

Characteristics of redox systems on self-assembled monolayer-covered electrodes

SHEELA BERCHMANS, V YEGNARAMAN* and
G PRABHAKARA RAO

Central Electrochemical Research Institute, Karaikudi 630 006, India

MS received 26 March 1997; revised 30 June 1997

Abstract. Electrochemical studies on gold electrodes covered with self-assembled monolayers (SAM) of aminoethane thiol (AET), mercaptobenzothiazole (MBT) and octadecyl mercaptan (ODM) have been carried out using cyclic voltammetry. Study of the influence of these monolayers on the double layer capacity of the interfaces involving the Au/SAM electrodes and of the electron transfer kinetics of chosen redox reaction probes, viz., $\text{Fe}(\text{CN})_6^{4-/3-}$, $\text{Fe}^{2+/3+}$, hydroquinone/quinone ($\text{H}_2\text{Q}/\text{Q}$) and Cu underpotential deposition, offers a wealth of information that can throw light on the role of SAMs in allowing/moderating/blocking the electron transfer at such interfaces. These details are presented and discussed in the paper.

Keywords. Self-assembled monolayer; redox system; electron transfer kinetics; underpotential deposition; voltammetry.

1. Introduction

Formation of organized molecular assemblies at interfaces, increasingly investigated (Lipkowski 1992; Bard *et al* 1993) in recent times, offers vast scope for manipulating the interfacial architecture that holds the key to proper understanding of several issues such as electron transfer (et), energy transduction etc. The method of self-assembly, where the binding of a monolayer of molecules to metal surfaces is achieved through chemical interactions, incidentally offers a simple and elegant approach to modify electrode surfaces at molecular levels (Wilner *et al* 1995; Zhong and Porter 1995; Upadhyay *et al* 1996). Molecular electronics (Carter 1982, 1987; Nuzzo *et al* 1987; Hong 1989; Bharathi *et al* 1993), sensors (Sun *et al* 1990; Steiberg *et al* 1991; Cheng and Toth 1992; Malem and Mandler 1993; Bharathi *et al* 1995) and tribology (Ulman *et al* 1991; Laibinis and Whitesides 1992) are typical application areas for such modified surfaces. Self-assembled monolayers (SAMs), serving as precision spacers with molecular resolution between the electrodes and the reaction centres, enabled, for the first time, the tailoring of model molecular interfaces for resolving some of the basic issues relating to et kinetics (Porter *et al* 1987; Sabatani *et al* 1987; Miller *et al* 1991; Finklea and Hanshaw 1992) that are hitherto unresolved. Typically, the SAMs of alkanethiols of the type $\text{CH}_3-(\text{CH}_2)_n-\text{SH}$ have enabled the understanding of the kinetics of the outer sphere et reactions as a function of the distance between the electrode and the redox centre by working with SAM-covered electrodes with varying values of n . These studies have also revealed that compact and impervious monolayers result when the methylene

*For correspondence

chain length is large (≥ 9), while non-compact and porous monolayers are the result of low values of n . Reports published so far are largely concerned with the use of aliphatic thiols for forming SAMs. On the other hand, studies with SAMs of thiols having aromatic substituents may prove to be rewarding (Bard *et al* 1993; Sabatani *et al* 1993), considering the additional interactions between the substrate metal and the π electrons of the aromatic ring on the one hand and the possibility of forming compact and impervious monolayers with thiols containing aromatic groups on the other (despite the absence of a long methylene chain length as in the case of long-chain aliphatic thiols). Accordingly, 2-mercaptobenzthiazole (MBT) which has a mercaptan group and a fused benzene ring that can contribute to rigid orientation of the molecule has been chosen for the present study. The thickness of the MBT monolayer is estimated to be around 8 Å (Bharathi *et al* 1993) from a space filling model. For comparison, two other alkyl mercaptans, namely, octadecyl mercaptan (ODM) and aminoethane thiol (AET), whose monolayer thicknesses correspond to about 30 Å (Porter *et al* 1987) and 6 Å from space-filling model calculations respectively, were included in the study.

Assessment of the influence of the above SAMs (on Au electrode) on *et* reactions was made through the use of (1) ferro/ferricyanide, ferrous/ferric and hydroquinone/quinone redox probes, and (2) underpotential deposition (upd) studies, which involve electrochemical phase formation of copper underpotential deposit. The latter, involving the formation of a new phase with the participation of metal ions from the solution and electrons from the Au substrate, is considered an additional useful tool in investigating charge transfer processes, particularly those involving both electron transfer and mass transfer across interfaces involving molecular spacers whose compact or porous nature is also to be probed.

2. Experimental details

A gold disk (BAS, Inc., USA) of area 0.036 cm² was polished using alumina slurry (0.05 μ m), washed, degreased and sonicated in water before being used as the working electrode. A Pt foil and a standard (1 M KCl) calomel electrode served as the counter and reference electrodes respectively. MBT (Fluka AG), ODM (Aldrich, USA), AET (Aldrich, USA) and other reagents were of AR grade and were used without further purification. Triple-distilled water was used for preparing the solutions. Monolayer coverage of the electrode was obtained by immersing the cleaned Au electrodes in an acetone solution of MBT/ODM (0.01 M) for about four hours and then rinsing them in alcohol and drying them in air. They are designated Au/MBT and Au/ODM respectively. Au/AET electrode was prepared by immersion of the cleaned electrode in an aqueous solution of AET (0.1 M). The cyclic voltammograms (CV) were recorded using Wenking (Model POS 73) potentiostan and Rikadenki (Model RW 201T) X-Y/t recorder. In the next section, the monolayer-covered gold electrode is generally represented as Au/SAM.

3. Results and discussions

3.1 Double-layer capacitance of Au/SAM electrodes

Double-layer capacitance (C_{dl}) values for the monolayer-covered electrodes have been estimated from the CV data using the expression (Cheng and Brajter-Toth 1995)

$$C_{dl} = I_c/2vA$$

Table 1. Double layer capacitance of Au/SAM electrodes.

Electrode	DL capacitance ($\mu\text{F}/\text{cm}^2$)
Au	100
Au/AET	83
Au/MBT	8
Au/ODM	4

Table 2. CV data of the redox systems on Au/SAM electrodes.

Electrode	Redox system	v (mV/s)	E_{Pa} (mV)	E_{Pc} (mV)	ΔE_P (mV)	I_{Pa} (μA)	I_{Pc} (μA)
Au	$[\text{Fe}(\text{CN})_6]^{4-/3-}$	20	370	300	70	4.9	4.4
Au	$[\text{Fe}(\text{CN})_6]^{4-/3-}$	50	380	300	80	6.7	5.7
Au	$[\text{Fe}(\text{CN})_6]^{4-/3-}$	100	380	300	90	9.0	7.0
Au	$\text{Fe}^{2+/3+}$	20	420	340	80	4.6	4.5
Au	$\text{Fe}^{2+/3+}$	50	430	340	90	5.6	5.1
Au	$\text{Fe}^{2+/3+}$	100	440	330	110	7.8	7.6
Au	$\text{H}_2\text{Q}/\text{Q}$	20	360	330	30	12.2	11.2
Au	$\text{H}_2\text{Q}/\text{Q}$	50	360	330	30	17.0	16.0
Au	$\text{H}_2\text{Q}/\text{Q}$	100	360	330	30	23.4	22.6
Au/AET	$[\text{Fe}(\text{CN})_6]^{4-/3-}$	20	380	320	60	4.4	4.6
Au/AET	$[\text{Fe}(\text{CN})_6]^{4-/3-}$	50	380	320	60	6.6	5.5
Au/AET	$[\text{Fe}(\text{CN})_6]^{4-/3-}$	100	380	320	60	9.0	7.0
Au/AET	$\text{Fe}^{2+/3+}$	20	460	300	160	3.0	2.3
Au/AET	$\text{Fe}^{2+/3+}$	50	480	330	150	3.9	3.3
Au/AET	$\text{Fe}^{2+/3+}$	100	500	250	250	5.9	4.4
Au/AET	$\text{H}_2\text{Q}/\text{Q}$	20	520	140	380	10.4	4.4
Au/AET	$\text{H}_2\text{Q}/\text{Q}$	50	530	130	400	15.8	8.0
Au/AET	$\text{H}_2\text{Q}/\text{Q}$	100	530	120	410	20.4	12.2
Au/MBT	$[\text{Fe}(\text{CN})_6]^{4-/3-}$	20	390	330	60	4.0	4.0
Au/MBT	$[\text{Fe}(\text{CN})_6]^{4-/3-}$	50	390	330	60	5.8	6.0
Au/MBT	$[\text{Fe}(\text{CN})_6]^{4-/3-}$	100	390	330	60	7.7	7.4
Au/MBT	$\text{Fe}^{2+/3+}$				No response		
Au/MBT	$\text{H}_2\text{Q}/\text{Q}$	20	680	a	—	7.4	—
Au/MBT	$\text{H}_2\text{Q}/\text{Q}$	50	700	a	—	10.0	—
Au/MBT	$\text{H}_2\text{Q}/\text{Q}$	100	710	a	—	14.4	—

'a' denotes absence of response

where I_c is the sum of the anodic and cathodic charging currents in mA, v is the scan rate in V/s and A is the electrode area in cm^2 . Table 1 lists the C_{dl} values for the different SAM-covered electrodes investigated. From the capacitance data, it can be seen that the C_{dl} of Au/AET is almost equal to that of the bare electrode and is significantly higher than that of the Au/MBT and Au/ODM, which are characterized by very low values of C_{dl} .

3.2 Response of the Au/SAM electrodes to the redox probes

The voltammetric behaviour of three different redox systems, viz (i) ferro/ferricyanide, (ii) ferrous/ferric, and (iii) quinone/hydroquinone on Au/SAM and bare Au electrodes have been studied. The Au/SAM electrode could be repeatedly used, after thorough washing, for investigations with different redox probes and the resulting voltammetric data were reproducible, thereby ensuring the stability of the monolayer modification. From typical CVs, the voltammetric features were measured and are presented in table 2. The heterogeneous rate constants for the electron transfer have been estimated from the CV data obtained at 20 mV/s, using the methods based on either ΔE_p values (Nicholson 1965) or scan rate dependence of peak-potentials (Reinmuth 1960); the results are given in table 3.

3.2a Ferro/ferricyanide: In figure 1 are depicted the CVs of ferrocyanide (2 mM) in 0.5 M H_2SO_4 at 20 mV/s on Au/SAM and bare Au electrodes. The redox system exhibits a fairly reversible behaviour on bare Au with ΔE_p values slightly higher than 60 mV which is in conformity with earlier observations (Porter *et al* 1987). Interestingly, the redox response is reversible with ΔE_p values of 60 mV at all sweep rates studied from 20 to 100 mV/s on Au AET (table 2). Similar observations were made on Au/MBT showing the facile redox kinetics in this case also. On the other hand, the electron transfer kinetics of ferro/ferricyanide is completely blocked on Au/ODM and these observations are in accordance with earlier reports (Porter *et al* 1987).

3.2b Ferrous/ferric: The CVs of 2 mM ferrous sulphate in 0.5 M H_2SO_4 at 20 mV/s on Au/SAM electrodes are presented in figure 2. $Fe^{2+/3+}$ exhibits near reversible redox behaviour on Au, with peak currents marginally lower than those obtained for $Fe(CN)_6^{4-/3-}$ (figure 1). On Au/AET, the redox kinetics of ferrous/ferric is found to be significantly slower as evidenced by large ΔE_p values (table 2). On the other hand, Au/MBT and Au/ODM completely blocked the et which has resulted in featureless voltammograms (figure 2).

3.2c Hydroquinone/quinone: The CVs of 3.3 mM hydroquinone in 0.5 M H_2SO_4 at 20 mV/s on Au/SAM electrodes are given in figure 3. This H_2Q/Q redox system exhibits a reversible et on bare Au, characterized by ΔE_p values of 30 mV at all sweep

Table 3. Heterogeneous et rate constants (k) of the redox systems based on CV data at 20 mV/s.
 $Fe(CN)_6^{4-}$: 2 mM; Fe^{2+} : 2 mM; Quinol: 3.3 mM

Electrode	k (cm/s)		
	$Fe(CN)_6^{3-/4+}$	$Fe^{2+/3+}$	H_2Q/Q
Au	@ 6.90×10^{-3}	@ 3.3×10^{-3}	@ 3.49×10^{-2}
Au/AET	@ 3.05×10^{-2}	@ 5.2×10^{-4}	# 1.48×10^{-5}
Au/MBT	@ 3.05×10^{-2}	NR	# 2.30×10^{-6}
Au/ODM	NR	NR	NR

@: Estimated using ΔE_p value (Nicholson 1965); #: Estimated using scan rate dependence of E_p (Reinmuth 1960)
 NR: No response

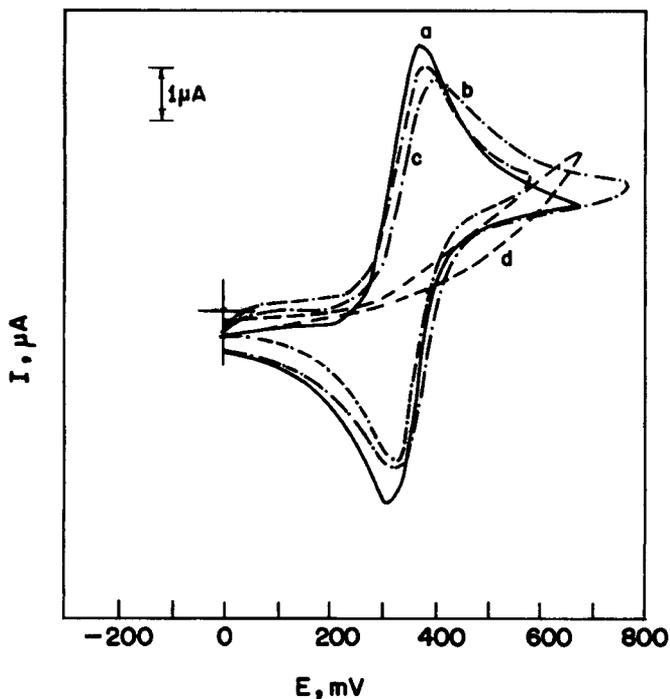


Figure 1. Redox behaviour of $\text{Fe}(\text{CN})_6^{4-/3-}$ on Au/SAM electrodes: Cyclic voltammograms in 0.5 M H_2SO_4 medium on (a) bare Au; (b) Au/AET; (c) Au/MBT; (d) Au/ODM at 20 mV/s; concentration of $\text{Fe}(\text{CN})_6^{4-} = 2 \text{ mM}$.

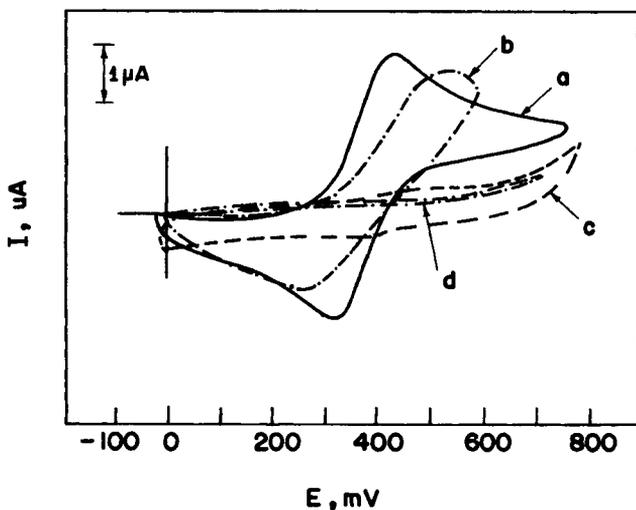


Figure 2. Redox behaviour of $\text{Fe}^{2+/3+}$ on Au/SAM electrodes: Cyclic voltammograms in 0.5 M H_2SO_4 medium on (a) bare Au; (b) Au/AET; (c) Au/MBT; (d) Au/ODM at 20 mV/s; concentration of $\text{Fe}^{2+} = 2 \text{ mM}$.

rates employed in this study. The redox kinetics of the same system becomes much slower on Au/AET with significant increase in ΔE_p values. When compared to the behaviour on the bare electrode, the cathodic reduction peak shifts cathodically by

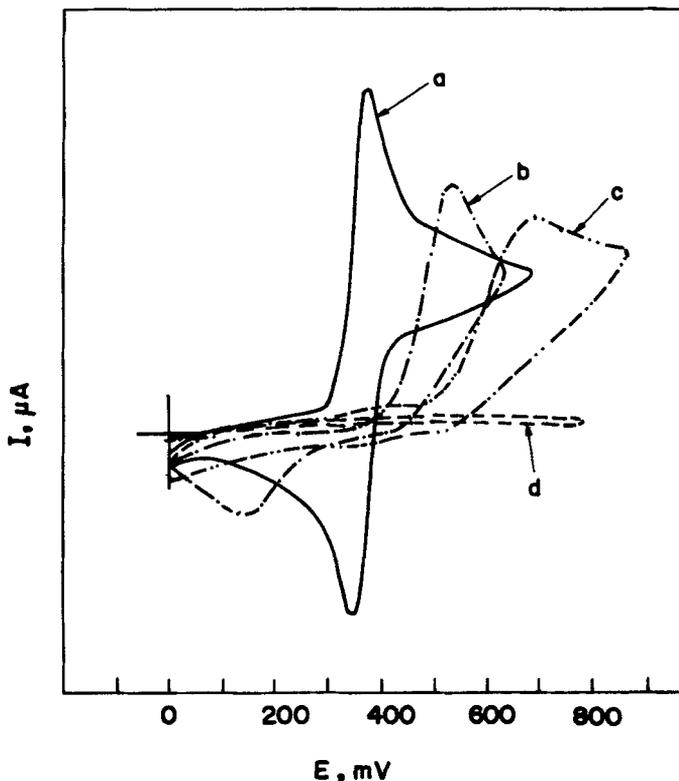


Figure 3. Redox behaviour of H_2Q/Q on Au/SAM electrodes: Cyclic voltammograms in $0.5\text{ M } H_2SO_4$ medium on (a) bare Au; (b) Au/AET; (c) Au/MBT; (d) Au/ODM at 20 mV/s ; concentration of hydroquinone = 3.3 mM .

about 200 mV while the anodic peak shifts by about 160 mV on the anodic side. Moreover, the cathodic peak currents are significantly reduced (about 50%) while the decrease in anodic peak currents is only marginal. On Au/MBT, the anodic peak is further shifted when compared to Au/AET (about 320 mV anodic with respect to bare Au) and the cathodic peak is absent. Also, the anodic peak currents are considerably reduced when compared to bare Au and Au/AET. Finally, the et of this redox system is totally absent on Au/ODM.

3.3 Response of Au/SAM electrodes to ECPF involving Cu upd

Figure 4 depicts the CVs resulting from the upd of copper on Au/SAM electrodes from $0.5\text{ M } H_2SO_4$ containing 6 mM of Cu^{2+} at 20 mV/s . The upd of Cu on bare Au takes place with characteristic deposition and stripping peaks occurring at 120 mV and 210 mV respectively, conforming to earlier literature (Kolb *et al* 1994). On Au/AET, the upd behaviour is similar to that on bare Au, except for a small reduction in currents. On Au/MBT and Au/ODM, upd behaviour is completely blocked.

A critical examination of the various observations presented above enables the derivation of the following inferences relating to the nature of SAMs and their influence on the interfacial et reactions.

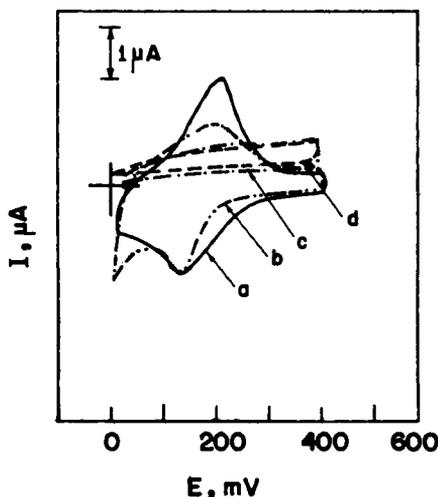


Figure 4. Cu up on Au/SAM electrodes: Cyclic voltammograms in 0.5 M H_2SO_4 medium on (a) bare Au; (b) Au/AET; (c) Au/MBT; (d) Au/ODM at 20 mV/s; concentration of $\text{Cu}^{2+} = 6$ mM.

Capacitance calculations (table 1) suggest that the C_{dl} of Au/AET is nearly the same as that of bare Au, suggesting that the AET film formed on the electrode surface is not compact, and thus allows permeation of water and the electrolyte into the monolayer (Cheng and Brajter-Toth 1995).

The capacitance of Au/MBT, on the contrary, is found to be very low, similar to that observed on Au/ODM which was characterized as an impervious monolayer (Porter *et al* 1987). Alkanethiols containing a long methylene chain length (≥ 9 methylene units) are known to form such compact monolayers due to van der Waals interactions between alkyl chains. The present observations about MBT molecules ($\approx 8 \text{ \AA}$ thick, containing no long methylene chains), perhaps yielding a compact and pore-free monolayer, are noteworthy and may be due to the following. The π - π interactions between the adsorbed MBT molecules and/or the interactions between the π electrons of MBT and the delocalized d -electrons of the metal surface may contribute to the compactness of the monolayer film (Lipkowski and Stolberg 1992). Despite the indications of a compact MBT films, the et kinetics of ferro/ferricyanide redox system is not hindered as shown by the experimental results. The ferro/ferricyanide reaction, being an outer sphere et reaction, is unlikely to be hindered by the MBT monolayer whose thickness is small (about 8 \AA). Further, it may be noticed that on Au/MBT, despite the presence of a compact MBT monolayer, the decrease in the i_p values in comparison to bare Au is only very small and reversibility also appears to improve, as evidenced by the ΔE_p values of 60 mV at all scan rates. In this context, it is relevant to note that a SAM of poly (octyl thiophene) when doped with I_2 exhibits increased reversibility to $\text{Fe}(\text{CN})_6^{4-/-3-}$ (Gao and Siong Siow 1996). On the contrary, our experimental results on Au/ODM where the thickness of the ODM monolayer is relatively large ($\approx 30 \text{ \AA}$) confirmed blocking of ferro/ferricyanide redox kinetics as per expectations based on the above arguments.

In the case of ferrous/ferric reaction, the values of ΔE_p show that the monolayer of AET on Au makes the et kinetics slower. Similar C_{dl} data observed with bare Au and

Au/AET suggest the formation of a non-compact AET film and therefore do not warrant any significant influence on kinetics by such electrodes. The reason for the disparity seen could be due to unfavourable electrostatic interactions between the $-\text{NH}_3^+$ groups of Au/AET and Fe^{2+} ions in solution. The blocking of $\text{Fe}^{2+/3+}$ et by the compact MBT film is to be expected considering the inner sphere nature of the et and the observed results are consistent with those expected. The ODM monolayer is known to be impervious and compact and the results on Au/ODM lend further support to the above Cu upd data fully substantiate all the above as can be seen from the following.

During upd reaction, Cu^{2+} ions have to come into contact with the gold surface to form adatoms that lead to the formation of the metal monolayer. It is seen from the figure that upd formation is totally blocked on Au/MBT and Au/ODM, while on Au/AET it is decreased on both the cathodic and anodic sides as compared to bare Au. The AET monolayer, being non-compact, may allow Cu upd formation to take place and the experimental results confirm this. However, the coverage by Cu upd on Au/AET is less than that observed on bare Au. The charge corresponding to stripping of upd estimated from CV in figure 3, yields $250 \pm 20 \mu\text{C}/\text{cm}^2$ on bare Au and $180 \pm 20 \mu\text{C}/\text{cm}^2$ on Au/AET. Half-peak-width is also higher (≈ 150 mV) on Au/AET as compared to that (≈ 100 mV) on bare Au. Reduced area for the electrode surface in the presence of the SAM of AET and the existence of repulsive electrostatic interactions due to protonated amino head-groups of adsorbed AET molecules could account for the above.

Monolayers of MBT and ODM, being compact and impervious are expected to prevent the permeation of Cu^{2+} ions and experimental results on Cu upd on Au/MBT and Au/ODM confirmed this. In this context, it is pertinent to recall that the investigations of Cu upd on SAM-covered electrodes have been reported to be a method for estimating defects in the monolayer (Sun and Crooks 1991).

The $\text{H}_2\text{Q}/\text{Q}$ redox system exhibits reversible et kinetics on Au. On Au/AET, et kinetics is much slower, while it becomes totally irreversible on Au/MBT. The retardation of et rate and the irreversibility observed in the case of Au/AET and Au/MBT respectively are not so easily understood and are perhaps so due to more than one reason, viz. the formation of intermediates, as noted in the case of sulphonate and phosphate esters of hydroquinone (Dryhurst *et al* 1982) and the irreversibility noted in hydrophobic SAMs for the hydroquinone system (Kunitake *et al* 1994). On Au/ODM, the et is completely blocked as expected since ODM monolayer is compact, impervious and relatively thick.

A critical appraisal of the results presented so far on et reactions would help to understand better the influence of SAMs, studied in terms of their molecular thickness, compact or porous structure, nature of SAM and its chemical structure etc.

At an electrode covered with a closely-packed monolayer, electron transfer to solution species could occur in two ways: (a) the electron could transfer through the monolayer via, a tunneling process (Miller *et al* 1991); (b) the electroactive species could permeate through the pinholes in the monolayer that would result in behaviour characteristic of ultramicro-electrodes (Amatore *et al* 1983; Sabatani and Rubinstein 1983).

In the present investigations, on bare Au, the et rate of reaction (2) (below) is marginally lower than that of reaction (1).



With Au/AET, on the other hand, the et kinetics of reaction (2) is significantly lower than that of reaction (1) (cf. ΔE_p values in table 2 and k values in table 3). The difference in trends observed for the two chosen redox reactions on the two electrode surfaces is readily understood in terms of the electrostatic interactions between the redox species and the protonated amino head-groups of the thiol (Takehara *et al* 1994). Attractive interactions between the protonated amino head-groups and the ferro/ferricyanide species facilitate et on Au/AET as compared to bare Au. On the other hand, repulsive interactions between the protonated amino groups and the ferrous/ferric species are possibly responsible for the decrease in the et kinetics on Au/AET when compared to bare Au. Nevertheless, the mechanism of et could be by path (b).

However, in the case of a hydrophobic neutral molecule like hydroquinone, et becomes quasi-reversible and the cathodic current is reduced to 50% when compared to the reversible character on the bare electrode. The reverse reaction, involving the addition of protons, could have been slowed down by one or more of the following factors viz., permeation rates through the film, irreversible adsorption of molecules on the electrode surface, kinetic restrictions due to formation of intermediates or non-availability of protons near the surface. Oxidation of hydroquinone, also, probably proceeds by path (b).

On Au/MBT, reaction (1) exhibits the usual reversible et whereas reaction (2) is completely blocked. Capacitance measurements suggest that MBT forms a pore-free and compact film and therefore the mechanism of et for reaction (1) could be presumed to be through tunneling involving the outer sphere et as mentioned earlier. The possibility of the electron transfer through pinholes in the monolayer, reported earlier (Amatore *et al* 1983; Sabatani and Rubinstein 1983), appears unlikely on Au/MBT, because of the following: (i) The plot of i_p vs \sqrt{v} obtained from the voltammetric data of ferro/ferricyanide redox system on Au/MBT reveals linear dependence of i_p on \sqrt{v} (figure 5). (ii) The CV data resulting at different scan rates under the present experimental conditions do not exhibit a sigmoidal shape characteristic of the ultra-

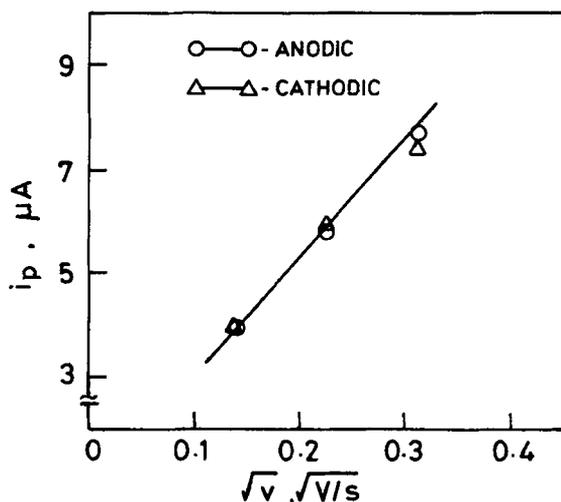


Figure 5. Plot of i_p vs $v^{1/2}$: Based on CV data for $Fe(CN)_6^{4-/3-}$ on Au/MBT in 0.5 M H_2SO_4 , presented in table 2.

microelectrode behaviour arising from the presence of pinholes in the monolayer. (iii) Recent STM investigations of holes in the SAMs of alkanethiols on Au have revealed the absence of pinholes (Schönenberger *et al* 1994).

Reaction (2), being an inner sphere et reaction, requires the direct contact of the species to the electrode surface and therefore is not allowed. Results with Cu upd, an unambiguous inner sphere et reaction have confirmed the compact nature of MBT monolayer. In the case of oxidation of hydroquinone, the observed reaction on the anodic side with the peak potential shifting to higher values and absence of cathodic reaction cannot be unequivocally assigned to any particular reason as mentioned above in the case of Au/AET. One has to still depend on tunneling mechanism to understand the observed et reaction through the compact MBT monolayer.

On Au/ODM, all reactions viz., the three chosen redox systems and Cu upd are seen to be totally blocked and serve as good models to demonstrate the blocking of et by a compact SAM on an electrode surface. On Au/ODM, the monolayer film is reported (Porter *et al* 1987) to have a thickness of about 30 Å. Hence, outer sphere et through such films is also ruled out due to the large distances involved.

4. Conclusions

Voltammetric investigations reveal that the ferro/ferricyanide system, an outer sphere et reaction is facile on Au/MBT and Au/AET while it is totally blocked on Au/ODM. The $\text{Fe}^{2+}/3+$ redox system, an inner sphere et reaction is found to be blocked on Au/MBT and Au/ODM while it is slightly hindered on Au/AET. The $\text{H}_2\text{Q}/\text{Q}$ system is considerably hindered on Au/AET, becomes irreversible on Au/MBT and is totally blocked on Au/ODM. The Cu upd reaction is completely blocked on Au/MBT and Au/ODM while on Au/AET it is partially hindered. Capacitance data suggest that the SAM of MBT, despite the absence of a long methylene chain is compact and pore-free like the SAM of ODM while AET SAM is not compact and allows permeation of electrolyte solution. The results suggest the possibility of SAMs, if sufficiently thin and impervious, distinguishing between outer sphere and inner sphere et reactions.

Acknowledgement

The authors express their sincere thanks to the Director, Central Electrochemical Research Institute, Karaikudi for his keen interest and encouragement.

References

- Amatore C, Saveant J M and Tessier D 1983 *J. Electroanal. Chem.* **147** 39
- Bard A J, Abruna H D, Chidsey C E D, Faulkner L R, Feldberg S W, Itaya K, Majda M, Melroy O, Murray R W, Porter M D, Soriaga M P and White H S 1993 *J. Phys. Chem.* **97** 7147
- Bharathi S, Yegnaraman V and Prabhakara Rao G 1993 *Langmuir* **9** 1614
- Bharathi S, Yegnaraman V and Prabhakara Rao G 1995 *Langmuir* **11** 666
- Carter F L 1982, 1987 *Molecular electronic devices* (New York: Marcel Dekker) vols. 1, 2
- Cheng Q and Toth A B 1992 *Anal. Chem.* **64** 1998
- Cheng Q and Brajter-Toth A 1995 *Anal. Chem.* **67** 2767
- Dryhurst G, Kadish K M, Scheller F and Renneberg R 1982 *Biological electrochemistry* (New York: Academic Press) vol. 7
- Finklea H O and Hanshew D D 1992 *J. Am. Chem. Soc.* **114** 3173
- Gao Z and Siong Siow K 1996 *J. Electroanal. Chem.* **412** 179

- Hong F T 1989 (ed.) *Biosensors and biocomputers* (New York: Plenum)
- Kolb D M, Prazanyski M and Gerischer H 1994 *J. Electroanal. Chem.* **54** 25
- Kunitake M, Deguchi Y, Kawatana K, Mahabe O and Nakashima N 1994 *J. Chem. Soc., Chem. Commun.* 564
- Laibinis P E and Whitesides G M 1992 *J. Am. Chem. Soc.* **114** 1990
- Lipkowski J 1992 In *Modern aspects of electrochemistry* (eds) B E Conway, J O'M Bockris and R E White (New York: Plenum) vol. 23, ch. 1
- Lipkowski J and Stolberg L 1992 In *Adsorption of molecules at metal electrodes* (eds) J Lipkowski and P N Ross (New York: VCH) p. 23
- Malem F and Mandler D 1993 *Anal. Chem.* **65** 37
- Miller C, Cuendet P and Gratzel M 1991 *J. Phys. Chem.* **95** 877
- Nicholson R S 1965 *Anal. Chem.* **37** 1351
- Nuzzo R G, Fusco F A and Allara D L 1987 *J. Am. Chem. Soc.* **109** 2358
- Porter M D, Bright T B, Allara D L and Chidsey C E D 1987 *J. Am. Chem. Soc.* **109** 3559
- Reinmuth W H 1960 *Anal. Chem.* **32** 1891
- Sabatani E and Rubinstein I 1983 *J. Phys. Chem.* **91** 6663
- Sabatani E, Rubinstein I, Maoz R and Sagiv J 1987 *J. Electroanal. Chem.* **219** 365
- Sabatani E, Cohen-Boulakia J, Bruening M and Rubinstein I 1993 *Langmuir* **9** 2974
- Schönenberger C, Sondag-Huethorst J A M, Jorritsma J and Fokkink L G J 1994 *Langmuir* **10** 611
- Steiberg S, Tor Y, Sabatani E and Rubinstein I 1991 *J. Am. Chem. Soc.* **113** 5176
- Sun L and Crooks R M 1991 *J. Electrochem. Soc.* **138** L23
- Sun L, Johnson B, Wade T and Crooks R M 1990 *J. Phys. Chem.* **94** 8869
- Takehara K, Takemura H and Ide Y 1994 *Electrochim. Acta* **39** 817
- Ulman A, Evans S D, Shnidman Y, Sharma R, Eilers J E and Chang J C 1991 *J. Am. Chem. Soc.* **113** 1499
- Upadhyay D N, Yegnaraman V and Prabhakara Rao G 1996 *Langmuir* **12** 4249
- Wilner I, Dagan M L, Tibbon S M and Katz E 1995 *J. Am. Chem. Soc.* **117** 6581
- Zhong C J and Porter M D 1995 *Anal. Chem.* **67** A709