CHAPTER 6

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

6.0 Introduction :

Ultramicroelectrodes are electrodes with extremely small dimensions, in the order of micrometer or less. Initially, microelectrodes were used for biological and medical research [1]. In early eighties, Fleischmann and his coworkers at the Southampton Electrochemistry group exploited the versatile properties of microelectrodes in electrochemical studies. The ultramicroelectrodes, due to their extremely small size, have certain unique characteristics which make them ideal for studies involving high resistive media, high speed voltammetry and *in vivo* electrochemistry in biological systems [2,3]. They exhibit very high rate of mass transfer which combined with low ohmic drop and double layer charging current make them powerful tool for studies of fast heterogeneous kinetics at very low concentrations. Due to the small electrode area, the current associated with microelectrode is very small, of the order of pA to nA and the current densities are very high. The combinations of high current densities and low currents provide new applications in the field of analysis, sensors and Scanning Electrochemical Microscopy (SECM) [4] and studies of corrosion processes in closely defined spaces.

Microelectrodes make it possible to carry out experiments which is not possible using conventional size macroelectrodes. This is due to the considerable difference in electrochemical responses between micro and macroelectrodes.

Due to the small area of microelectrodes, the double layer capacitance is reduced relative to macroelectrodes. This allows the electrode potential to be changed rapidly, which can be utilized in voltammetric measurements in submicrosecond time scale [5,6]. At normal time scales, cyclic voltammograms obtained with ultramicroelectrodes are different from that of macroelectrodes. The voltammograms is sigmoidal shaped analogous to the s-shaped polarograms obtained with dropping mercury electrode or rotating disk electrodes. The rate of mass transport (diffusion) plays important role for the shape of voltammograms. At large electrodes, mass transport occurs mostly perpendicular to the electrode surface (planar diffusion). The result is a typical peak-shaped voltammogram for large area macroelectrodes. For a reversible redox process, the peak current follows Randles-Sevcik equation [7,8] given below.

$$I_p = (2.69 \times 10^5)\, n^{3/2}\, C_o^*\, D^{1/2}\, \nu^{1/2},$$

in which I_p is the peak current density (A cm^{-2}), n is the electron stoichiometry, D is the diffusion coefficient (cm^2 s^{-1}) of the electroactive species, C^* is the bulk concentration of the electroactive species, ν is the scan rate (Vs^{-1}). On the other hand, for a microelectrode a s-shaped voltammogram is obtained at lower scan rates, which changes into peak shaped at very high scan rates. At lower scan rates, the rate of electrolysis is almost equal to the rate of diffusion and the diffusion takes place in a hemispherical fashion, which is a time-independent process. Hence, it produces steady-state s-shaped voltammogram. At higher scan rates, the rate

of electrolysis exceeds the rate of diffusion to a larger extent. At such a fast time scales, redox species take longer time to diffuse. Hence, the current changes with time, and peak shaped voltammograms are obtained in those cases. The diffusion processes occurring at the ultramicroelectrodes can be understood by solving the diffusion problems for dropping mercury electrodes used in polarography. For a spherical electrode (radius r), current is given by,

$i_{spherical} = nFADC* [1/(\pi Dt)^{1/2} + 1/r]$,

where $A = 4\pi r^2$ is the area for a spherical electrode. According to this equation at large time scales, the current should be time independent. For a macroelectrode, the current due to semi-infinite planar diffusion is given by the Cottrell equation

$i_{planar} = nFADC*/(\pi Dt)^{1/2}$ i.e. $i_{spherical} / i_{planar} = 1 + (\pi Dt)^{1/2}/r$.

The parameter $(Dt)^{1/2}/r$ will determine when the current will be predominantly steady state in nature. Saito [9] has examined the steady state nature of current at disk microelectrodes and obtained the following expression $i = 4nFDCr$, where the steady state current is related to the electrode radius r. Hence, one can determine the dimension of a microelectrode by directly measuring the steady state current from the s-shaped voltammogram, provided the value of D is known. Since the steady state current is proportional to the bulk concentration of electroactive species, the above expression can also be used in determining unknown concentration of some electroactive species. Microelectrodes of different geometries are commonly found in the literature [2,10]. Among the common geometries are disks, rings, and bands.The current associated with microelectrode is very small, of the order of pA to nA and consequently the

current densities are very high compare to normal sized macroelectrodes. Current densities of upto 70 A cm^{-2} have been reported [11]. Since current density determines the ratio of faradaic to non-faradaic current for a cyclic voltammograms, the cyclic voltammograms obtained in case of microelectrodes are almost unaffected by background current. Since the current is very small, the corresponding iR drop for a microelectrode is negligible. Hence, microelectrodes can be used to study voltammograms in absence of supporting electrolytes and also in highly resistive media like non-aqueous solvents, polymers, gaseous interfaces, which is not possible with macroelectrodes. Due to small iR drop, microelectrodes are utilized to carry out voltammograms at very high scan rates (10^6 Vs^{-1}). The voltammograms are also free from double layer charging current. Microelectrodes also possess large mass transport coefficient m (m=D/r), where D is the diffusion coefficient and r is the electrode radius. Due to high rate of mass transfer, microelectrodes can be used to measure the rate constants and other kinetic parameters of very fast heterogeneous charge transfer reactions. Kinetic parameters for rapid homogeneous processes can also be determined only if the diffusion limited current is dependent on the homogeneous kinetics.

AC impedance spectroscopy has been used as a powerful technique to characterize an electrochemical system, since both the faradaic and non-faradaic process can be readily measured using conventional size macroelectrode[12]. Only a limited number of impedance studies have been carried out using ultramicroelectrodes [13-16]. Several authors have tried to derive appropriate equations for the ac impedance at a microdisk electrode [16-20], but the most comprehensive treatment is that of Fleischmann and Pons [18]. Abrantes et al. [21] have carried out ac impedance experiments

with microdisk electrode in solution containing ferrocyanide/ferricyanide redox couple to compare their experimental results with the theoretical predictions of Fleischmann and Pons [18].

Ultramicroelectrodes are available commercially from most companies specializing in electrochemical apparatus, but the cost is very high and electrodes of variable diameters are not available. In this chapter, we have described a simple method of fabricating disk shaped gold and platinum microelectrodes with diameters of 10-50 μm by sealing sodalime glass with metal microwires. The electrodes were characterized by performing cyclic voltammetry in aqueous and acetonitrile solution. We have observed the characteristic sigmoidal voltammogram, from which the electrode dimensions have been calculated. We have performed impedance spectroscopy using 50 and 40 μm microelectrodes to study ferrocyanide/ferricyanide redox couple in aqueous medium.

We have studied the barrier properties of SAM modified ultramicroelectrodes using ferrocene/ferricenium redox couple in acetonitrile and ferrocyanide/ferricyanide redox couple in water and also studied on the effect of solvents on the barrier properties of alkanethiol SAMs formed on microelectrodes, as there has been no study on the formation of SAM of alkanethiol molecules on gold microelectrode. Microelectrode can provide several advantages in electrochemical studies, over the conventional sized macroelectrode.

6.1 Experimental :

6.1.1 Microelectrode fabrication

Ultramicroelectrodes are available commercially from most companies specializing in electrochemical apparatus, but the cost is comparatively very

high and variable electrode diameters may not be available. Our aim is to fabricate microelectrodes of different diameters by sealing glass with metal microwires of required diameters. A wide variety of methods are available for constructing ultramicroelectrodes [2,22]. Disks, bands and rings are some of the common geometries of ultramicroelectrodes.The ultramicroelectrode disk is easiest to fabricate and can be made by encapsulating metal microwire in a matrix of glass or epoxy [22]. Glass is the best choice to be embedded with metal, as it has the properties of good insulation, transparency, inertness and is easy to polish and seal with metals. Perfect metal to glass sealing is an important step in modern scientific glass-blowing. To assure a satisfactory seal, glass must wet the surface of the metal, and the metal must have a coefficient of thermal expansion similar to that of the glass. This will give perfect glass to metal sealing without any leakage. While platinum and gold have a thermal expansion coefficient of 91×10^{-7} and 143×10^{-7} /^{0}C respectively, the soft glass which we have used has a thermal expansion coefficient of 92×10^{-7} /^{0}C. This was found to be suitable for platinum due to exact matching in thermal expansion coefficient. Though the thermal expansion coefficient of our glass is almost two third of gold, we have successfully achieved excellent glass-metal seal and fabricated gold microelectrodes which show no leakage when kept in electrolytes even for days.

The glass used by us is a sodalime lamp glass of the following composition available commercially. It has a softening point of 700^0 C and very high percentage of sodium monooxide. The composition of sodalime lamp glass :

SiO_2 73.5 %, Na_2O 16.3 %, CaO 4.7 %, K_2O 0.3 %, Al_2O_3 1.6 %, Sb_2O_3 0.17 %, MgO 3.4 %, FeO 0.03 %.

The following method was adopted by our glass blower to achieve a perfect metal-glass seal. The gold and platinum microwires (diameters 10, 12.5, 40 and 50 μm) were obtained from Advent (U.K). A 10 cm length of gold or platinum microwire was soldered with a thin copper wire for electrical contact without any blob at the soldered part, as any blob will cause obstruction while drawing this soldered microwire through a narrow capillary jet. The length of the microwire depends on the height of the electrochemical cell along with the cap. The soldered gold/platinum wire was inserted carefully through the fine capillary jet and drawn to the other side and positioned. The wire end just protrudes outside the jet capillary. A pinpoint low temperature flame was set at the burner and the capillary tube was sealed with the gold/platinum wire. High temperature, broad flame and prolong heating may spoil the wire and conduction of heat may sometimes desolder the wire. The sealing must take place from one end progressively to the other end to avoid air trapping between the glass and metal interface which will definitely weaken the sealing. The other end of the soldered copper wire was conveniently folded at the top of the cone and this was used as the external electrical contact. The electrode tip was shaped to a disk by grinding in 1000 grade carborandum, 1500 grade emery paper and the resulting electrode was smoothed by polishing on a micro cloth having a slurry of 1.0, 0.3 and 0.05 μm alumina powder (Buehler made) successively. The metal-glass sealing portion was examined under the microscope for any imperfections, although the quality of the electrode should ultimately be assessed electrochemically by cyclic voltammetric studies of some standard redox couples like ferrocyanide/ferricyanide in aqueous media, ferrocene/ferricenium in acetonitrile.

6.1.2 Electrode and cells

This gold disk electrode was used as the working electrode in our study. A conventional three electrode electrochemical cell was used. A platinum foil of large surface area was used as counter electrode. Saturated calomel electrode (SCE) was used as reference electrode in aqueous medium, whereas a silver rod was used as a quasi-reference electrode in acetonitrile [23,24]. The silver quasi-reference electrode has a potential of −0.2 V with respect to saturated calomel electrode (SCE) [25]. This quasi-reference electrode has a stable potential in acetonitrile and free of any liquid junction potential. The cell has a provision for inserting an inlet and outlet for nitrogen gas. Before each experiment, the cell was completely deaerated by passing 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 100^0 C for atleast one hour before the start of the experiment. Immediately before use, the gold electrode was polished using aqueous slurries of progressively finer alumina (1.0, 0.3 and 0.05 μm alumina), sonicated to remove alumina particle. The electrode was rinsed with distilled water. Ferrocyanide solution was prepared with millipore water. The whole electrochemical cell containing the electrode was put into a Faraday cage to suppress the background noise.

6.1.3 Chemicals

Ethanol 99.95% (Emerck), tetrabutylammonium tetrafluroborate (Aldrich), lithium perchlorate (Fischer), ferrocene (Acros Organics), hexadecanethiol (Aldrich),potassium ferricyanide(Qualigens), potassium ferrocyanide(Loba), acetonitrile (Ranbaxy), sodium fluoride (Qualigens), potassium chloride (Ranbaxy) were used in this study.

6.1.4 Instrumentation

Cyclic voltammetry was carried out using a home-made potentiostat and also with an EG&G potentiostat (Model 263 A) interfaced to a PC through a GPIB card (National Instruments). We describe here the fabrication of a simple operational amplifier (Op Amp) based potentiostat along with the low current measuring device. The current associated with microelectrodes is of the order of pA to nA. The problems associated with measurement of very small currents and elimination of noise can be overcome by the use of ultra low noise, low bias current amplifiers. We have used Op Amp CA 3140 for the control amplifier and voltage follower and AD 515 (Analog Devices) as current amplifier in our potentiostat. AD 515 is a low noise amplifier, having ultra low bias current of 75 fA, with low offset and thermal drift and is ideal for measuring very low currents. However, measurement of such low currents is beset with the problem of line frequency (50 Hz) and its harmonic noise. We got excellent signal to noise ratio by using unity gain sallen-key type low-pass filter having a cutoff frequency of 1 Hz. We have used low noise, low drift Op Amp AD 743 (Analog devices) for fabricating the low pass filter. The current amplifier output was recorded using Hewlett Packard X-Y recorder (7044 A model), while a SRS function generator (model DS340, 15 MHz) was used as a voltage source for supplying suitable voltage ramp. The schematic diagram of our experimental set up is shown below. 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. The impedance measurements were carried out at 0.240 V vs SCE.
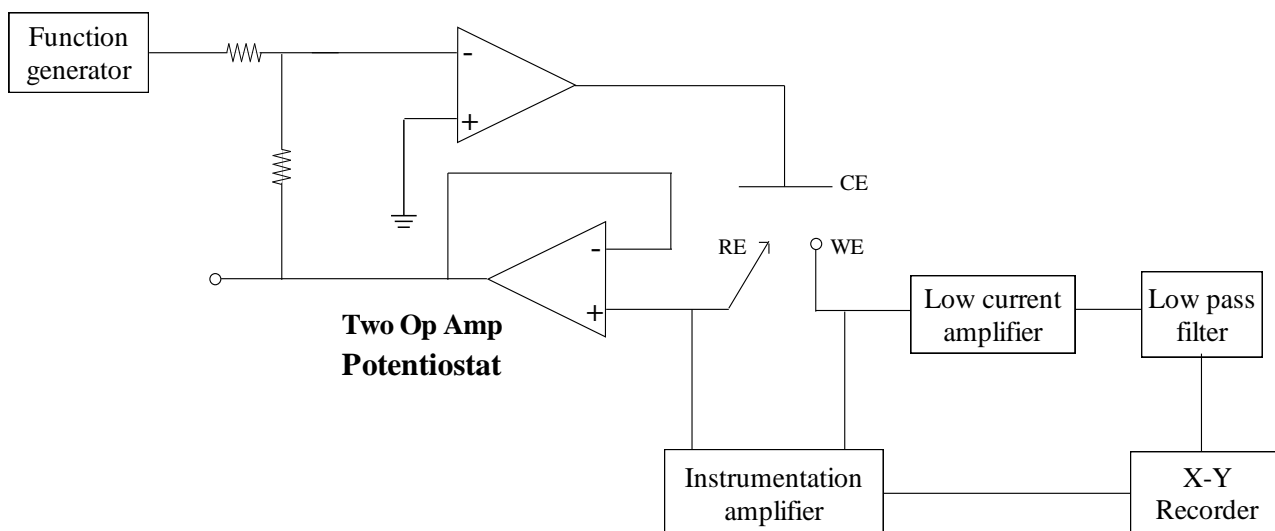
Schematic diagram of experimental setup used for microelectrode studies

6.2 Results and discussion :

6.2.1 Characterization of microelectrode by cyclic voltammetry

We have fabricated 10 μm and 50 μm diameter platinum and 12.5 and 40 μm diameter gold microdisk electrodes. The electrodes were characterized by performing cyclic voltammetry of 10 mM potassium ferrocyanide with 1M NaF in water and also of 1 mM ferrocene in 0.1 M TBAFB/acetonirile solution. For a disk-shaped microelectrode, we get typical sigmoidal voltammogram and the limiting plateau current from CV is given by the following equation (1).

i_{lim}= 4nFrC*D -------------(1)

where i_{lim} is the steady state limiting current(A), F is Faraday constant (1F=96500C), and r is electrode radius(cm). By measuring the limiting current from steady-state sigmoidal shaped voltammogram one can determine r, provided C* and D value are known. We observed sigmoidal shape voltammograms in all the experiments indicating microelectrode characteristics. The cyclic voltammograms are highly reproducible even

157

after keeping 24 hours in the solution, indicating very good metal-glass sealing without any leakage. The cyclic voltammograms for 10 mM ferrocyanide with 1 M NaF with 40 μm Au and 10 μm Pt microdisk electrodes are shown in Figure 1. We have also determined the radius of microelectrode using equation (1). In determining r value, we have used the following diffusion coefficient values (D) from the literature at 25^0 C.

$D_{ferrocyanide/water} = 9.2 \times 10^{-6}$ cm^2/s , $D_{ferrocene/acetonitrile} = 2.4 \times 10^{-5}$ cm^2/s

Table 1 shows the calculated r values for different microelectrodes obtained from the steady state voltammograms.

Table 1

Calculated radius values (in μm) for different microelectrodes from sigmoidal shaped steady state voltammograms

Redox system	Type of microelectrode	$r_{calculated}$ (μm)
10 mM ferrocyanide with 1 M NaF in water	50 μm diameter platinum microelectrode	31.5
10 mM ferrocyanide with 1 M NaF in water	10 μm diameter platinum microelectrode	5.2
10 mM ferrocyanide with 1 M NaF in water	12.5 μm diameter gold microelectrode	7.9
10 mM ferrocyanide with 1 M NaF in water	40 μm diameter gold microelectrode	21.1
1 mM ferrocene with 0.1 M TBAFB in acetonitrile	12.5 μm diameter gold microelectrode	10.3
1 mM ferrocene with 0.1 M TBAFB in acetonitrile	40 μm diameter gold microelectrode	29.1

The difference in value between the measured radius and the used wire radius may be due to the fact that the wire may not have uniform diameter throughout the length of the wire.

6.2.2 Electrochemical impedance spectroscopy using microelectrode

Figures 2A and 2B illustrate the complex plane impedance plot (Nyquist plot) of the real and imaginary components for 10 mM ferrocyanide/ferricyanide in 1 M NaF using 50 and 40 μm diameter Pt and Au microelectrode respectively over a frequency range of 0.01 Hz to 30 kHz. In both the cases, the ac response at higher frequencies is determined by charge transfer resistance of the ferrocyanide redox reaction, which is in parallel to double layer capacitance. The mass transfer impedance (diffusional impedance) predominates at lower frequencies. We have observed a large semicircle at lower frequency region (from 0.01 Hz to 80 Hz), where reaction is diffusion controlled. A much smaller semicircle is observed at higher frequency region (from 90 Hz onwards) due to kinetic control. The main advantage using microelectrodes in ac impedance spectroscopy is the significant reduction of diffusional impedance compared to conventional sized macroelectrode and therefore it is possible to characterize fast heterogeneous redox reaction like the ferrocyanide/ferricyanide.

6.2.3 Electrochemical studies on the effect of solvents on the barrier properties of alkanethiol SAM formed on gold microelectrodes :

6.2.3.1 <u>Study of ferrocene redox reaction in acetonitrile</u>

Figure 3 shows the cyclic voltammograms of ferrocene redox reaction on 40 μm diameter bare Au electrode (Figure 3a) and hexadecanethiol (HDT) coated electrode in acetonitrile containing 0.1 M TBAFB. The first cycle CV of 1 mM HDT coated electrode exhibits a s-shaped voltammogram with

much lower current compared to bare Au microelectrode (Figure 3b). As scanning continues however, we get voltammogram with current similar to bare Au electrode (Figure 3c). In order to check whether there is any desorption of thiol monolayer that might have occurred during potential cycling in acetonitrile, we have carried out cyclic voltammetry with the same electrode which was already scanned in acetonitrile, in another redox system viz., 10 mM ferrocyanide in water containing 1 M KCl. Figure 4a shows the cyclic voltammogram of bare gold electrode for ferrocyanide redox reaction in water with usual characteristics of a microelectrode exhibiting s-shaped voltammogram, while 4b shows the CV of hexadecanethiol coated electrode for the same system which was subjected to potential scanning in acetonitrile. It can be seen that initially the electrode shows almost no blocking to ferrocyanide redox reaction with a peak in the voltammogram (Figure 4b). The peak in the voltammogram can be attributed due to two opposite effects due to monolayer disorganization (by first potential scanning in acetonitrile) and gradual organization (by later potential scanning in aqueous medium). But after some time, this electrode shows very good blocking to ferrocyanide redox reaction (Figure 4c) which is a clear indication that hexadecanethiol molecules are still existing on the gold surface. It is interesting to note that an alkanethiol coated macroelectrode, which was subjected to potential scanning in acetonitrile previously, shows excellent blocking behaviour to ferrocyanide redox reaction in aqueous media on initial scan. This can be explained as follows : For an alkanethiol coated macroelectrode, the electron transfer kinetics of ferrocyanide redox reaction is masked by diffusion process through the pinholes and defects as discussed in Chapter 3. On the other hand, the effect of diffusion on the electron transfer kinetics of ferrocyanide redox reaction is

minimized for an alkanethiol coated microelectrode. Hence, the kinetically controlled current becomes prominent in an alkanethiol coated microelectrode. This is manifested in the voltammogram exhibiting prominent current (Figure 4b). Next, we scanned the potential to a very negative value (below –1 V vs SCE) in acetonitrile, as it is known that the thiol monolayer desorbs at this potential. This electrode, after washing in millipore water is cycled again in ferrocyanide containing electrolyte and the CV (Figure 4d) obtained clearly resembles that of bare gold microelectrode. The above series of experiments proves that hexadecanethiol monolayer was stable in ferrocene-acetonitrile medium within the potential range of scanning but undergoes some kind of disorganization which results in significant faradaic current during ferrocene redox reaction. We have found that electron transfer reaction of ferrocene-ferricenium redox couple is unimpeded for an alkanethiol coated Au microelectrode. This behaviour is similar to alkanethiol coated Au macroelectrode in acetonitrile. This was explained as arising from the ability of acetonitrile to solvate the alkyl chain of alkanethiol monolayer to disorganize [26-28] and allowing the ferrocene or ferricenium molecule to penetrate through the monolayer. These results are very much in agreement with our previous studies on the barrier properties of alkanethiol SAMs in different non-aqueous solvents [26,27].

6.2.3.2 Study of ferrocyanide redox reaction in water

We have studied the ferrocyanide/ferricyanide redox reaction in water with 40 μm diameter Au disk electrode coated with alkanethiol monolayer. The alkanethiol coated electrode was kept for 30 minutes in solvents like ethanol and acetonitrile. Figure 5a shows the s-shaped cyclic voltammogram for 10 mM ferrocyanide in 1M NaF with 40 μm diameter Au disk microelectrode. Figures 5b and c illustrate the CVs of 1 mM HDT coated electrode after

keeping in ethanol for 30 minutes immediately after the formation of monolayer (initial scan) and after several scans (after keeping longer time in aqueous medium) respectively. We find that the ferrocyanide redox reaction is slightly impeded by alkanethiol coated microelectrode (Figure 5b) initially, after keeping the electrode in ethanol for 30 minutes. However, after keeping the same electrode in the aqueous medium for longer duration, it shows gradual blocking of ferrocyanide reaction (Figure 5c). However, the alkanethiol coated microelectrode shows complete blocking to ferrocyanide redox reaction without keeping in ethanol (Figure 5d). We have also observed similar results for alkanethiol coated microelectrode after keeping in acetonitrile for 30 minutes.

This behaviour can be explained as follows: The alkanethiol monolayers are disorganized in solvents like ethanol and acetonitrile due to ability of these solvent molecules to extensively solvate the alkyl tails of the monolayer. This is caused by two factors. Firstly, there is no or little 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.

More ordered solvents such as 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 hydrophobic interaction among the terminal methyl groups of the alkanethiol.

The alkanethiol coated Au microelectrode, previously kept in acetonitrile and ethanol shows almost no blocking toward ferrocyanide/ferricyanide redox reaction initially due to the disorganization of the alkanethiol monolayer in these solvents. However, keeping longer time in the aqueous solution, the alkanethiol coated Au microelectrode eventually blocks the ferrocyanide/ferricyanide redox reaction. On keeping longer time in water, there is enhanced hydrophobic interaction among the disorganized alkanethiol molecules as the alkyl chains repels water molecule and thereby forming more compact and organized monolayer.

6.2.3.3 <u>Study of ferrocyanide redox reaction in water+ethanol mixture</u>

Figure 6 shows the cyclic voltammograms of bare (Figure 6a) and 1 mM (Figure 6b) and neat HDT (Figure 6c) coated Au microdisk electrode (40 μm diameter) for the ferrocyanide redox reaction in 0.1 M LiClO$_4$ in (1:1) ethanol+water mixture. We have obtained a diffusion coefficient (D) value of 6×10^{-6} cm^2 s^{-1} for ferrocyanide in 1:1 ethanol+water mixture using expression (1) from the s-shaped voltammogram (Figure 6a). We find that neat HDT coated microelectrode blocks the ferrocyanide redox reaction to a greater extent compared to 1 mM HDT coated microelectrode. These results prove that neat HDT coated gold electrode exhibits better barrier properties for ferrocyanide redox reaction in ethanol+water mixture compared to dilute ethanolic HDT coated electrode. Our result is in good agreement with our previous results [26,29], where neat alkanethiol coated Au electrode exhibits better barrier properties both in aqueous and non-aqueous media compared to dilute ethanolic alkanethiol coated Au surface.

Figure 7 shows the cyclic voltammograms of bare (Figure 7a) and 1 mM (Figure 7b) and neat HDT (Figure 7c) coated Au microdisk electrode

(40 μm diameter) for the ferrocyanide redox reaction in 0.1 M LiClO$_4$ in (1:2) ethanol+water mixture. We have obtained a D value of 2×10^{-6} cm^2 s^{-1} for ferrocyanide in (1:2) ethanol+water mixture.

A study of the relative barrier properties of alkanethiol coated microelectrode for ferrocyanide redox reaction in (1:1) and (1:2) ethanol+water mixture has been carried out by directly measuring the faradaic current from the s-shaped cyclic voltammograms. The barrier efficiency of alkanethiol coated microelectrode is calculated from the following formula.

B.E. = (1- I$_m$/ I$_b$) × 100

where B.E. is the barrier efficiency, I$_m$ is the faradaic current of 1 mM HDT coated Au microelectrode (40 μm diameter), and I$_b$ is the faradaic current of bare gold microelectrode for ferrocyanide redox reaction in ethanol+water mixture. We have obtained B.E. values of 77.21 % and 94.22 % for 1 mM HDT coated Au microelectrode (40 μm diameter) for ferrocyanide redox reaction in (1:1) and (1:2) ethanol+water mixture respectively. Ethanol and water are completely miscible and both contain hydrogen bonded structure. 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. On the other hand, ethanol can form ring like one dimensional H-bonding with the nearest neighbours [30,31]. However, it lacks the orderness of water. Ethanol has the ability to solvate the alkyl tail of alkanethiol monolayer and disorganize it due to this lack of solvent

orderness. Hence, ethanol and water play contrasting role in their ability to order the alkanethiol SAM on gold.

6.3 Conclusions :

The following conclusions can be inferred from our studies :

1. 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.

2. 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.

3. 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.

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