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Application of 2-mercaptobenzothiazole self-assembled monolayer on polycrystalline gold electrode as a nanosensor for determination of Ag(I)

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Abstract

Fabrication and application of a voltammetric sensor based on gold 2-mercaptobenzothiazole self-assembled monolayer (Au-MBT SAM) for determination of silver ion is described. Preliminary experiments were performed to characterize the monolayer. The surface pK_a determined for the MBT monolayer is 7.0. This value was obtained by impedimetric titration of the monolayer in the presence of $Fe(CN)_6^{3-/4-}$ as a redox probe. The extent of surface coverage was evaluated as 1.52×10^{-9} mol cm^{-2} based on charged consumed for reductive desorption of the monolayer in the 0.50 M NaOH solution. Then the sensor was used for determination of Ag(I) by square wave voltammetry. The parameters affecting the sensor response, such as pH and supporting electrolyte, were optimized. A dynamic calibration curve with two linear parts was obtained in the concentration ranges of 5×10^{-8}–8×10^{-7} and 1×10^{-6}–1×10^{-5} M of Ag(I). The detection limit adopted from cathodic striping square wave voltammetry was as 1×10^{-8} M for $n = 7$. Furthermore, the effect of potential interfering ions on the determination of Ag(I) was studied, and an appropriate method was used for the elimination of this effect.

Keywords: 2-Mercaptobenzothiazole; Self-assembled monolayer; Silver ion; Square-wave voltammetry

1. Introduction

Spontaneous adsorption of organic molecules as thiols and lipids from solution onto the solid surface of coinage metals such as copper, silver, and gold can give rise to self-assembled monolayers (SAMs). The affinity of the sulfur for the metals and the strength of the bond formed, predominantly covalent with some polar character, are significant and have led to applications in nanometer scale modification of the surface [1–6]. Gold is the most frequently used substrate because it does not have a stable oxide under ambient conditions. The thiol groups chemisorb onto the gold surface via the formation of a gold–thiol bond [3,4] to produce a densely packed and highly ordered monolayers [5,6].

The SAMs have been used in electroanalytical chemistry for some 20 years. The most frequent application of SAMs in electroanalytical chemistry is in the development of sensors and biosensors where the SAM is used to impart selectivity onto an electrode for a particular analyte. Sensors using SAMs have been applied to monitor pH [7], inorganic species [8–23], and organic molecules [24–42] using both chemical and biological recognition elements.

The 2-mercaptobenzothiazole (MBT) is a well-known analytical reagent for silver ion. It has been widely used as a ligand for preconcentration of Cu(II) [43], Ag(I) [44,45], Hg(II) [46], Bi(III) [47], Au, Pt, and Pd [48], followed by spectroscopic determination of these ions. In electroanalytical chemistry MBT was used for construction of Ag(I) [49] and Hg(II) [50] ion-selective electrodes, and as a ligand for simultaneous stripping analysis of Hg(II), Cu(II), and Bi(III) [51]. However, determination of Ag(I) using SAM modified electrodes was reported by Zeng et al. [52a] and Nagaoka et al. [52b], but, the Au-MBT SAM has never been tested to determine any inorganic ion, specially Ag(I). So far several attempts have been made to characterize the MBT SAM on gold (Au-MBT SAM) electrode. For example, Zhou et al. [53] have studied the "opening and closing" behavior of MBT as a function of solution pH in the presence of $Fe(CN)_6^{3-/4-}$ redox probe. Bharathi et al. [54] have proposed

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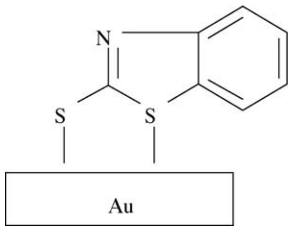

Scheme 1. Schematic representation of Au-MBT SAM structure proposed by Bharathi et al. [54].

that MBT adsorbs on gold surface in thiol form (Scheme 1). In contrast, Pradeep et al. [55] have suggested that MBT adsorbs on the gold surface in the thione form. This controversy makes it difficult to understand the true bond structure of Au-MBT SAM and consequently leads to failure for decision about probable mechanism of silver ion interaction with Au-MBT SAM. However, investigation of the bond structure and molecular orientation on the gold electrode surface is out of the goals of this work.

Thus, modification of the gold electrode by MBT should provide suitable sensor for voltammetric determination of Ag(I). In this paper, the characterization of Au-MBT SAM by electrochemical impedance spectroscopy (EIS) followed by its application for determination of Ag(I) using adsorptive cathodic stripping square wave voltammetry (SWV) (i.e., accumulation of Ag(I) on Au-MBT SAM under open circuit potential followed by voltammetric reduction) are presented and discussed.

2. Experimental

2.1. Chemicals

MBT was purchased from Riedel® and used as received. All other chemicals used in this investigation were of analytical reagent grade. High-purity nitrogen was used for deaeration. All glasswares were cleaned with a sulfochromic acid solution (saturated $K_2Cr_2O_7$ in concentrated H_2SO_4), followed by thoroughly washing with double-distilled water to avoid contamination. A stock solution of 0.1 M Ag(I) was prepared by dissolving ca. 1.70 g of $AgNO_3$ and diluting to 0.1 L. This solution was standardized against carefully prepared solution of NaCl (as a primary standard) using chromate indicator (Mohr's method). More dilute solutions were prepared by diluting the standardized solution with deionized water. Since silver ions may undertake the reduction to zero valent silver and this leads to fading some of ionic silver, for the analytical daily work, stock solutions of Ag(I) were prepared and kept into the polyethylene vessel.

2.2. Electrochemical equipments

All electrochemical measurements were performed with P/G AUTOLAB®30 (Eco Chemie, Utrecht, The Netherlands) in conjunction with an electrode stand VA663 (Metrohm®, Switzerland), equipped with Frequency Response Analyzer, interfaced with a personal computer, and controlled by General Purpose Electrochemical System (GPES 4.9) and FRA 4.9 softwares (Eco Chemie, Utrecht, The Netherlands). The measurements were performed in a three-electrode glass cell including a gold disk (2 mm diameter, Azar Electrode Co., Urmia, IRAN) as working electrode, a large area Pt plate as auxiliary electrode, and a saturated calomel electrode (SCE) as reference. All reported potentials are referenced to the SCE electrode. An ultrasonic bath (Bandlin, HF 35 kHz) was used for electrode sonication.

2.3. Electrode preparation

Before use, the gold working electrode was kept in Piranha solution (1:3 v/v, 30% H_2O_2 and concentrated H_2SO_4. Caution: Piranha solution is extremely corrosive and must be handled carefully) for 3.0 min and rinsed thoroughly with double-distilled water. Then, the electrode was polished with 0.05 μm alumina slurry on a polishing cloth (Buehler®), rinsed with water and sonicated in water/chloroform/water each step 5 min, to remove any physically adsorbed particle and contaminant. The cleanliness of the electrode surfaces was ascertained by recording the cyclic voltammogram (CV) for oxidation and reduction of the gold electrode surface in 0.1 M H_2SO_4 between 0.00 and +1.50 V with 50 mV s^{-1} scan rate for about 40 min and comparing with the CV of the clean Au reported by Brett et al. [1c]. The real surface area of the gold electrode was calculated by the integration of cathodic peak obtained on bare gold in 0.1 M H_2SO_4 and comparing with 482 μC cm^{-2} charge for reduction of one monolayer of AuO on Au (1 1 1). A roughness factor of 1.6 ± 0.2 was calculated from the ratio of the real to the geometric surface area, and attemped to reach to this value in all experiments. It should be emphasized that the state of the surface, including the surface roughness, is very important for reproducible formation of high quality SAMs on gold electrode [56]

The clean gold electrode was immersed in a 10 mM ethanolic solution of MBT for 12 h to form Au-MBT SAM. Finally, the modified electrode was removed, sonicated in ethanol, washed thoroughly with ethanol and water to remove physically adsorbed MBT, and used for electrochemical measurements.

2.4. Electrochemical measurements

The EIS measurements were carried out as follows: An electrolyte solution was prepared using the method of Smalley et al. [57]. The initial pH was ca. 2.1 for 0.1 M $NaClO_4$ + 0.01 M H_3PO_4. The higher pH was adjusted by the addition of 0.11 M NaOH. Ionic strength was constant over the entire range of pH. The electrochemical cell was filled with the pH-adjusted electrolyte solution containing 0.5 mM of each one of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ as a redox probe.

A sine wave with 5 mV amplitude was applied at the formal potential of the redox probe, and the impedances were measured for 30 frequencies in logarithmic scale starting from 10 kHz down to 100 mHz. The EIS data were approximated using electronic equivalent circuits. For this purpose, commercial software (ZView® version 2.3, Scribner Associates Inc.)

was employed. A modified Randles' model in which C_{dl} was replaced by frequency dependent constant phase element (CPE), ($Z_{\mathrm{CPE}} = Y_0(j\omega)^{-\alpha}, \alpha = 1 - \varphi$, and $\varphi = 0$ for complete smooth electrodes), was enough to explain the experimental data, from which the model parameters as interfacial charge transfer resistance (R_{ct}) for $\mathrm{Fe(CN)_6}^{3-/4-}$ at different pH were extracted [58–61]. For quantitative determination of Ag(I), the square wave voltammetric measurements were performed based on the following optimized parameters; pulse height, 10 mV, scan rate, 100 mV s^{-1} and interval time, 0.04 s. All peak currents in calibration plot were obtained by subtracting the blank voltammogram from the respective voltammograms using GPES 4.9. This feature facilitates obtaining the net faradaic current from experimental data. The corrected peak currents were used for construction of the cabilration curves.

3. Results and discussion

3.1. Blocking of Au-MBT SAM against $\mathrm{Fe(CN)_6}^{3-/4-}$ as a function of pH

The $\mathrm{Fe(CN)_6}^{3-/4-}$ was used as an electrochemical redox probe to investigate effect of pH on R_{ct} at the Au-MBT SAM. The complex plane plots obtained on modified electrode at different pH values are presented in Fig. 1. The diameter of the semicircles demonstrates a rough estimation of R_{ct}, which increases with increasing the solution pH. This behavior reveals that charge transfer for $\mathrm{Fe(CN)_6}^{3-/4-}$ on Au-MBT SAM becomes less favorable in higher pH values. However, at lower pHs, the nitrogen atom of MBT molecule is protonated [53], and the electrode surface is positively charged. Therefore, the R_{ct} is dramatically decreased due to the electrostatic attraction between redox probe and surface charges. A surface pK_{a} may be evaluated using the method reported in literature [62]. We obtained a surface pK_{a} from the midpoint of impedimetric-pH titration curve (p$K_{1/2}$), assuming that half of the surface functions are deprotonated at that point. The R_{ct} was approximated from the EIS data and plotted as a function of pH (Fig. 2). A good agreement is observed between experimental (R_{ct} versus pH) and theoretical (f versus pH, $\Psi = 0$ for equation 2 in Ref. 62b) results. The approximated pK_{a} for the Au-MBT SAM is 7.0.

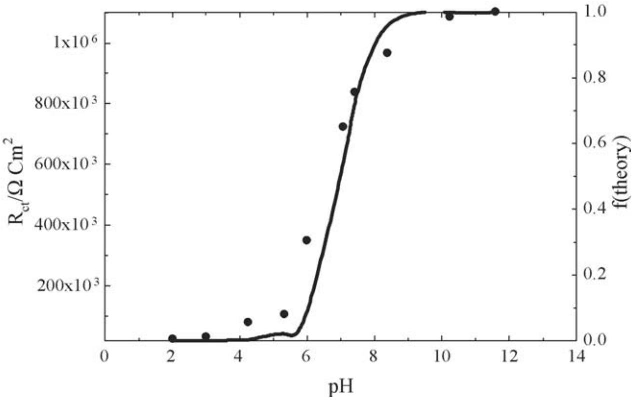

Fig. 2. Faradaic impedance titration curve for Au-MBT SAM electrode, points are experimental R_{ct} obtained by approximation of the EIS data (Fig. 1) using CPE model, line is calculated f using equation 2 in Ref. [62b].

Due to the electrostatic repulsive interaction, the positive charge of the surface hinders the adsorption of positive species (e.g., Ag^+ in this work), and the working pH has to be studied. However, it is more reasonable for similar works, to choose surfactants (e.g., MBT in this work) that have a relatively lower pK_{a} when adsorb on the electrode surface, because, the lower the surface pK_{a}, the narrower the pH range in which hydronium ion can compete with analyte for binding sites of surfactant.

3.2. Analytical behavior of the Au-MBT SAM

Analytical behavior and possibility for the application of Au-MBT SAM as a nanosensor for recognition of Ag(I) was studied by SWV. Thus, the bare gold and Au-MBT SAM electrodes were tested. When the bare gold was preconcentrated in Ag(I) solution, no current peak was observed (Fig. 3a) in spite

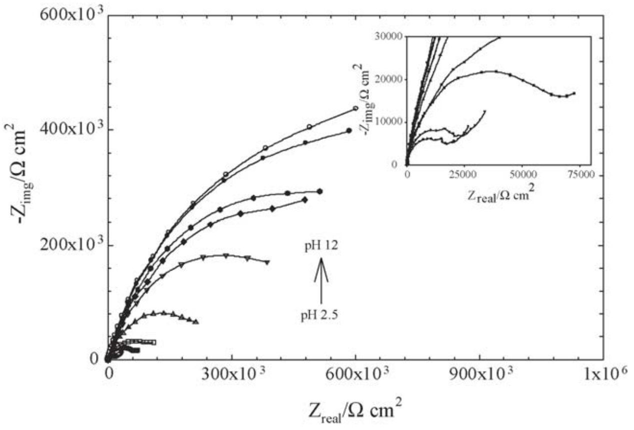

Fig. 1. Complex plane plots obtained on Au-MBT SAM electrode in the presence of 0.5 mM $\mathrm{Fe(CN)_6}^{3-}$/$\mathrm{Fe(CN)_6}^{4-}$ and different pH ranging from 2.5 to 12. Conditions: DC potential, +0.200 V; AC amplitude, 5 mV; frequency range, 10 kHz–100 mHz. Symbols show experimental data and lines the approximated results obtained using CPE model.

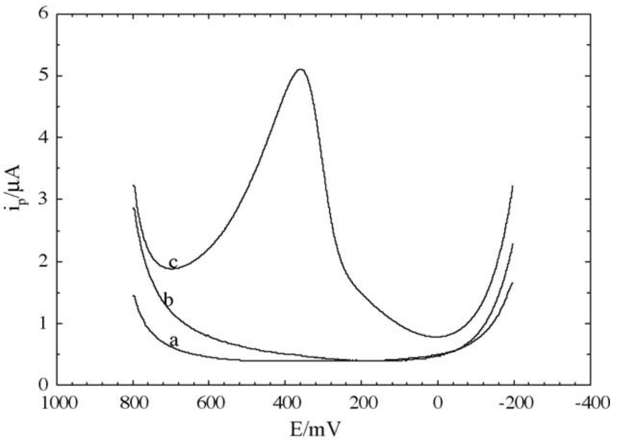

Fig. 3. Square wave voltammograms obtained in 0.1 M $\mathrm{KNO_3}$ solution, pH 4.0 on bare Au (a) and Au-MBT SAM electrode (b and c) preconcentrated in a 0.05 M $\mathrm{KNO_3}$ solution, pH 6.0 containing 0.0 M (b) or 1×10^{-5} M (a and c) Ag(I). Scan rate, 100 mV s^{-1}; pulse height, 10 mV; interval time, 0.04 s; preconcentration time, 5 min.

of Au-MBT SAM that reveals a cathodic wave around +0.350 V (Fig. 3c). Also, the Au-MBT SAM did not exhibit any wave over this potential range after preconcentration in the blank solution (Fig. 3b). So, the observed wave was attributed to the reduction of Ag(I). These results indicate that the chemical preconcentration of Ag(I) takes place only on the Au-MBT SAM.

3.3. Regeneration of Au-MBT SAM

In general, the regeneration of the sensors for eliminating the memory effect is one of the most important aspects that have to be considered in designation and fabrication of these devises [63–65]. The simple regeneration procedure enhances the potential applicability of the sensor. The attachment of analyte to the modified surface should not be so strong that not allow analyte elution and sensor regeneration. In most of the cases a complexing agent is used for modification of the electrode surfaces, which imparts selective accumulation of the analyte onto the electrode. When these sensors are used in voltammetric stripping analysis, the accumulated metal ions are reduced to their metallic or non-conventional oxidation state [64]. Therefore, the sensitivity of the method will decrease upon repetitive application of the sensor (e.g., this will be the case if a gold thiol SAM based sensor is used for determination of heavy metal ions). If this happens to the sensor, the electrode surface needs to be regenerated for its next use. There are two common methods for the regeneration purposes, namely chemical and electrochemical. The chemical methods are simple, and should be preferably used if the experimental conditions tolerate their application [66,67]. After several considerations and using various chemicals, we found that solutions of chemical species bearing sulfur atom, such as thiourea, thiocyanate, and thiosulphate, are good choices for our purpose. However, these species are susceptible to chemical adsorption on the surface of gold electrode and consequently causing the properties of the monolayer to be altered. Thus, to overcome this problem, we chose the acidic–ethanolic solution of MBT for regeneration of the electrode. This choice had two advantages over other tested chemicals as; (i) leaving the monolayer unchanged (even being repaired) after regeneration of the electrode and (ii) higher regeneration efficiency with respect to other chemicals (except for thiosulphate). Thus, regeneration was performed by dipping the Au-MBT SAM electrode into the stirring acidic–ethanolic solution of MBT for a required time, followed by recording the square wave voltammograms for several times, in the same conditions as for measurement step, until reaching characteristic voltammogram of the blank test. The simple chemical regeneration procedure through utilization of surface modifier itself (i.e. MBT), which was applied here, enhances the potential applicability of this sensor.

3.4. Influence of pH on the analytical efficiency

According to the preliminary investigations we found that both pH of the preconcentration and stripping solutions influence the response of the Au-MBT SAM toward Ag(I). The pH effect of the accumulation medium on the current response of Au-MBT SAM was investigated in the range of 3.0–8.0. Fig. 4(A) shows the plot of the cathodic peak current of Ag(I) as a function of the preconcentration solution pH, at the given conditions. The stripping peak current increased as the pH of the preconcentration solution was increased and a maximum was appeared at pH 5.0. At upper and lower pH values the response was decreased. This behavior may be attributed to; (i) the hydration of Ag(I) ions at higher and (ii) the competition of hydronium ions with Ag(I) ions at lower pH values.

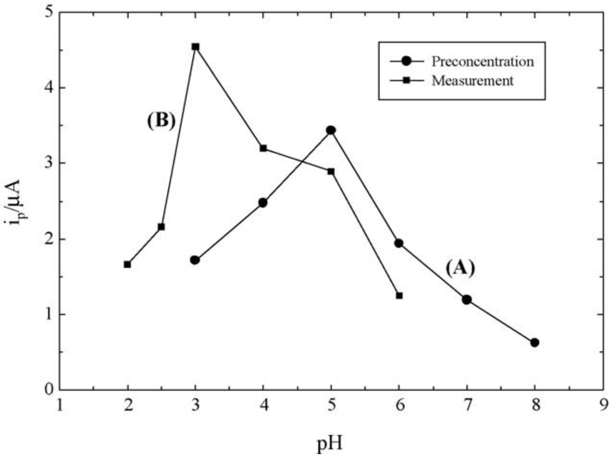

Fig. 4. Variation of the stripping peak current as a function of pH of the preconcentration (A) and stripping (B) solutions obtained on Au-MBT SAM conditioned in 0.05 M KNO_3 solution, containing 1.0×10^{-5} M Ag(I), preconcentration time 5 min. Stripping conditions: the same as Fig. 3.

The pH effect of the stripping medium was also investigated in the range of 2.5–6.0. Fig. 4(B) shows dependency of the cathodic peak current on pH of stripping solution. As it reveals from the plot, the peak current reaches a maximum at pH 3.0 and afterward begins to decrease. Thus, pHs 5.0 and 3.0 were chosen for preconcentration and stripping solutions, respectively.

3.5. Influence of the electrolyte solution

Various electrolyte solutions (whether being buffered or not) were tested, both as preconcentration and stripping media. Solutions including sulfuric, nitric, chloridric, citric, boric, phthalic, benzoic, and acetic acid were tested as stripping medium. These acids were added to 0.1 M of KNO_3 and their pH were adjusted to 3.0. Among these solutions, acetate was found to be the best suited medium. Various buffer solutions (all 0.05 M and pH of 5.0) including; acetate, borate, phthalate, benzoate, and citrate were also tested as preconcentration media. Again, voltammetric response in the case of using acetate buffer solution was the higher under the same experimental conditions. Therefore, acetate solutions with appropriate pH, 5.0 and 3.0, were chosen as preconcentration and stripping media, respectively.

3.6. Dependence of stripping current on the Ag(I) concentration

The cathodic stripping square wave voltammograms at different concentrations of Ag(I) under optimum conditions are shown in Fig. 5. The logarithm of the peak current is proportional

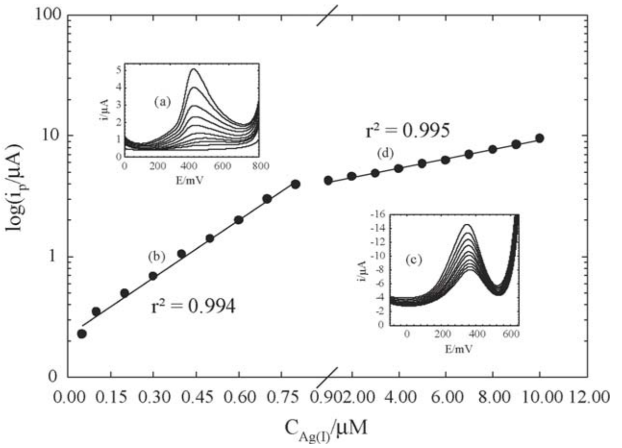

Fig. 5. Square wave voltammograms (a and c), and calibration curves (b and d) obtained on Au-MBT SAM electrode from variation of the stripping peak current as a function of Ag(I) concentrations from 5×10^{-8}–8×10^{-7} M (a and b) and 1×10^{-6}–1×10^{-5} M (c and d) of Ag(I) in 0.05 M acetate buffer solution pH 5.0 with 10 and 5.0 min preconcentration times, respectively. Stripping conditions: 0.1 M acetate solution pH 3.0; scan rate, 100 mV s^{-1}; pulse height, 10 mV; interval time, 0.04 s.

to the concentration of the Ag(I) ion. A dynamic calibration curve with two linear parts was obtained in the concentration ranges of 5×10^{-8}–8×10^{-7} and 1×10^{-6}–1×10^{-5} M of Ag(I). The detection limit of Ag(I) ion was 1×10^{-8} M for $n = 7$ ($S/N = 3$) and 10 min preconcentration time. Better detection limits could be reached using longer condition times. However, it was avoided for three reasons; (i) fading of some of Ag(I) ions due to the reduction to zero valent, (ii) loosing the dynamic range at higher concentrations due to saturation of the electrode surface, and (iii) increasing the probability of interference of other species.

3.7. Influence of some coexistent ions

We define the interfering effect as the concentration of interfering species that can change the electrode response toward the analyte by more than $3S_A$, where S_A is standard deviation of the replicate analyte measured signals. Effect of some anions and cations on the response of Au-MBT SAM to the Ag(I) ions was investigated. The results showed that the peak current of 1.0×10^{-5} M Ag(I) was decreased in the presence of above two-fold of Cl^-, Br^-, I^- and equimolar amount of $S_2O_3{}^{2-}$. This is due to the formation of compounds such as AgCl, AgBr, AgCl and $Ag_2S_2O_3$, which make the Ag(I) concentration to decrease. The interference of some cations including: Na^+, K^+, Pb^{2+}, Cd^{2+}, Hg^{2+}, Fe^{3+}, Ni^{2+}, Co^{2+}, Mg^{2+}, Mn^{2+}, Fe^{2+}, Zn^{2+}, Cu^{2+}, and Sn^{2+} were also examined. Most of these cations interfered in the determination of Ag(I) by Au-MBT SAM electrode. The peak current of 1.0×10^{-5} M Ag(I) was changed by less than 10% when 1 M of Na^+ and K^+, 1 mM of Cd^{2+}, Fe^{3+}, Ni^{2+}, Co^{2+}, Mg^{2+}, Mn^{2+}, Fe^{2+}, Zn^{2+}, Cu^{2+}, and 100 μM of Pb^{2+} and Sn^{2+} were presented. An equimolar amount of Hg^{2+} strongly affected the peak current. However, when 0.01 M of EDTA was added to the preconcentration solution the interferences of 1000-fold excess of above cations were eliminated.

4. Conclusions

The Au-MBT SAM electrode was fabricated and employed for determination of Ag(I) at trace levels by using adsorptive cathodic stripping SWV. The EIS studies in the presence of $Fe(CN)_6{}^{3-/4-}$ at different pHs allowed us evaluation of the surface pK_a as 7.0, which in turn helped to find the suitable pH for chemical accumulation of silver onto the surface of Au-MBT SAM. The SWV reduction peak potential of the silver ion was found around +0.35 V enabling the quantitative determination of Ag(I) in the two ranges of 5×10^{-8}–8×10^{-7} and 1×10^{-6}–1×10^{-5} M of Ag(I). The analytical conditions such as pH and type of electrolyte were studied. The method offers simplicity for electrode preparation and regeneration, and selectivity toward Ag(I) in the presence of a number of cations, which might be resulted from the electron affinity of Ag(I) towards the MBT. The detection limit adopted from the SVW measurements was 1×10^{-8} M Ag(I) with 4.5% relative standard deviation for $n = 7$. The interferences of coexisting cations, especially Hg^{2+}, were completely eliminated using 0.01 M EDTA.

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