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Effect of pH on the barrier properties of 11-mercapto undecanoic acid and 4-amino thiophenol SAMs on gold

Ujjal Kumar Sur
Department of Chemistry, Behala College, University of Calcutta, Kolkata-60, West Bengal, (INDIA)
E-mail: uksur99@yahoo.co.in

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ABSTRACT

To understand the influence of surface charge on the electron transfer properties of ionic SAMs, the effect of pH of electrolytic solutions and applied potential on the barrier properties of 11-mercapto undecanoic acid and 4-aminothiophenol SAMs on gold were carried out. We find that 11-mercapto undecanoic acid SAM exhibits poor blocking behaviour towards ruthenium (III) redox reaction at low pH, but shows excellent blocking behaviour at high pH. On the other hand, the same monolayer shows excellent blocking behaviour to ferrocyanide redox reaction even at low pH. On the other hand, 4-aminothiophenol SAM shows poor blocking behaviour towards ferrocyanide and ruthenium (III) redox reaction at low pH, but shows good blocking behaviour at high pH.

KEYWORDS

Self-assembled monolayers;
Alkanethiol;
Cyclic voltammogram;
4-aminothiophenol;
11-mercapto
undecanoic acid.

INTRODUCTION

Self-assembled monolayers of alkanethiols form a (v3×v3) R 30° overlayer structure on Au (111) surfaces. The monolayers provide an ideal model systems for studying a large variety of interfacial phenomena, which are difficult to study in natural interfaces. Organic disulphides[1, 2], thiols[3, 4], sulphides[5] on gold surfaces and carboxylic acids[6] and silanes[7] on various oxide surfaces have been utilized extensively as model systems in recent times. Among various interfacial phenomena, long range electron transfer can provide useful information in biological research. In the recent times, various groups[3, 4, 8, 9] have shown interest in the studies of interfacial electron transfer between a metal electrode and a molecular donor or acceptor using alkanethiol coated gold as the model system. Electron donors or acceptors can be attached with the functional groups at the outer surface (terminal groups) of the monolayer to study the electron transfer phenomena. Chidsey and Loiacono[10] have studied the structural and electrochemical properties of alkanethiol monolayers ($HSC_{10}X$, X=H, CH_2OH, CN, COOH) with very simple functional groups at their outer surface. They have examined the defect properties and permeability of monolayers of long-chain organic molecules bound to gold electrode in aqueous medium. The defect and pinhole currents for redox couples and their interfacial capacitances increase in the order H < CH_2OH < CN < COOH. They found that there was no clear correlation of the permeability of monolayers with their wettability and structure.

With the exception of the SAMs with terminal COOH groups, the blocking SAMs are uncharged. The blocking behaviour can be dramatically affected by the introduction or creation of charge sites on the external surface of the monolayer. Various theoretical studies[11-13] on the surface potential of an SAM with ionic terminal group show that there is changes in ϕ_{DL} on the order of 100 mV due to ionization of the terminal group (e.g., $Au/SC_nCOOH \rightarrow Au/SC_nCOO-$) in concentrated electrolyte. The concentration of an ionic redox molecule with charge z at the SAM is related to the surface potential ϕ_{DL} by the relation $C_s = C_b \exp(-zF\phi_{DL}/RT)$, where C_s and C_b are the surface and bulk concentration of the redox species. Therefore, ionization of terminal groups can be observed by following the barrier property of the SAM towards a charged redox couple. Hanshew and Finklea have studied the blocking behaviour of $HSC_{10}COOH$ and pendant pyridine SAMs to $Ru(NH_3)_6^{+3}$ as a function of electrolyte pH[14]. The $HSC_{10}COOH$ SAM at low pH is sufficiently blocking to Ru(III) ions. However, cathodic current for Ru(III) increases as the pH of the solution is enhanced to a value of 5, and both the anodic and cathodic peaks are visible at pHs 6 to 8. Lowering the pH reverses the block behaviour, indicating the SAM is not desorbed or damaged. The SAM with pendant pyridine exhibits the same behaviour as $HSC_{10}COOH$ SAM, but for the opposite reason. Ru(III) reduction current decreases as the pH is lowered, but increases as the pH reaches a higher value. Protonation of the pyridines appears to start by pH 7 and continues to pH 4 or 5.

In order to understand the effect of surface charge on the barrier property of ionic SAMs towards ionic electroactive species, we have studied the barrier properties of SAMs of 11-mercapto undecanoic acid and 4-amino thiophenol (ATP) on gold using ferrocyanide and hexaammine ruthenium (III) chloride as redox probe molecules at different pH values of electrolytic solution.

EXPERIMENTAL

Evaporated gold substrates on glass were used as working electrode in of our studies. Evaporation of gold (~100 nm thickness) on glass was carried out using vacuum evaporation unit (Hindhivac) at a pressure of 2×10^{-5} mbar. Chromium underlayers (2-5 nm thickness) were deposited on glass before gold evaporation to improve the adhesion of gold on glass. The substrate was heated to 350^0C during gold evaporation, a process which normally yields a substrate with predominantly Au (111) orientation. The gold samples were used as strips for electrochemical studies with a well defined area exposed to the electrolyte solution, rest of the portion being insulated with parafilm and teflon. These gold samples were cleaned with Piranha solution (mixture of concentrated sulphuric acid and 30% hydrogen peroxide in 3:1 ratio) for 30 s before each experiment and finally rinsed in millipore water. Before each experiment, the electrolyte was completely deaerated by passing oxygen free nitrogen gas. During the experiment a blanket of nitrogen gas was maintained on top of the solution. The cell was cleaned thoroughly before each experiment and kept in a hot air oven at 100^0C for at least one hour before the start of the experiment. A conventional three electrode electrochemical cell was used in this study. A platinum foil of large surface area was used as counter electrode. A saturated calomel electrode (SCE) was used as reference electrode.

We have conducted experiments where the monolayer is formed by dipping the electrode in 1 mM ethanolic solution for 24 hours.

RESULTS AND DISCUSSIONS

Figure 1 shows the reversible voltammogram of bare evaporated gold electrode for the ruthenium (III) redox reaction in 0.1 M $LiClO_4$. On the other hand, Figure 2 illustrates the cyclic voltammograms showing the blocking behaviour of the 11-mercapto undecanoic acid SAM ($HSC_{10}COOH$) to $Ru(NH_3)_6^{3+}$ as a function of electrolyte pH (adjusted by adding H_2SO_4 or NaOH solution to an unbuffered electrolyte). The carboxylic acid SAM at a pH of 4.5 shows cathodic peak, but the anodic peak is absent (Figure 2 A). As the pH of the electrolyte solution containing ruthenium (III) is increased to 6 the cathodic and anodic peaks due to pinholes become visible and we observed quasi-reversible voltammogram with very large peak separation, but

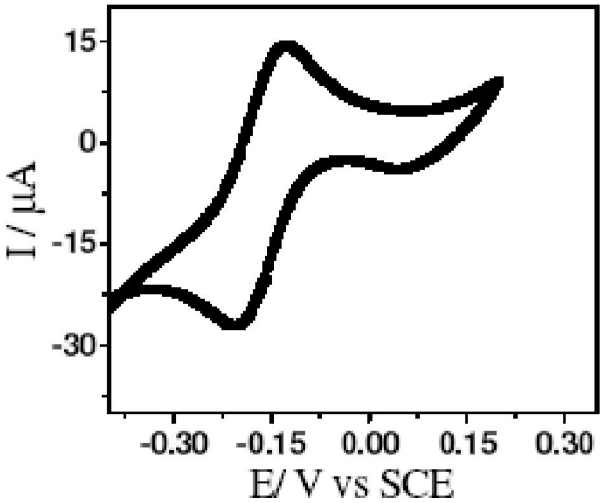

Figure 1 : Cyclic voltammogram of bare evaporated gold electrode for 1 mM ruthenium (III) redox reaction in 0.1 M LiClO$_4$. Scan rate =50 mV s^{-1}, geometric area = 0.16 cm^2.

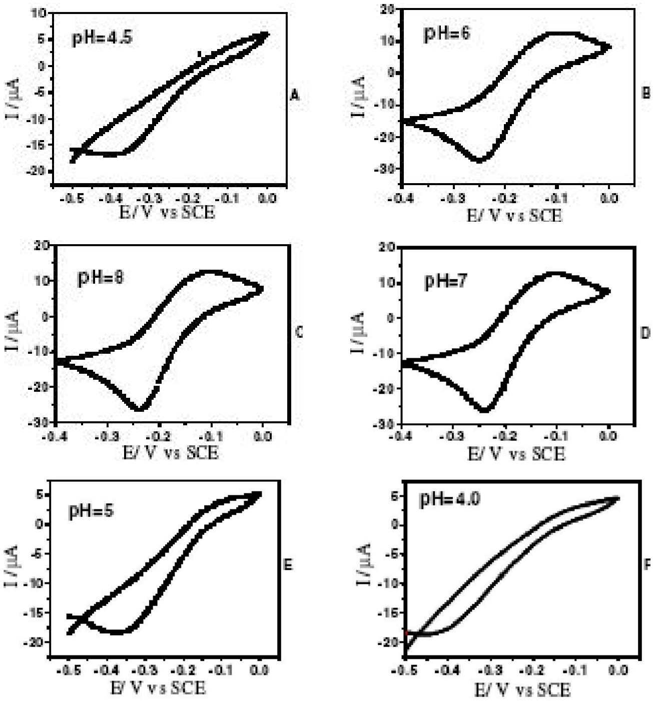

Figure 2 : Cyclic voltammograms of 1 mM 11-Mercapto undecanoic acid coated evaporated gold electrode for 1 mM ruthenium (III) redox reaction in 0.1 M LiClO$_4$ as a function of electrolytic pH. Scan rate = 50 mV s^{-1}, geometric area = 0.16 cm^2. (A) pH = 4.5, (B) pH = 6, (C) pH = 8, (D) pH =7, (E) pH = 5, (F) pH = 4.0.

current almost same as bare gold electrode (Figure 2 B). Peaks due to cathodic and anodic current are visible in the pH range 6-8 (Figure 2 B-D). The current due to cathodic reaction is greater than the anodic current in all these cases. To check whether the SAM is desorbed or damaged during the increase of pH of the electrolyte solution, we have reduced the pH of the electrolyte solution. Figure 2 F shows the voltammogram at a pH of 4.0. At this pH, the voltammogram shows very good blocking behaviour. Our results suggest that the SAM has not desorbed or damaged during the increase of pH. Our results can be explained as follows: The charge of the ionic monolayer terminal group will affect the distribution of the redox species near the electrode surface. The positively charged surface will attract the anionic species, whereas it repels the cationic species. Opposite effect is observed in case of negatively charged surface. The surface concentration of the electroactive species (C_s) is related to the bulk concentration (C_b) by the expression $C_s = C_b \exp(-zF\phi_{DL}/RT)$, where ϕ_{DL} is the electrical potential drop across the diffuse layer and z is the charge of the electroactive species. The poor blocking behaviour of 11-mercapto undecanoic acid SAM to ruthenium (III) redox reaction in pH range 6-8 can be attributed to electrostatic attraction of positively charged ruthenium redox species towards negatively charged carboxylic acid SAM (the carboxylic acid SAM starts to ionize at pH 5). At pH 4.5, a few –COOH groups start to ionize, but most of the –COOH groups remain unionized. At this pH, application of positive potential (for anodic reaction) will try to neutralize the slight negative charge attained by the ionization of a few –COOH groups. On the other hand, application of negative potential (cathodic reaction), the carboxylic acid SAM has slight negative charge. So at this pH, the carboxylic acid SAM exhibits better blocking behaviour towards anodic reaction compared to cathodic reaction of ruthenium (III) redox molecules. The applied potential (positive or negative potential) affects the charge on the terminal groups of the ionic carboxylic acid SAM. Between pH values 6 to 8, the complete ionization of the –COOH groups of the carboxylic acid SAM can take place. Hence, due to the effect of applied potential on the surface charge of ionic SAM, the cathodic current will be always greater than the anodic current.

Figure 3 shows the voltammograms corresponding to the blocking behaviour of 11-mercapto undecanoic acid SAM towards ferrocyanide redox reaction as a function of electrolyte pH (4-10). It can be seen at all pH values (4-10), the carboxylic acid

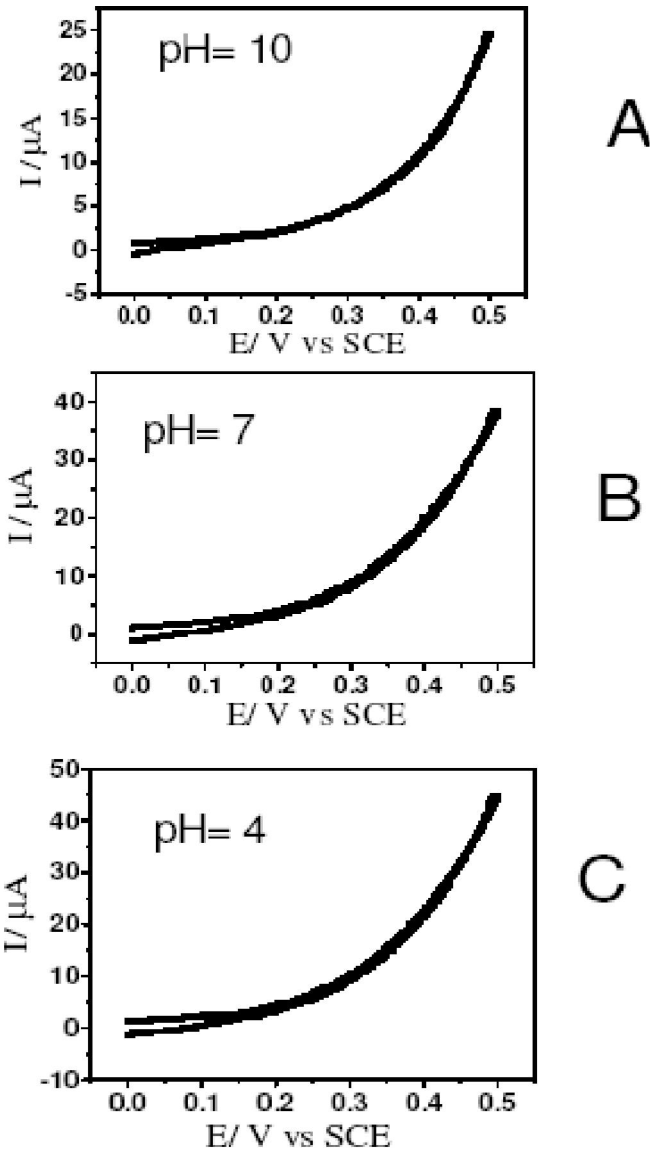

Figure 3 : Cyclic voltammograms of 1 mM 11-Mercapto undecanoic acid coated evaporated gold electrode for 10 mM ferrocyanide redox reaction in 1 M NaF as a function of electrolytic pH. Scan rate =50 mV s^{-1}, geometric area = 0.16 cm^2. (A) pH = 10, (B) pH = 7, (C) pH = 4.

SAM exhibits good blocking behaviour to ferrocyanide redox reaction (Figure 3 A-C). However, the faradaic current due to ferrocyanide redox reaction is lower in basic pH (Figure 3 A; pH=10) than in neutral (Figure 3 B; pH =7) or acidic pH (Figure 3 C; pH =4). At basic pH, the negatively charged carboxylic acid SAM repels negatively charged $[Fe(CN)_6]^{4-}$, which can be attributed to its excellent blocking behaviour. Similarly, neutral carboxylic SAM at acidic pH also shows good blocking behaviour to ferrocyanide redox reaction just like other uncharged SAMs.

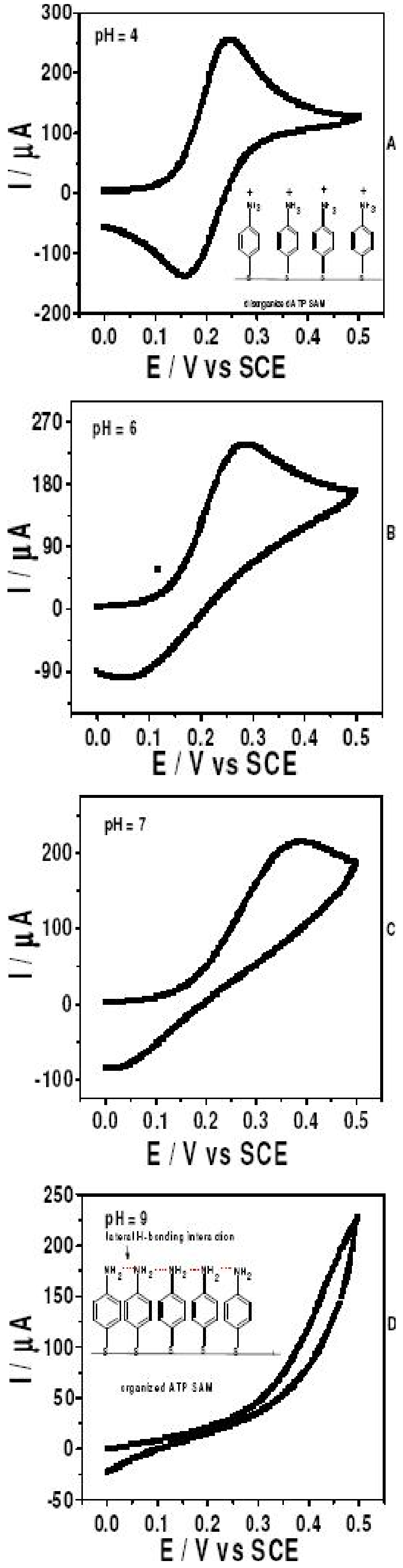

Figure 4 : Cyclic voltammograms of 4-amino thiophenol (ATP) SAM on gold for 10 mM ferrocyanide redox reaction in 1 M NaF as a function of electrolyte pH. Scan rate =50 mV s^{-1}, geometric area = 0.16 cm^2. (A) pH = 4, (B) pH = 6, (C) pH = 7, (D) pH = 9.

Figure 4 shows the cyclic voltammograms of 4-amino thiophenol (ATP) SAM on gold for 10 mM ferrocyanide redox reaction in 1 M NaF as a function of electrolyte pH. At low pH, the SAM exhibits poor blocking behaviour to ferrocyanide redox reaction (Figure 4 A). The voltammogram shows cathodic and anodic peaks due to ferrocyanide redox reaction. However, as the pH of the electrolyte solution is enhanced, the ATP SAM shows very good blocking behaviour to ferrocyanide redox reaction with no peak current. The blocking behaviour of the ATP SAM changes reversibly with electrolyte pH, as can be seen from the voltammograms. At a pH of 7, the amino group of ATP SAM starts to be protonated and become positively charged. However, at basic pH, when the ATP SAM becomes uncharged, it can block the ferrocyanide redox reaction like other uncharged SAMs.

Figure 5 shows the voltammograms of ATP SAM for the ruthenium (III) redox reaction in 0.1 M $LiClO_4$ as a function of pH. At low pH, the ATP SAM exhibits its poor blocking behaviour to ruthenium (III) redox reaction (Figure 5 A). This is rather surprising, as we expect the positively charged ATP SAM to impede the ruthenium (III) redox reaction due to electrostatic repulsion. However, on increasing the pH of the solution, the redox reaction is gradually impeded as can be observed from the decrease in current in the voltammogram (Figure 5 C-D). Probably, the effect of charge of the monolayer on the faradaic reaction of electroactive species become unimportant for shorter chain thiol monolayer like 4-amino thiophenol. At basic pH, there is strong lateral hydrogen bonding interactions between the terminal uncharged NH_2 groups of the neutral ATP SAM, which is responsible for the excellent blocking behaviour of ATP SAM towards both ferrocyanide and ruthenium (III) redox reactions. At low pH, the NH_2 terminal group is protonated and probably there is strong ionic repulsion between the terminal NH_3^+ groups of the ATP SAM. This effect can weaken the lateral hydrogen bonding interaction and thus disorganize the SAM. This disorganization makes the blocking behaviour of ATP SAM poor towards the ruthenium (III) and ferrocyanide redox reactions.

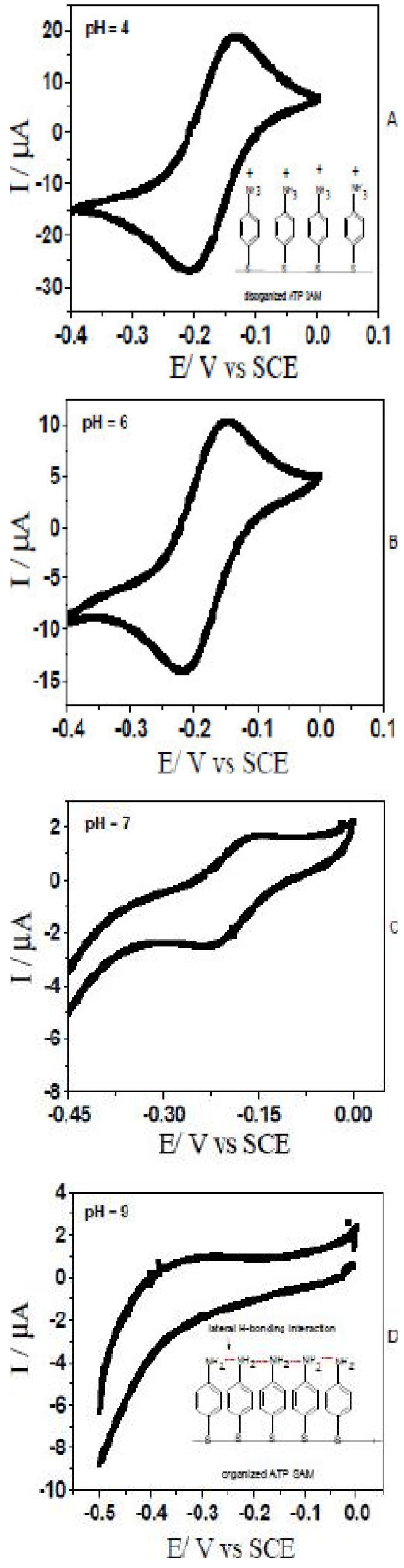

Figure 5 : Cyclic voltammograms of ATP SAM for the ruthenium (III) redox reaction in 0.1 M $LiClO_4$ as a function of pH. Scan rate =50 mV s^{-1}, geometric area = 0.16 cm^2. (A) pH = 4, (B) pH = 6, (C) pH = 7, (D) pH = 9.

CONCLUSIONS

In summary, blocking behaviour of ionic SAMs towards ionic electroactive species depends on the pH of the electrolytic solution and applied potential. We find that 11-mercapto undecanoic acid SAM exhibits poor blocking behaviour towards ruthenium (III) redox reaction at low pH, but shows excellent blocking behaviour at high pH. On the other hand, the same monolayer shows excellent blocking behaviour to ferrocyanide redox reaction even at low pH. The effect of charge of the ionic carboxylic acid thiol plays important role in the blocking behaviour towards redox reactions involving ionic electroactive species. The ATP SAM shows poor blocking behaviour towards ferrocyanide and ruthenium (III) redox reaction at low pH, but shows good blocking behaviour at high pH. In this case, the effect of charge of the ionic SAM becomes unimportant for short chain length thiol SAM like ATP. In this case, the structure of ATP SAM will determine the barrier property, which will change with the pH of the electrolytic solution. The lateral hydrogen bonding interaction between the terminal NH_2 groups of the ATP SAM will determine the structural integrity and hence the blocking behaviour towards ionic electroactive species. Further work is going on to develop a novel pH sensor using these systems, which will be communicated later.

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