

SHORT COMMUNICATION

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Self-assembled monolayers on electrode surfaces: a probe for redox kinetics

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Abstract The formation and characterization of self-assembled monolayers of organosulfur compounds like alkanethiols and dialkyl (di)sulfides on metal surfaces such as gold are areas of current research interest. The presence of an aromatic ring in a thiol molecule can enhance the binding between Au and the thiol, resulting in the formation of compact and impervious self-assembled monolayers. The formation of a monolayer of 2-mercaptobenzothiazole (MBT), containing an aromatic group with a fused thiazole ring but no long alkyl chain, is achieved on a gold electrode surface. Voltammetric investigations of ferro/ferricyanide and ferrous/ferrous redox systems carried out on this Au|MBT electrode are reported. Further, the possibility of using such an Au|MBT electrode to distinguish between inner and outer sphere electron transfer reactions is indicated.

Key words Self-assembled monolayers · Redox systems · Voltammetry · Organosulfur compounds · Electron-transfer reactions

Introduction

Formation of organized molecular assemblies at electrode surfaces, extensively studied [1–3] in recent times, offers vast scope to manipulate the interfacial architecture that holds the key to the proper understanding of several issues such as electron transfer (ET), energy transduction, etc. In this context, the method of self-assembly, which enables the binding of a monolayer of molecules to metal surfaces through chemical interactions, offers a simple and elegant approach to modify electrode surfaces at molecular levels, facilitating appli-

cations in diverse areas such as molecular electronics [4–7], sensors [8–12] and tribology [13, 14]. Significantly, these self-assembled monolayers (SAM), serving as precision spacers with molecular resolution between the electrodes and the reaction centres, enable the tailoring of model interfaces for the understanding of heterogeneous ET kinetics [15–18]. The SAMs of alkanethiols of the type $\text{CH}_3\text{-(CH)}_n\text{-SH}$ have enabled a better understanding of the kinetics of outer sphere ET reactions as a function of the distance between the electrode and the redox centre by varying the value of 'n'. Again, studies on such SAMs have revealed that compact and impervious monolayers result when n is large (≥ 9), while low values of n yield non-compact and porous monolayers.

Generally, most of the published reports invariably concern aliphatic thiols. On the other hand, the behaviour of SAMs formed from thiols containing π -electron-rich aromatic substituents may prove interesting. However, investigations of only a few such systems have been reported. Co-adsorption of short aromatic thiols along with alkanethiols [19] and the influence of a polar aromatic group present in the middle of the aliphatic chain of an alkanethiol [20] have been studied. The SAM formation of 4-aminothiophenol on Au and the $\text{p}K_a$ determination of the surface-confined molecules have been described [21]. Investigations on the SAM of 4-mercaptobenzoic acid on Au have shown that the aromatic ring imparts conformational rigidity to the monolayer [22]. Surface spectroscopic measurements show that, on an Ag surface, the aromatic thiols form monolayers having long-range order [23]. Studies on the SAMs of thiols containing a chain of aromatic rings reveal that a monolayer of thiophenol containing a single benzene ring does not have good stability [24]. Further, the order and the stability of the monolayer film is reported to increase with the increase in chain length [24, 25]. In this context, it is worth investigating if thiols with fused aromatic rings can form compact and impervious monolayers despite the absence of a long methylene chain. This paper describes the formation of the SAM using 2-mercaptobenzothiazole (MBT), an

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aromatic thiol having a fused thiazole ring but no methylene chain, and the influence of such a monolayer on the ET actions.

Experimental

A gold disk (Bio-Analytical Systems) of area 0.036 cm^2 was polished using alumina slurry ($0.5 \mu\text{m}$ size), 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 the reference electrodes, respectively. MBT (Fluka), octadecanethiol (octadecyl mercaptan; ODM) (Aldrich) and other reagents were of analytical grade and were used as such without further purification. Triple distilled water was used for preparing the solutions. Monolayer coverage of the electrode was obtained by immersing the cleaned Au electrode in an acetone solution of MBT/ODM for about 4 h and then rinsing the electrode in alcohol followed by drying in air. The modified electrodes, denoted as Au|MBT and Au|ODM, respectively, were subjected to voltammetric studies. The cyclic voltammograms (CV) were recorded using a Wenking (model POS 73) Potentiostat and a Rikadenki (model RW 201 T) X-Y/t recorder.

Results and discussions

The CVs recorded on bare Au, Au|MBT and Au|ODM electrodes at 20 mV s^{-1} from $0.5 \text{ M H}_2\text{SO}_4$ containing 2 mM ferrous ammonium sulfate are depicted in Fig. 1, while Fig. 2 presents CVs resulting from $0.5 \text{ M H}_2\text{SO}_4$ containing $2 \text{ mM K}_4\text{Fe}(\text{CN})_6$. The voltammetric response of the above electrodes to the underpotential deposition (UPD) of copper from $0.5 \text{ M H}_2\text{SO}_4$ containing 3.5 mM CuSO_4 was also studied (CV not presented). The double layer capacitance (C_{dl}) of the electrodes was estimated from the CVs recorded at 20 mV s^{-1} in the presence of the background electrolyte only, by dividing the sum of the anodic and cathodic currents at 0.3 V by twice the scan rate [17].

It is seen from Fig. 1 that the redox behaviour of the $\text{Fe}^{2+/3+}$ system is totally blocked on both Au|MBT and Au|ODM, while it is almost reversible on bare Au. It is known that ODM forms a compact and impervious monolayer on Au [16]. The observed voltammetric

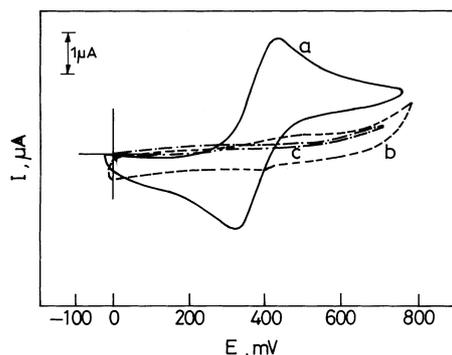


Fig. 1 Redox behaviour of $\text{Fe}^{2+/3+}$ on Au|SAM electrodes: CVs of $2 \text{ mM Fe}^{2+/3+}$ in $0.5 \text{ M H}_2\text{SO}_4$ on **a** bare Au, **b** Au|MBT and **c** Au|ODM, at 20 mV s^{-1}

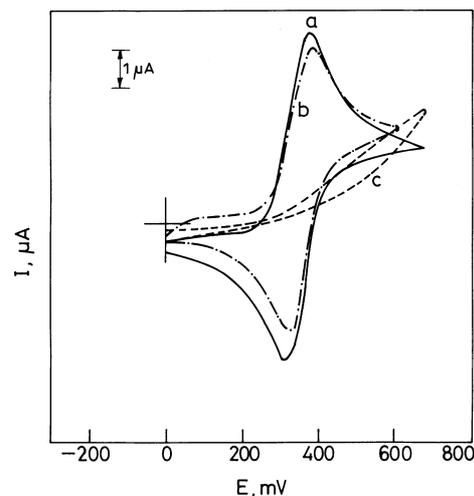


Fig. 2 Redox behaviour of $\text{Fe}(\text{CN})_6^{4-/3-}$ on Au|SAM electrodes: CVs of $2 \text{ mM Fe}(\text{CN})_6^{4-/3-}$ in $0.5 \text{ M H}_2\text{SO}_4$ on **a** bare Au, **b** Au|MBT and **c** Au|ODM, at 20 mV s^{-1}

response on Au|MBT, being almost identical to that on Au|ODM, indicates that MBT also forms a compact and impervious monolayer on Au. It is pertinent to note that MBT does not have a long methylene chain, which is reported to be responsible for the formation of impervious monolayers by aliphatic thiols like ODM. Moreover, the formation of a pore-free and impervious monolayer by MBT receives confirmatory evidence from the C_{dl} data. The low C_{dl} value ($4.1 \pm 1.0 \mu\text{F cm}^{-2}$) for Au|ODM arises from the formation of compact and impervious monolayers on Au by thiols having a long methylene chain [16]. The fact that Au|MBT is also characterized by such a low C_{dl} value ($8.1 \pm 1.1 \mu\text{F cm}^{-2}$) shows that MBT molecules, despite the absence of a long methylene chain as in ODM, form a compact monolayer that prevents the permeation of the electrolyte. A marginally higher C_{dl} value for Au|MBT as compared to Au|ODM can be attributed to the thickness of the ODM monolayer ($\approx 30 \text{ \AA}$ [16]), being higher than that of the MBT monolayer ($< 10 \text{ \AA}$ [7]), since C_{dl} is known to increase with decrease in thickness.

The presence of an aromatic ring in MBT possibly tethered to Au in a lateral configuration [7] will facilitate, through interactions between the electrons of the aromatic ring and the delocalized polarizable free electrons of the metal [26], additional binding, besides the Au-thiolate linkage, between the adsorbate and the substrate.

Figure 2 shows that reversible redox behaviour is exhibited by the $\text{Fe}(\text{CN})_6^{4-/3-}$ system on Au|MBT, similar to that on bare Au. However, the voltammetric behaviour of the above redox system is seen to be totally blocked on Au|ODM, which is in agreement with that reported earlier [16]. This difference in the voltammetric behaviour of $\text{Fe}(\text{CN})_6^{4-/3-}$ noted on the two different monolayers covering Au, viz., Au|MBT and Au|ODM, can be substantiated as follows. The outer sphere ET reaction, to which the $\text{Fe}(\text{CN})_6^{4-/3-}$ system belongs, in-

volves no direct electronic interaction between the electrode and the redox centre and it can proceed through a tunnelling mechanism which predicts a rapid decrease in kinetics with the increase in distance between the redox centre and the electrode surface. Thus the difference in thickness of the monolayers of the two molecules concerned (MBT and ODM) can give rise to the blocking of ET on Au|ODM and the near transparency on Au|MBT.

Finally, the dissimilarity in charge transfer response yielded by Au|MBT towards the $\text{Fe}^{2+/3+}$ and $\text{Fe}(\text{CN})_6^{4-/3-}$ redox systems (viz., blocking the former and allowing the latter charge transfer reactions) could be rationalized on the basis of their inner or outer sphere ET character. Thus the thin, compact and impervious MBT monolayer (of thickness approximately 10 Å) can be visualized to effectively prevent the direct access of the Au electrode surface to the redox $\text{Fe}^{2+/3+}$, which is an essential prerequisite in inner sphere ET reactions.

The above suggestion gains strength further from the voltammetric data on copper UPD on Au|MBT and Au|ODM electrodes. The CV behaviour, characteristic of the Cu UPD on bare Au, is totally absent on both the monolayer covered electrodes. The monolayer coverage by MBT and ODM, being compact and pore-free, does not allow direct interaction between Cu^{2+} and the Au surface and hence inhibits UPD on both Au|MBT and Au|ODM.

Conclusions

The investigations reveal that the presence of an aromatic substituent in the thiol molecule can be favourably exploited for forming compact and impervious ad-monolayers that could normally be achieved only with thiols having a long methylene chain. Further, the formation of such impervious and relatively thin monolayers of aromatic thiols can help to distinguish between inner and outer sphere ET reactions. Thus, the present investigations have opened up the possibility of tailormaking interfaces for distinguishing ET mechanisms, of the inner sphere vis-à-vis outer sphere types.

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