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Electron transfer studies through mixed self-assembled monolayers of thiophenol and thioctic acid

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Abstract

Mixed self-assembled monolayer of thiols were formed on the electrode surface using aromatic and aliphatic thiols and the modified interface were used to demonstrate charge trapping behavior at the modified interface. The electrode surface was modified by two schemes. In Scheme 1, electrode surface modified with methylene blue (MB) shows charge trapping behavior when contacts the electrolyte containing potassium ferricyanide. In Scheme 2, a redox-active bilayer is constructed using hexamineruthenium (II) chloride and methylene blue. This redox-active bilayer assembly exhibits unidirectional flow of current.

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Keywords: Mixed self assembled monolayers; Thiophenol; Thioctic acid; Electron transfer; Charge trapping

1. Introduction

Formation of organized monolayers by the self-assembly of organosulfur molecules viz. thiols and disulfides at the electrode/electrolyte interface has been investigated in the recent years for their capacity to modify electrode surface in such a way to study the fundamental electron transfer kinetics [1–9] to produce highly electro catalytic surface [10,11], to form patterned surfaces [12], and to exhibit molecular recognition [13–15]. Such self-assembled monolayers (SAMs) behave as model systems for understanding the characteristics of organic and biological interfaces. Besides, they offer a vast technological scope in the fabrication of sensors [16,17], corrosion protective and wear-resistant layers [18], tribiology and in the miniaturization of electronic device [19].

In recent years, a lot of work is being done towards molecular electronics such as wires [19,20], gates [21,22] and rectifiers [23,24] using single molecules [25,26] to organized monolayer [27]. The concept of rectification introduced by Aviram and Ratner [28] was based on asymmetric electron tunneling. Metzer and co-workers [23,29] demonstrated this idea using experimental LB technique. Rectifiers based on MIM [30] junctions with donor–acceptor compounds are being studied. In 1980s, Murray and co-workers [31,32], Wrighton and co-workers [33,34] have fabricated rectifiers based on redox-active polymer derivatives of Ruthenium and Osmium. Later in 1990, the possibility of constructing rectifying interfaces using SAM modification [27] was shown.

Earlier, we have demonstrated the phenomenon of charge trapping [35a,b] at an electrode/electrolyte interface with the help of redox-active bilayer assembly based on donor-(sigma-bridge) [36–40] acceptor

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configuration. In the present investigations, inner layer (also called the first layer), incorporating the redox moieties, is a mixed monolayer comprising of SAMs of two types of molecules viz. thiophenol and cysteamine, and thiophenol and thioctic acid. Charge trapping behavior is also studied at the above modified interface by coupling it with the second redox species kept either in the solution phase or in a polymeric layer formed on the first layer, i.e., redox-active bilayer assembly. The importance and novelty of the present work are:

(i) the use of mixed self-assembled monolayer consisting of aromatic and aliphatic thiol, aromatic thiols (thiophenol) and heterocyclic thiol;
(ii) the functionalization of the above mixed monolayer with the redox molecules; and
(iii) the use of new type of modified interface (comprising of thiol and polymeric layer) for rectification purpose, which will stimulate further studies.

2. Experimental

2.1. Materials and methods

Thiophenol (TP), nafion and hexaamineruthenium (II) chloride were purchased from Aldrich Sigma. Thioctic acid (TOA), polystyrene sulfonate, polyvinyl alcohol, glutaraldehyde, methylene blue (MB), and cysteamine (CYS) were obtained from SRL, India. HCl and sulphuric acid were obtained from Rankem, India, potassium ferricyanide, potassium hydrogen pthalate and sodium hydroxide were purchased from BDH. All the above materials were used without further purification.

A gold disc of area 0.0314 cm^2, embedded in an epoxy resin coating served as the working electrode. A Pt foil and an Hg/Hg_2SO_4 were used as the counter and reference electrodes, respectively. Potential values mentioned in this study are against this reference electrode. Cyclic voltammetric (CV) experiments were carried out using a Potentioscan (Model – POS 88, Wenking, Germany), and X-Y/t recorder (Model – RW 201T, Rikadenki, Japan).

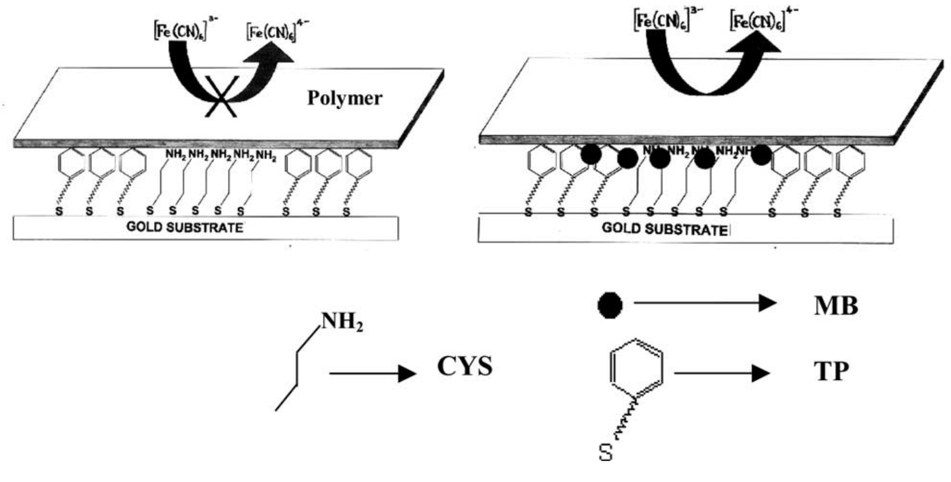
Prior to modification, the electrode surface was thoroughly polished with emery sheets of grade (4/0), and (5/0) using alumina slurry. The polished electrode was cleaned and then cycled in 0.5 M sulfuric acid solution for 5 min in the potential range −0.2 to +1.2 V at 50 mV/s scan rate [41]. The cleanliness of the electrode surface was ensured by obtaining a reproducible and reversible cyclic voltammogram with $\Delta E_p = 60$ mV in 0.5 M sodium sulphate solution containing 10 mM potassium ferricyanide. Electrodes standardized as above were used for modification and subsequent voltammetric investigations.

2.2. Modification of the electrode

The modification of the electrode surface was effected using two different configurations, and depicted as Schemes 1 and 2. The essential difference between the two configurations is that the second redox species is kept in solution phase in one case, while in the other, the second redox species is also immobilized on the electrode over the first layer.

2.2.1. Scheme 1

2.2.1.1. Construction of the first layer. Gold electrodes were dipped in TP for 7 h and dried in Nitrogen atmosphere and dipped in 20 mM of CYS solution in ethanol for 3 h for the formation of mixed self-assembled monolayer. A few drops of methylene blue was put on the mixed SAM and allowed to dry. This is then covered with a protective polymeric layer formed by placing few drops of the solution containing polystyrene sulfonate (5%), polyvinylalcohol, glutaraldehyde (0.5 ml), HCl (0.5 ml) and water (2 ml).



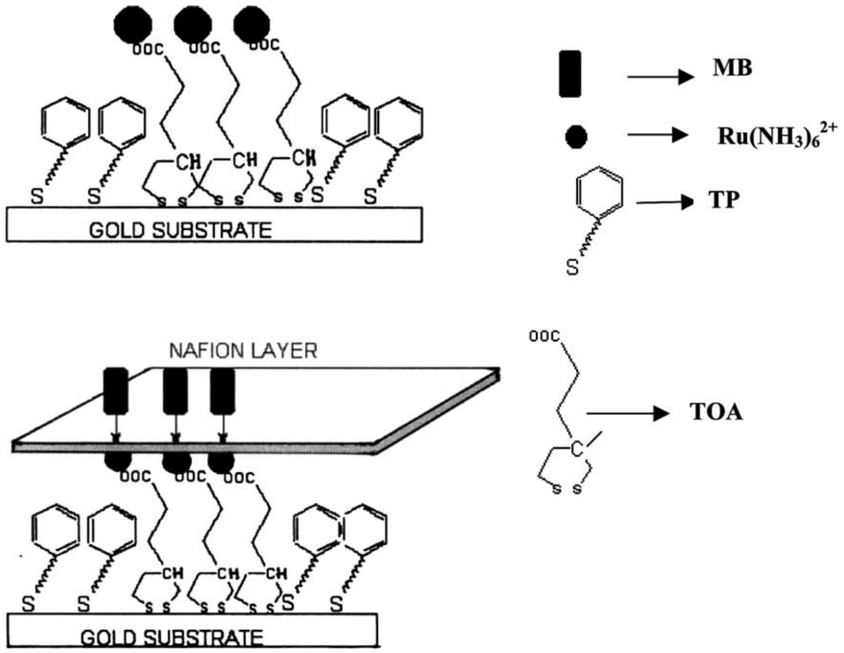
2.2.2. Scheme 2

2.2.2.1. Construction of the first layer. Gold electrodes were dipped in thiophenol for 7 h and dried in the presence of Nitrogen. For the formation of a mixed monolayer, the above electrode was dipped in TOA (20 mM ethanol) for 3 h and then the electrode was rinsed with ethanol, dried in the nitrogen atmosphere.

Gold electrode modified with mixed SAM (TP + TOA) is then dipped in pthalate buffer solution of pH 5.5 for 2 h, so that the –COOH group dissociates to COO^- [42a,b]. The above modified electrodes were made redox-active by spreading few drops of $Ru(NH_3)_6^{2+}$ solution over the mixed monolayer and the redox moiety was trapped in the mixed monolayer by coating a thin film of nafion (1% ethanol solution).

2.3. Construction of the second layer

A second redox-active layer was constructed using nafion (1%) and methylene blue. Few drops of methylene blue in 0.5 M sulfuric acid solution was coated over the second layer (nafion) and allowed for drying. The modified electrode was rinsed before use.



In Scheme 1, the first redox species is present on the mixed monolayer and trapped by the anionic polymer layer. The second redox species $K_3[Fe(CN_6)]$ is kept in the solution. Direct electron transfer from methylene blue is blocked by the mixed monolayer and hence, it takes place through MB trapped on the monolayer. In Scheme 2, both the redox species are immobilized in two different layers. In this redox-active bilayer assembly, the electron transfer from second layer redox species MB is mediated by $Ru(NH_3)_6^{2+}$ present in the first layer. Hence, in both the schemes, unidirectional flow of current is observed.

3. Results and discussion

3.1. Characterization of modified surface

The electrodes covered with single and mixed monolayers were initially subjected to voltammetric studies in the presence and absence of the standard redox system to understand their blocking characteristics. With the redox-immobilized electrodes, cyclic voltammograms were recorded in supporting electrolyte solutions to evaluate the electron transfer characteristics of the modified electrodes.

3.1.1. Scheme 1

Cyclic voltammogram (CV) of gold electrode modified with TP, CYS monolayer and their mixed monolayer (i.e., TP + CYS) were featureless indicating that no electroactivity taking place in the particular potential range used. These CVs are not shown here. The double layer capacitance, C_{dl} value for the electrode modified with TP is 6.0 μF/cm^2 (see Table 1) which shows that it forms a relatively compact monolayer. Compared to aliphatic long chain thiols, thiophenol does not form an ordered layer [43] and hence, it is less compact. The C_{dl} value for the mixed monolayer of thioctic acid and cysteamine is 5.25 μF/cm^2 (see Table 1), which shows that the mixed monolayer is still more compact.

Table 1
The double layer capacitance (C_{dl}) values for the electrode surface modified with TP, CYS, TOA and their mixed monolayers by Schemes 1 and 2

Electrode surface modified with	C_{dl} values (μF/cm^2)
Scheme 1	
TP	6.0
CYS	7.2
TP + CYS	5.25
Scheme 2	
TP	6.0
TOA	9.5
TP + TOA	4.7

3.1.2. Scheme 2

Cyclic voltammogram of gold electrode modified with TP and TOA monolayers and their mixed monolayer (i.e., TP + TOA) were also featureless indicated that no electroactivity taken place in the potential region used. The C_{dl} value for TOA is 9.5 μF/cm^2 (see Table 1), which is lower than TP since TOA forms a loosely packed layer due to the absence of second alkyl chain in the asymmetric disulfide ring [44] and the tendency to break the disulfide bond resulting in a monolayer with defects leading to a less compact layer. The C_{dl} value of TP and TOA mixed monolayer is 4.7 μF/cm^2 (see Table 1) suggests that it is compact compared to individual monolayer modified electrodes. When the mixed SAM modified electrode is dipped in phthalate buffer of pH 5.5, the COOH group of TOA dissociates to COO$^-$. Hence, $Ru(NH_3)_6^{2+}$ spread on the mixed SAM is immobilized through electrostatic interaction and further trapped by 1% nafion layer.

Although the C_{dl} values for the above mixed monolayers are more than that of the mixed monolayer formed by aliphatic long chain thiols, these mixed monolayers (formed by Schemes 1 and 2) are compact enough to prevent the direct electron transfer between the redox moiety and electrode surface.

3.2. Charge trapping studies

3.2.1. Scheme 1

Fig. 1 shows the cyclic voltammogram of MB immobilized in mixed monolayer of CYS + TP and trapped with the polymeric layer by Scheme 1. The CV shows a quasireversible response with the formal potential value of −170 mV. The mixed monolayer assembly consists of aromatic thiol and CYS and hence, the electron transfer from MB takes place by intercalation. The charge corresponding to the reduction peak of MB$^+$ is found to be 1×10^{-9} mol/cm^2.

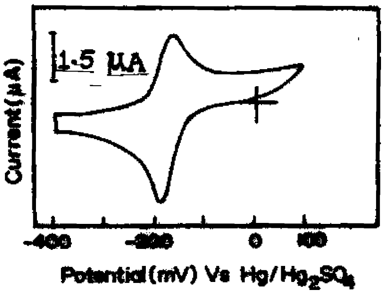


Fig. 1. Cyclic voltammogram in 0.5 M of sulfuric acid of Au electrode modified with mixed SAM of (TP + CYS) further functionalized with MB by Scheme 1.

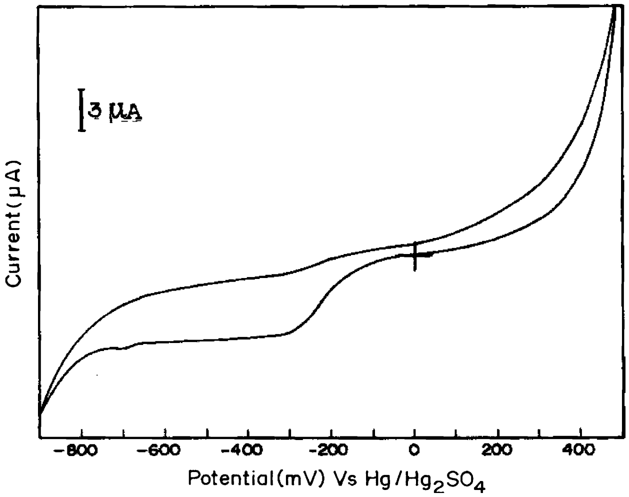


Fig. 2. Cyclic voltammogram in 0.5 M of sulfuric acid of Au electrode modified with mixed SAM of (TP + CYS) further functionalized with MB by Scheme 1 in 5 mM potassium ferricyanide solution.

Fig. 2 represents the cyclic voltammogram of electrode modified by Scheme 1, when transferred to a cell containing 5 mM of $K_3[Fe(CN_6)]$ in 0.5 M of sulfuric acid. When the electrode potential is scanned in negative direction from −0.4 to −0.8 V, cathodic peak at −260 mV with the enhancement in current corresponding to the reduction of MB$^+$ is observed. The reduction of ferricyanide ion at its formal reduction potential value is not observed, since the mixed monolayer is impermeable to ferricyanide ion. Hence, ferricyanide ion undergoes mediated reduction [35b,45] through the reduction of MB$^+$ ion and the increase in the peak current at −260 mV supports this fact. Moreover, the charge corresponding to the reduction peak at the above potential is 7×10^{-9} mol/cm^2 (which is greater than the charge due to the trapped MB alone) and the shift in the reduction potential of ferricyanide ion indicates that it undergoes mediated electron transfer.

When the scan direction is reversed the anodic peaks of both the redox species were absent and hence, unidirectional flow of current is observed. In other words, modified surface allows the electron transfer to take place in one direction, which is essential criterion for rectification at the interface. Fig. 2 also confirms the charge trapping behavior occurring at the modified interface, which leads to the unidirectional flow of current.

3.2.2. Scheme 2

Fig. 3 represents the cyclic voltammogram of $Ru(NH_3)_6^{2+}$ immobilized in mixed monolayer and trapped with nafion layer. The cyclic voltammogram shows quasireversible response of $Ru(NH_3)_6^{2+}$ with the formal potential value of -700 mV. Electron transfer from $Ru(NH_3)_6^{2+}$ to the electrode surface takes place very slowly by diffusion and hence, ΔE_p is not equal to zero (deviation from the ideal behavior). This type of slower kinetics has been reported earlier [46,47]. Charge corresponding to the reduction peak of $Ru(NH_3)_6^{3+}$ is found to be 1.98×10^{-9} mol/cm^2.

Fig. 4 represents the cyclic voltammogram of MB bound inside nafion layer. MB shows a reversible response as reported earlier [48]. The E^0 value of MB is -170 mV.

Fig. 5 represents the voltammetric response of $(TP + CYS)/Ru(NH_3)_6^{2+}$/nafion/MB in 0.5 M of sulfuric acid at the Au electrode. In this bilayer assembly, the reduction starts only at -730 mV, which is far negative to the reduction potential of MB$^+$. However, the increase in the reduction peak current (cathodic region) clearly shows that the electron transfer from MB$^+$ to the substrate is mediated by $Ru(NH_3)_6^{3+}$ ion. Comparison of formal potential values of both the redox species suggests that the mediation during the reduction process is thermodynamically a downhill process, whereas during the reverse scan the energy levels are not favorable for the mediated electron transfer in the anodic region and hence, oxidation is thermodynamically unfavorable [32, 35a,b]. Fig. 5 also supports the above fact.

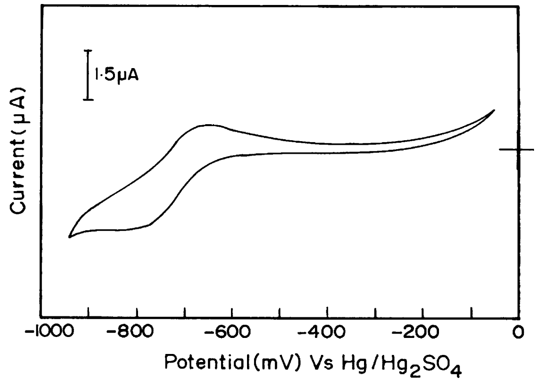


Fig. 3. Cyclic voltammogram in 0.5 M sulfuric acid of Au electrode modified with mixed self-assembled monolayers of thiophenol + thioctic acid and further functionalized with ruthenium hexamine (II) chloride. Scan rate: 50 mV/s.

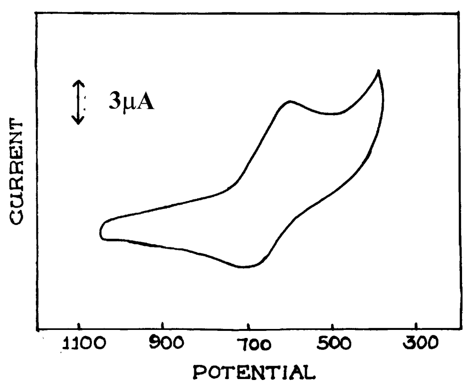


Fig. 4. Cyclic voltammogram of Au surface modified with nafion + MB in 0.5 M sulfuric acid.

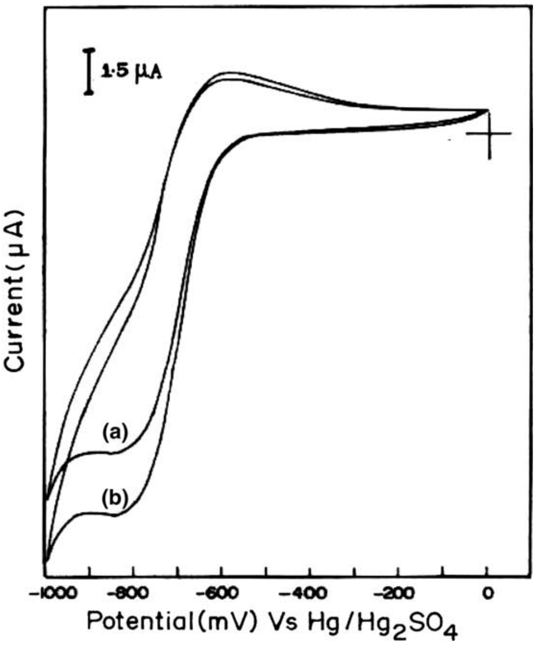


Fig. 5. Cyclic voltammogram in 0.5 M sulfuric acid of Au electrode modified with mixed self-assembled monolayers of thiophenol + thioctic acid and functionalized with ruthenium hexamine (II) chloride initially and MB subsequently at different scan rates: (a) 25 mV/s; (b) 50 mV/s, respectively.

Thus, unidirectional flow of current analogous to the electrochemical rectification is observed at the redox-active bilayer assembly. The charge corresponding to mediated reduction is 8.9×10^{-9} mol/cm^2 also confirms the electrochemical rectification behavior occurring at modified interface.

However a slight anodic current in Fig. 5 may be due to the fact that mixed SAM formed using TOA + TP is not as compact as the mixed SAM of aliphatic thiols. In redox-active bilayer assembly, mechanisms for releasing the trapped redox moieties present in the outer layer has been discussed by Abruna et al. [31]. However, in our present investigation, MB trapped in the outer layer is not released to get the continuous current flow in one direction.

4. Conclusions

This study describes the fabrication of redox-active bilayer assembly through mixed self-assembled monolayers (SAMs) of thioctic acid and thiophenol without covalent linkage between redox moieties. We have also demonstrated this fabrication through mixed SAMs and polymer layer. The electron transfer from the second redox layer (MB) has taken place through $Ru(NH_3)_6^{3+}$ ion resulting in the unidirectional flow of current, which allows to have a control over the monolayer film and its electron transfer properties by choosing appropriate adsorbates and redox moieties.

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