

Evaluation of monolayers and mixed monolayers formed from mercaptobenzothiazole and decanethiol as sensing platforms

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Abstract

In this investigation, the characterisation of monolayer and mixed monolayers formed from mercaptobenzothiazole (MBT) and decanethiol (DT) has been carried out with cyclic voltammetry. The SAMs have been tested for their stability and electron transfer blocking properties. The redox probes used in the present study are $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Ru}(\text{NH}_3)_6]^{2+}$ and Cu underpotential deposition (upd). The electron transfer kinetics is investigated in acid and neutral pH range. Electron transfer kinetics is altered by the nature of charge on the redox probe and the charge on the monolayer. Electron transfer kinetics of negatively charged redox probes like ferrocyanide ions is blocked when the surface $\text{p}K_a < \text{pH}_{\text{medium}}$ and at $\text{p}K_a > \text{pH}_{\text{medium}}$ reversible features is observed for negatively charged probes. An exactly reverse effect is observed in the case of positively charged redox species like $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$.

Cu under potential deposition studies reflects the structural integrity and compactness of the SAM layer. The utility of these monolayers and mixed monolayer for selective sensing of dopamine is discussed based on their ability to discriminate between positively and negatively charged redox species at different pH.

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Keywords: Mercaptobenzothiazole; Self-assembled monolayers; Mixed monolayers; Electron transfer kinetics; Molecular recognition

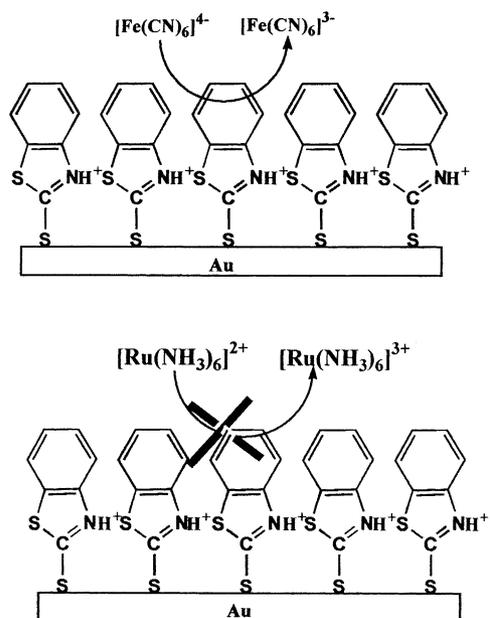
1. Introduction

Molecular self assembly is gaining importance in recent years as it has become a popular surface derivatisation procedure due to its simplicity, versatility and establishment of high level order on a molecular scale [1–3]. Some application of the high level order monolayers include catalysis, electron transfer, lithography, electronic devices and lubrication [4–11]. This type of surface modification can be used to control the fundamental interfacial charge transfer phenomena. In addition, interest in such monolayers arises largely from their characteristics of good microstructural definition which provides the needed platform for further functionalisation of the monolayer with the redox species, catalysts, photoactive species etc. [12–16]. The formation of highly ordered monolayers is often done by the spontaneous adsorption of alkanethiols. This provides a convenient approach for studying electron transfer reactions between an electroactive group and an electrode where the electroactive group is held at a fixed distance from the electrode

surface or if in solution is separated from the electrode by a fixed monolayer and also for electron transfer studies in the case of the ion permeation model systems for biological membranes. Studies on hetero aromatic thiols are still rare. Imidazoles are important constituent of enzymes like ascorbate oxidase and superoxide dismutase whose metal complexes are responsible for important biological reactions. Hence mercaptobenzothiazole being a biomimetic analogue is chosen for the formation of SAM and the structural integrity and compactness of SAM formed with MBT and mixed monolayers of MBT are characterised by following the electron transfer kinetics with standard redox species (Scheme 1). The investigations are aimed at evaluating the performance of these monolayers as suitable sensor materials for the analysis of neurotransmitters like dopamine. The electron transfer kinetics is carried out with standard redox species such as potassium ferrocyanide, hexa amine ruthenium (II) chloride and also by the underpotential deposition of copper on the films explained below. The films evaluated as sensor material are a monolayer of MBT, a mixed monolayer of DT + MBT and polymeric thin film of MBT (PMBT) and a mixed monolayer of DT + PMBT (Scheme 2).

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Scheme 1. Scheme showing the ability of the MBT film to discriminate between positively and negatively charged species at $\text{pH} < \text{p}K_a$.

2. Experimental

2.1. Instrumentation

All electrochemical experiments are carried out with Wenking LB75L potentiostat using a standard 3-electrode cell. The triangular input waveform was generated using universal programmer (Model 175, PAR). Scanning electron

micrographs (SEM) are recorded using Scanning Electron Microscope, Model S.3000H from Hitachi Science Systems Ltd., Japan. Gold electrode is used as the working electrode. Mercury/mercurous sulphate (MMS) is used as the reference electrode and platinum foil as the counter electrode. All the potentials are reported with respect to MMS. All the solutions are prepared using triply distilled water.

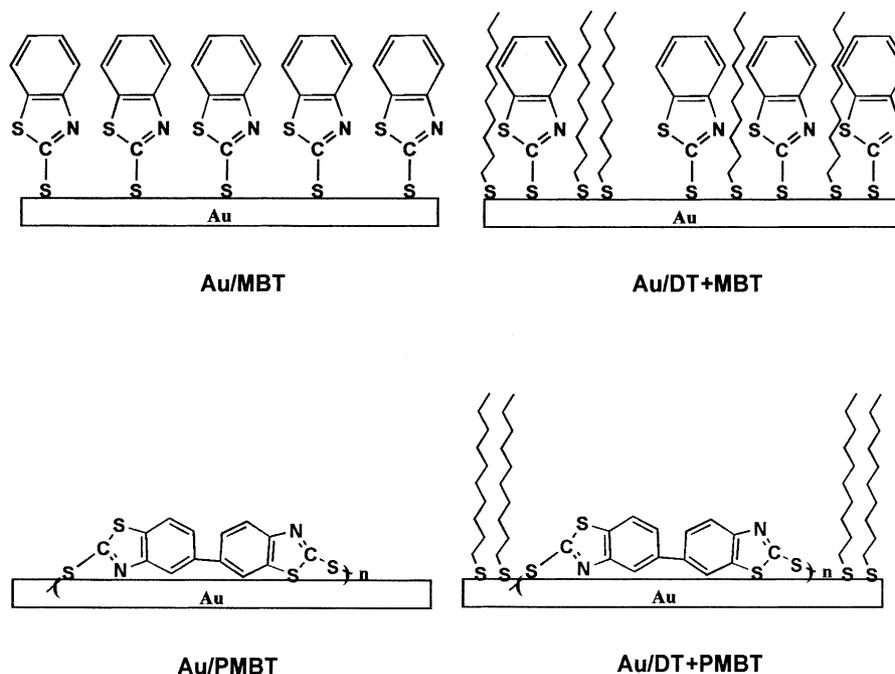
2.2. Chemicals

The chemicals used in the present investigation are listed as follows:

- 2-Mercaptobenzothiazole (MBT) (Fluka).
- Decanethiol (DT) (Aldrich).
- 3-Hydroxytyramine hydrochloride or dopamine (DA) (Acros Organics).
- Ascorbic acid (AA) (Indian Drugs and Pharmaceuticals).
- Hexa amine ruthenium (II) chloride (Aldrich).
- $\text{K}_4[\text{Fe}(\text{CN})_6]$ (Merck).
- $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Indian Drugs and Pharmaceuticals).
- NaOH (Merck).
- Potassium dihydrogen orthophosphate (Sarabhai M Chemicals).
- Dimethyl formamide (DMF) (Merck).
- Na_2SO_4 (Merck).
- H_2SO_4 (Merck).

2.3. Standardisation of the electrode

- (a) Gold electrodes of area 0.07065 cm^2 are polished using emery sheets of 3,4,5 grade and were sonicated in



Scheme 2. Different electrode configuration used in the present investigation.

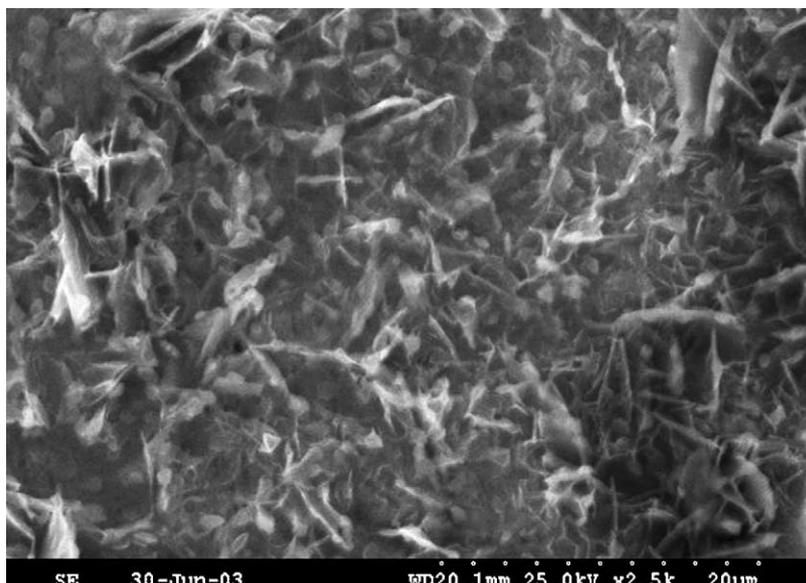


Fig. 1. SEM picture of polymerised mercaptobenzothiazole on Au substrate—magnification used 2.5K.

triply distilled water for about 5 min. Then the electrode is given electrochemical treatment by cycling in 0.5 M sulphuric acid between -0.4 and $+1.2$ V for 5 min. The reproducibility of the gold surface is checked by recording the gold oxide formation peak and its reduction peak.

- (b) The electrochemically pretreated electrode is then standardised using 5 mM $K_4[Fe(CN)_6]$ in sulphuric acid and sodium sulphate and the reversibility of the electron transfer reaction is confirmed by the ΔE_p value (difference between the anodic and cathodic peak potential values = 60 mV for reversible charge transfer).

2.4. Modification of the electrode

1. *Au/MBT*. The standardised Au electrode is dipped in 1 mM of recrystallised MBT dissolved in acetone overnight.
2. *Au/DT + MBT*. The standardised electrode is dipped in decanethiol overnight and then dipped in MBT dissolved in acetone for 3 h.

Composition of *Au/DT + MBT*: based on the peak current measurement (from Fig. 3b and c), we have estimated that roughly 33% of the DT was replaced by MBT. The composition of the mixed monolayer will be DT:MBT (3:1).

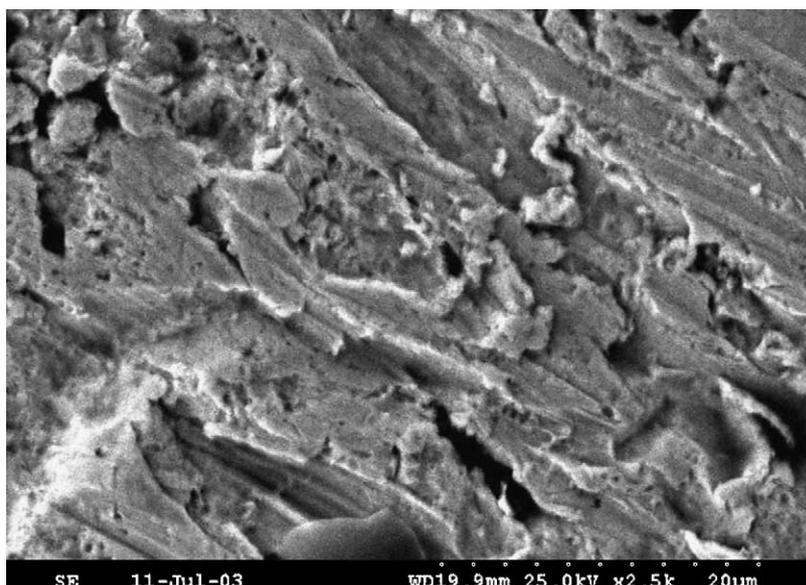


Fig. 2. SEM picture of *Au/DT + PMBT* on Au substrate—magnification used 2.5K.

3. *Au/PMBT*. The standardised electrode is cycled in an organic solvent of DMF:0.05 M H₂SO₄ mixture (2:1) containing 1 mM MBT at potentials between 0 and +1.5 V. The number of cycles is 20 and the scan rate used is 50 mV s⁻¹ [8,17,18].

A compact polymeric film with needle structure was obtained during electropolymerisation and this is clearly seen from the SEM picture (Fig. 1).

4. *Au/DT + PMBT*. The standardised electrode is dipped in decanethiol for 1 h and polymerised in DMF:H₂SO₄ mixture containing 1 mM MBT. The film morphology can be seen from the SEM picture (Fig. 2).
5. Cu underpotential deposition was recorded between the potential limits +0.2 and -0.4 V with the bare/modified electrode in acid or neutral medium containing 1 mM CuSO₄.
6. Analysis of dopamine was performed in phosphate buffer at pH 7.6.

3. Results

The electron transfer characteristics is studied using the cationic redox species [Ru(NH₃)₆]^{2+/3+}, anionic redox species [Fe(CN)₆]^{4-/3-} and also by the underpotential deposition (upd) of copper on bare gold and four modified surfaces.

3.1. Electron transfer kinetics using [Fe(CN)₆]^{4-/3-} redox species

- (a) *Bare electrode*. It is seen from Figs. 3a and 4a that on a bare electrode the electron transfer kinetics is reversible in both acidic and neutral media indicating fast electron transfer kinetics.
- (b) *Au/MBT modified electrode*. In acidic medium, we observed that (Fig. 3b, Table 1) the electron transfer remains perfectly reversible, with reduced current. However, in neutral medium the film becomes completely impermeable and no response is observed (Fig. 4b).
- (c) *Au/DT+MBT modified electrode*. In the presence of the mixed monolayer, the ferrocyanide electron transfer is slowed and the nature of the voltammogram is plateau shaped in acidic medium. The plateau current is found to be independent of the scan rate whereas in neutral medium no response is observed (Figs. 3c and 4c).
- (d) *Au/PMBT modified electrode*. Polymeric film formed by electrochemical cycling is found to be permeable for the anionic redox species ferrocyanide. However, there is a slow down in the electron transfer kinetics as indicated by large ΔE_p in acidic medium as compared to bare electrode response. In neutral medium the reaction becomes more irreversible and the cyclic voltammogram takes the shape of a plateau (Figs. 3d and 4d).
- (e) *Au/DT + PMBT modified electrode*. In the case of the mixed monolayers, the film exhibits reversibility in

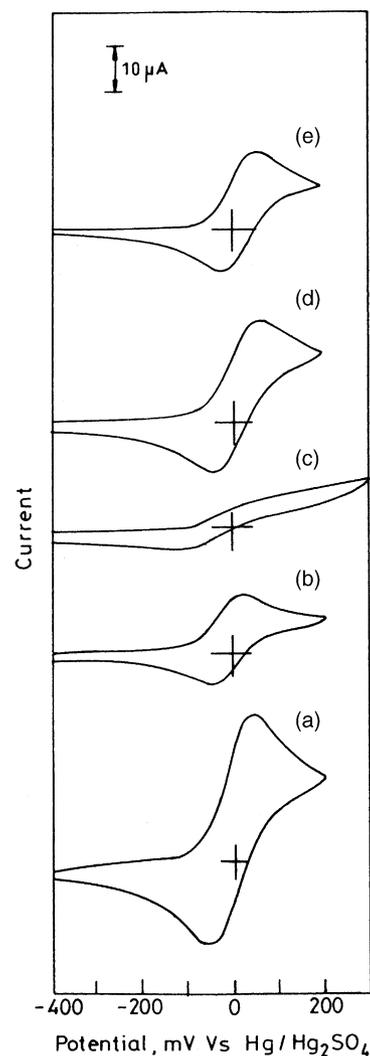


Fig. 3. Cyclic voltammograms representing the response of 1 mM [Fe(CN)₆]^{4-/3-} for: (a) bare Au, (b) Au/MBT, (c) Au/DT + MBT, (d) Au/PMBT and (e) Au/DT + PMBT in 0.5 M H₂SO₄ at the scan rate 50 mV s⁻¹.

acidic medium. In neutral medium the electron transfer kinetics slows down compared to acidic medium (Figs. 3e and 4e).

3.2. Electron transfer kinetics using [Ru(NH₃)₆]^{2+/3+} redox species

- (a) *Bare electrode*. [Ru(NH₃)₆]^{2+/3+} is another standard redox probe that is used in many investigations to test the compactness and structural integrity of the monolayers. This species show reversible features in acidic and neutral medium indicating fast electron transfer kinetics on a bare electrode (Figs. 5a and 6a).
- (b) *Au/MBT modified electrode*. In this case, the cationic redox species exhibits a very low current in acidic medium with near reversible features and in the case of neutral medium the current is reduced only by 50% compared

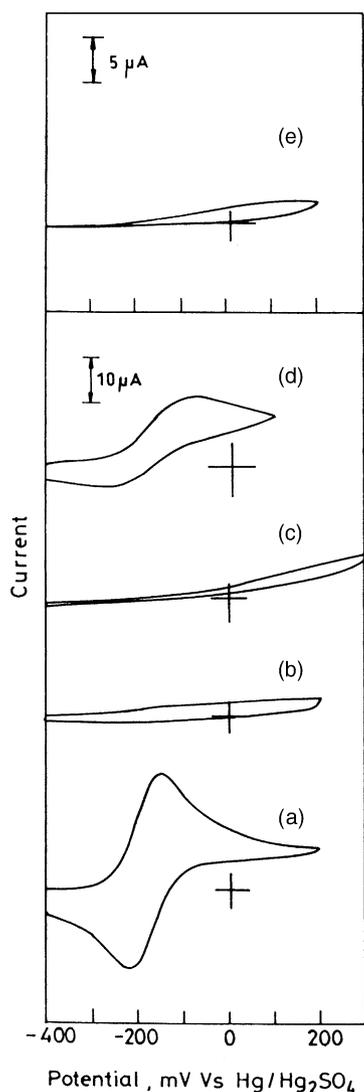


Fig. 4. Cyclic voltammograms representing the response of 1 mM $[\text{Fe}(\text{CN})_6]^{4-/3-}$ for: (a) bare Au, (b) Au/MBT, (c) Au/DT + MBT, (d) Au/PMBT and (e) Au/DT + PMBT in 0.5 M Na_2SO_4 at the scan rate 50 mV s^{-1} .

to the bare electrode and the reversibility is maintained (Figs. 5b and 6b).

- (c) *Au/DT + MBT modified electrode.* In the case of mixed monolayers the $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$ species exhibits a plateau shaped voltammogram in acidic medium and in neutral medium a near reversible characteristics is observed (Figs. 5c and 6c).
- (d) *Au/PMBT modified electrode.* In the case of polymeric film the response obtained is similar to the case of mixed monolayer (DT + MBT), no response is observed in acidic medium whereas a reversible response is observed in the case of neutral medium (Fig. 5d and 6d).
- (e) *Au/DT + PMBT modified electrode.* In the case of acidic medium no response is obtained and in neutral medium a voltammogram with reversible response is obtained (Figs. 5e and 6e).

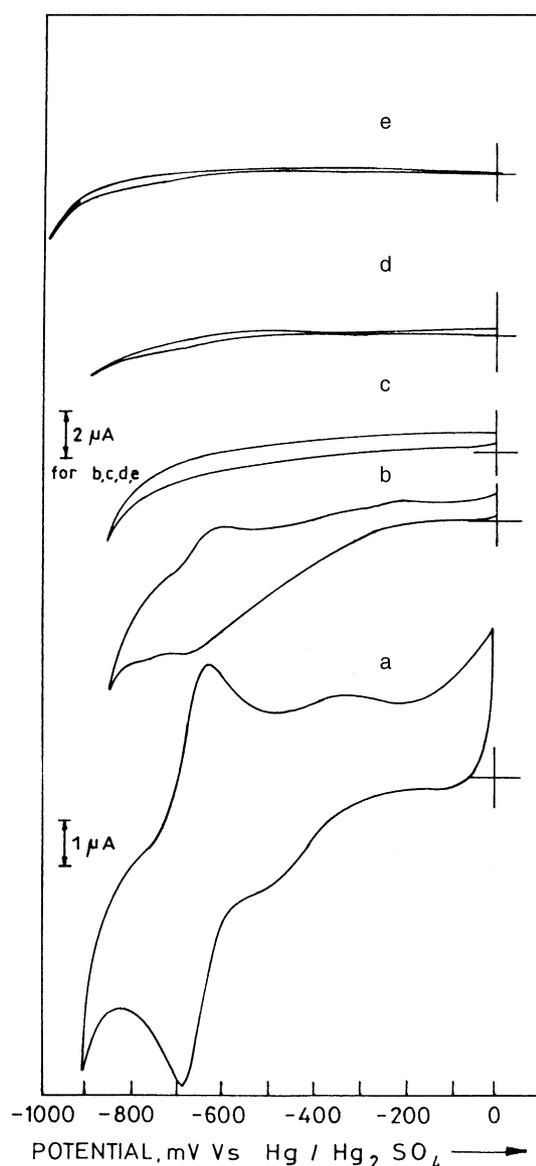


Fig. 5. Cyclic voltammograms representing the response of 1 mM ruthenium hexa amine (II) chloride for: (a) bare Au, (b) Au/MBT, (c) Au/DT + MBT, (d) Au/PMBT and (e) Au/DT + PMBT in 0.5 M H_2SO_4 at the scan rate 50 mV s^{-1} .

3.3. Under potential deposition of copper

- (a) *Bare electrode.* The characteristic feature of Cu upd is well observed in the case of Na_2SO_4 and H_2SO_4 medium (Figs. 7a and 8a).
- (b) and (c) *Au/MBT and Au/DT + MBT.* Cu upd is not observed in acidic medium, whereas it is observed in neutral medium (Figs. 7b, 8b and 7c, 8c).
- (d) *Au/PMBT.* In the case of the polymeric film, Cu upd is not observed in acidic medium, whereas the upd of Cu is present in neutral Na_2SO_4 medium (Figs. 7d and 8d).
- (e) *Au/DT + PMBT.* Cu upd is not observed in both acidic and neutral medium (Figs. 7e and 8e).

Table 1

Nature of the modified electrode	i_p (μA)	ΔE_p (mV)	k_s^a (cm s^{-1})	Shape of the curve
Ferro cyanide				
Bare Au/H ₂ SO ₄	22			Reversible
Au/MBT/H ₂ SO ₄	15	65	0.0334	Reversible
Au/MBT/Na ₂ SO ₄	Plateau			Plateau
Au/DT/MBT/H ₂ SO ₄	Plateau			Plateau
Au/DT/MBT/Na ₂ SO ₄	Plateau			Plateau
Au/PMBT/H ₂ SO ₄	14	100	0.00401	Quasi-reversible
Au/PMBT/Na ₂ SO ₄	5	150	0.001339	Plateau
Au/DT/MBT/H ₂ SO ₄	10	70	0.01473	Quasi-reversible
Au/DT/PMBT/Na ₂ SO ₄				No response
Ruthenium hexa amine				
Bare Au/H ₂ SO ₄	3.2			Reversible
Au/MBT/H ₂ SO ₄	0.6	61	0.1207	Reduced response
Au/MBT/Na ₂ SO ₄	1.4	61	0.1207	Reversible
Au/DT/MBT/H ₂ SO ₄	Plateau			Absent
Au/DT/MBT/Na ₂ SO ₄	1	70	0.0132	Quasi-reversible
Au/PMBT/H ₂ SO ₄	No response			Absent
Au/PMBT/Na ₂ SO ₄	0.4	70	0.0132	Plateau
Au/DT/MBT/H ₂ SO ₄	No response			Absent
Au/DT/PMBT/Na ₂ SO ₄	2	80	0.00072	Plateau

^a Based on Nicholson method [28].

Fig. 9 represents the cyclic voltammetric response obtained for different additions of dopamine on Au/MBT modified electrode. Each addition corresponds to 1.6×10^{-4} M DA. The oxidation current for DA increases with increase in concentration of DA. It appears at a slightly higher potential as compared to the bare electrode [19]. Since the measurement is carried out at a pH of 7.6 using phosphate buffer, MBT layer remains negatively charged and it is found to be impermeable to ascorbic acid.

Fig. 10 represents the cyclic voltammetric response obtained for different additions of dopamine in Au/DT+MBT electrode in phosphate buffer. In this SAM, DA oxidation occurs at a negative potential (lower than the potential of oxidation of DA at bare electrode) and the oxidation current increases with increase in concentration of DA. Au/DT+MBT film is impermeable to AA at pH 7.6. However, when DA is present along with AA, the film is able to tolerate about 10 times the concentration of AA (Fig. 10e). AA gets catalytically oxidised in the presence of DA, when the concentration of AA exceeds 10 times the concentration of DA.

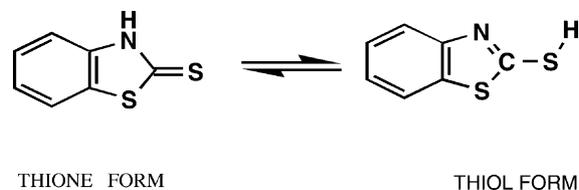
4. Discussion

4.1. Electron transfer in bare Au, Au/MBT, Au/DT + MBT, Au/PMBT and Au/DT + PMBT using an anionic redox species $[\text{Fe}(\text{CN})_6]^{4-/3-}$

The results indicate the general trend that the anionic species ferrocyanide is reversibly oxidised on a bare electrode in acidic and neutral medium. It is observed from the results that the species is found to be more permeable through all the films studied in acidic medium compared to

that observed in neutral medium. This observation could be explained on the basis of structural considerations on gold surface and on the charge acquired by the film at different pH.

It is well known from the literature that thiols substituted with aromatic ring increases the binding between Au and thiol, which thereby forms a compact and impervious SAM [5,6]. MBT, which is a derivative of thiazole, contains an aromatic ring fused with a thiazole ring through which the monolayer is formed. It was reported earlier that MBT monolayers on gold have higher thermal stability when compared to other alkane thiol monolayers [7]. MBT adsorbs with its molecular plane perpendicular to the surface of gold [7,20–22]. The $\text{p}K_a$ of 2-MBT is 6.93 [20,23] at 20 °C and it exists in two forms [24]. The thione form and the thiol form as follows:



In the acid medium MBT is present as the unionised protonated form [25,26], i.e. the thione form. In the basic medium it exists as the anionic form (MBT^-). Surface enhanced Raman spectroscopy (SERS) as well as molecular orbital calculations suggest that MBT adsorbs on gold surface in the thione form [21,22].

As the redox species is an anionic species, i.e. $[\text{Fe}(\text{CN})_6]^{4-/3-}$ which is negatively charged and as mentioned above since MBT exists in its thione form in acid medium, the nitrogen atom gets protonated and hence the

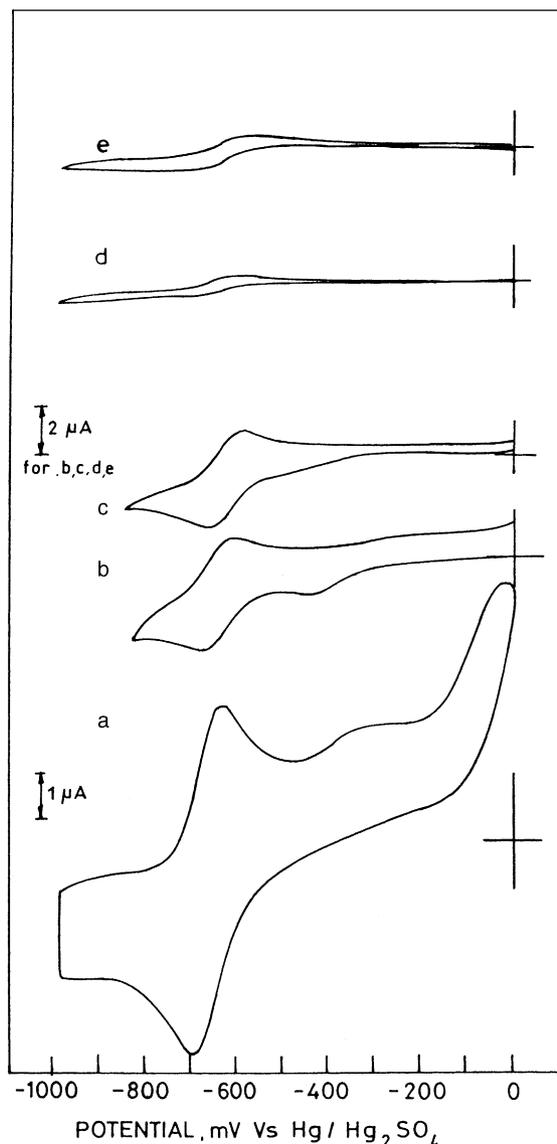


Fig. 6. Cyclic voltammograms representing the response of 1 mM ruthenium hexa amine (II) chloride for: (a) bare Au, (b) Au/MBT, (c) Au/DT+MBT, (d) Au/PMBT and (e) Au/DT+PMBT in 0.5 M Na_2SO_4 at the scan rate 50 mV s^{-1} .

monolayer attains a positive charge. Therefore, the positive charge on the monolayer attracts the negatively charged redox species and hence a redox peak is observed. The i_p (peak current) is reduced when compared to the redox reaction at the bare electrode as observed in the case of other thiols.

In case of neutral medium, as MBT exists in its thiolate form (MBT^-). Au/MBT monolayer and Au/DT + MBT (mixed monolayer) acquire a negative charge and these films naturally repel the redox species, which is also negatively charged thereby reducing electron transfer through the monolayer and mixed monolayer resulting only a charging current.

In Au/PMBT modified electrode, a reversible response is obtained in acidic medium due to the attraction between the negatively charged redox species and the positively charged

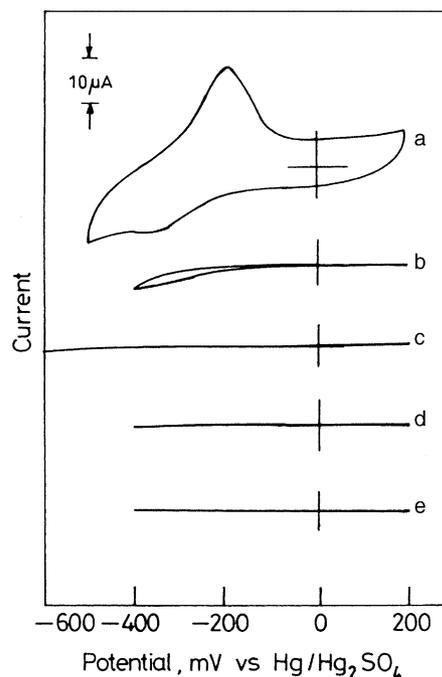


Fig. 7. Cyclic voltammograms representing the response for the underpotential deposition (upd) of Cu (1 mM Cu^{2+}) for: (a) bare Au, (b) Au/MBT, (c) Au/DT + MBT, (d) Au/PMBT and (e) Au/DT + PMBT in 0.5 M H_2SO_4 at the scan rate 50 mV s^{-1} .

monolayer with an increase in current compared to that of Au/DT + MBT mixed modified electrode. An irreversible peak is obtained in neutral medium. This shows that polymerised MBT does not form a compact layer compared to

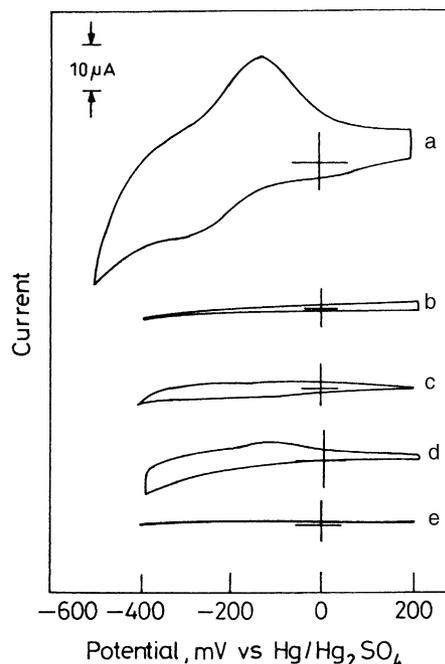


Fig. 8. Cyclic voltammograms representing the response for the underpotential deposition (upd) of Cu (1 mM Cu^{2+}) for: (a) bare Au, (b) Au/MBT, (c) Au/DT + MBT, (d) Au/PMBT and (e) Au/DT + PMBT in 0.5 M Na_2SO_4 at the scan rate 50 mV s^{-1} .

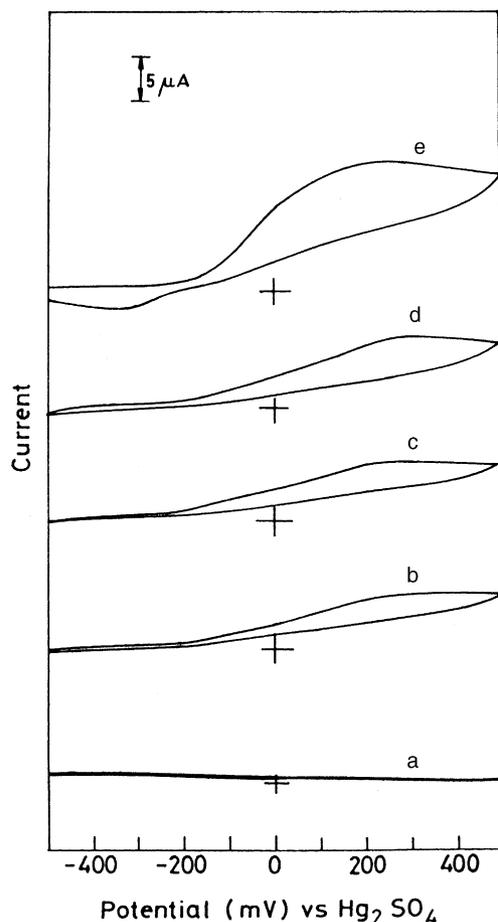


Fig. 9. Cyclic voltammograms representing the response for different concentrations (mM) of dopamine (DA) on Au/MBT electrode: (a) 0 mM, (b) 0.16 mM, (c) 0.33 mM, (d) 0.5 mM and (e) 0.66 mM at the scan rate 50 mV s^{-1} in phosphate buffer.

Au/DT + MBT mixed monolayer. In neutral medium as the monolayer and the redox species are negatively charged the redox species should be repelled from the monolayer and as a result redox peak should be absent but because of the formation of the less compact layer electron transfer occurs which is less compared to that in acidic medium and greater than that of the Au/DT + MBT mixed monolayer.

In Au/DT + PMBT layer in acidic medium a redox peak is obtained. In acidic medium due to the attraction of the negatively charged species a reduced current compared to that of Au/PMBT is observed. In neutral medium, almost no response is obtained as a result of the repulsion of the redox species by the polymerised layer.

4.2. Electron transfer in bare Au, Au/MBT, Au/DT + MBT, Au/PMBT, Au/DT + PMBT using cationic redox species $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$

The cationic redox species exhibits a reversible response in bare gold in both acidic and neutral medium.

In Au/MBT modified electrode in acidic medium as the redox species and the monolayer are positively charged, they

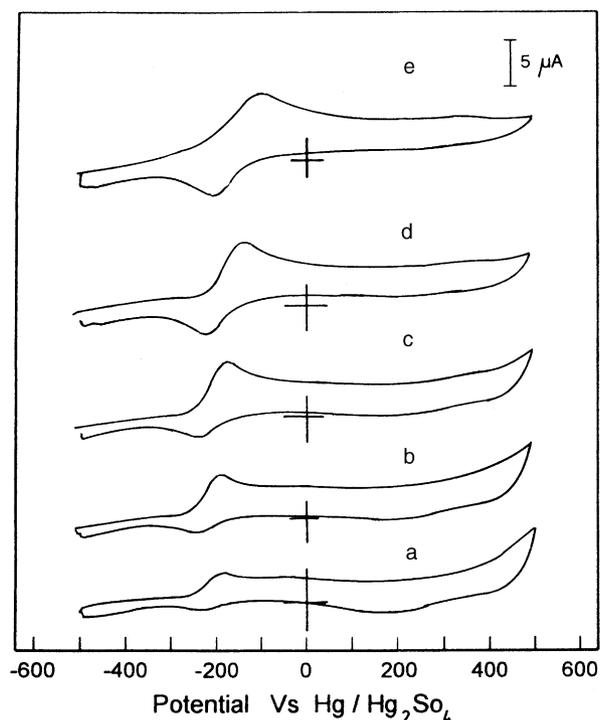


Fig. 10. Cyclic voltammograms representing the response for different concentrations (mM) of dopamine (DA) on Au/DT + MBT electrode: (a) 0.16 mM, (b) 0.33 mM, (c) 0.5 mM, (d) 0.66 mM and (e) 0.66 mM DA + 8.3 mM ascorbic acid (AA) at the scan rate 50 mV s^{-1} in phosphate buffer.

are repelled from each other and hence a redox peak with reduced current compared to the bare is obtained. In neutral medium, since the monolayer is negatively charged and the redox species is positively charged they attract each other and hence a reversible redox peak with a reduced current compared to that of the bare is obtained. The reduction in the current is due to the presence of the monolayer as observed in other cases.

In Au/DT + MBT mixed monolayer, no reversible response is obtained in presence of acidic medium because of the repulsion between the monolayer and the redox species as they carry the same charge and a plateau is obtained which is due to the presence of pinholes which behave like an array of microelectrodes. In neutral medium as the redox species and the monolayer are oppositely charged they are attracted by each other and hence electron transfer occurs through the mixed monolayer with a reduced current compared to that of the Au/MBT monolayer.

In Au/PMBT modified electrode, in acidic medium no response is obtained, whereas in neutral medium as the redox species and the monolayer are oppositely charged a reversible peak is obtained with a reduced current.

In Au/DT + PMBT modified electrode, in acidic medium the redox species is repelled from the surface and hence no response is observed. In neutral medium as the redox species and the modified layer are oppositely charged the layer

attracts them and hence electron transfer occurs through the layer and a redox peak is obtained.

4.3. Electron transfer studies in bare Au, Au/MBT, Au/DT + MBT, Au/PMBT and Au/DT + PMBT modified electrodes using Cu upd

In bare gold the upd of Cu is easily observed in acidic medium and neutral medium. In Au/MBT modified electrode, in acidic medium Cu upd is completely absent thereby showing that as the monolayer and Cu^{2+} are positively charged Cu^{2+} ions are repelled from the surface and hence electron transfer is not permitted through the monolayer. In neutral medium as the monolayer is negatively charged, it attracts the positively charged species and hence the upd of Cu is observed with reduced current because the electron transfer has to occur through the pin holes and defects in the monolayer.

In Au/DT+MBT modified electrode in acidic medium the Cu upd is completely absent as the monolayer and species are of the same charge. The absence of upd also explains the absence of any pinholes thereby providing a compact mixed monolayer. In neutral medium Cu upd is present with reduced current, which shows that the positively charged species Cu^{2+} is attracted by the monolayer, and hence electron transfer through the mixed monolayer is possible.

In Au/PMBT monolayer in acidic medium Cu upd is absent, whereas in neutral medium upd of copper is present which is greater than that of Au/DT + MBT mixed monolayer which shows that the polymer layer is less compact compared to Au/DT + MBT mixed monolayer.

The Au/DT + PMBT modified electrode in acid medium and in neutral medium shows that the monolayer is highly compact and pore free and hence there is no scope for nucleation and hence upd is not observed.

4.4. Selective recognition of dopamine

The foregoing discussion explains clearly that the monolayer Au/MBT and mixed monolayer Au/DT + MBT of mercaptobenzothiazole are able to discriminate between positively and negatively charged redox species depending upon the pH of the medium. Dopamine being positively charged is selectively sensed in presence of negatively charged ascorbate ions as revealed in Figs. 9 and 10. The SAM layers are impermeable to ascorbic acid at pH 7.6. In MBT layer the oxidation of DA occurs at a higher potential compared to the oxidation of DA on the bare electrode (+130 mV). In the mixed monolayer of Au/DT + MBT, the oxidation occurs at a negative potential. DT molecules being hydrophobic, repel the Na^+ ions (from the supporting electrolyte) to reach the surface and avoids pairing up of Na^+ ions with MBT^- anions [27]. Hence more anions are free in this case (compared to Au/MBT monolayer) and dopamine is recognised by the mixed monolayer favourably.

The hydrophobic DT layers decrease the over potential for DA oxidation and it provides an advantageous method for the selective recognition of DA.

5. Conclusions

This paper summarises the electron transfer characteristics of three standard probe reactions through self-assembled monolayers formed from MBT and mixed monolayers of MBT and DT. Polymerisation of MBT has also been tried to check the nature of the film formed with the polymer in terms of its electron transfer blocking capabilities, compactness and structural integrity. The results observed are in accordance with the nature of the charge on the monolayer and charge on the redox probe. These results are being utilised for developing molecular recognition units for some biological species like dopamine. Selective recognition of DA could be achieved in monolayers and mixed monolayers of MBT without interference from ascorbic acid.

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