of the electrode dipped in neat dodecanethiol. While both the electrodes block ferrocene redox reaction even after continued potential scanning in acetic acid, the one adsorbed in neat thiol has much better barrier property as can be seen from the figure. This excellent blocking property of alkanethiol monolayer to ferrocene in acetic acid can be attributed to the intermolecular dimeric hydrogen bonded structure of acetic acid molecules [20,21]. Due to the association of acetic acid molecules by strong hydrogen bonding, acetic acid cannot solvate the alkyl tails of alkanethiol molecules and consequently, no disorganisation of the monolayer takes place to permit entry of ferrocene molecules. The above results with acetic acid shows that its behaviour is quite similar to that of formamide.

Hence, in terms of the ability to disorganise the monolayer, the solvents can be arranged in the order, propylene carbonate $\cong$ acetonitrile > ethanol $\cong$ DMF $\cong$ DMSO > formamide $\cong$ acetic acid.

Probable mechanism of Electron transfer across the alkanethiol monolayer film in non-aqueous electrolytic solvents

The electron transfer process across a blocking SAM can take place at pinholes or defect sites or by electron tunneling mechanism. The SAM is not perfectly blocking towards redox reaction due to the presence of pinholes and defects. The faradaic current at pinholes are mass transfer controlled at low overpotentials, whereas the tunneling current is kinetically controlled. Electron transfer by tunneling mechanism can only take place for a perfectly blocking pinholes and defects free SAM. Miller et al. [14,25] have studied the electron tunneling mechanism for faradaic reaction in aqueous medium across the perfectly blocking SAMs of ω-hydroxy thiol. The strong lateral hydrogen bonding between the terminal –OH groups is responsible for the excellent blocking behaviour for ω-hydroxy thiol SAM, which provides ideal system for the study of electron tunneling mechanism.

We have suggested a probable mechanism of ferrocene electron transfer reaction in the presence of highly insulating alkanethiol monolayer on gold in acetonitrile and propylene carbonate as electrolytic medium. The ferrocene redox reactions in propylene carbonate and acetonitrile can take place through either or both of the following processes occurring in parallel :

(1) Diffusion of the redox species through the pinholes and access to the electrode surface followed by electron transfer reaction.

(2) Permeation of the redox molecule through the assembly and access to a region close to the electrode surface. This is followed by electron transfer by tunneling process.

From our work, we can infer that the possible scenario appears to be that the solvent molecules such as propylene carbonate and acetonitrile disorganise the monolayer. This is caused by two factors. Firstly, there is no interaction among terminal methyl groups unlike in water. Secondly, since the solvent molecules are not bound to each other, they are free to interact with the alkyl chain of the thiol monolayer. These two effects create free spaces or gaps between the thiol molecules which will now be inhabited by solvent molecules under dynamic motion and the redox species. Thus, the redox species can permeate through the monolayer and enter closer to the electrode which is otherwise prohibited in a fully organised compact monolayer.

3.2 Conclusions :

The following conclusions can be inferred from our studies :

1. We find that the alkanethiol monolayers are quite stable in solvents studied in this work, namely propylene carbonate, acetonitrile, formamide, acetic acid, DMF, DMSO and ethanol.

2. 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.

3. 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.

4. There is a clear correlation between the internal order of solvent molecules with the structural integrity and barrier properties of organic thiol monolayers.

5. We also find that neat alkanethiol SAMs exhibit excellent barrier properties in non-aqueous media compared to the monolayers formed in ethanol.

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