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Corrosion Inhibition of Brass in 3% NaCl Solution by Electrosynthesized Poly 4-amino-3-méthyl-1,2,4-triazole-5-thione

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This paper describes the kinetics of the electropolymerization of 4-amino-3-methyl-1,2,4-triazole-5-thiol (MTSNH) on a brass substrate in alkaline solution containing methanol. Our laboratory has developed a new synthesis strategy for MTSNH. This compound was purified and characterized by ^{1}H NMR and ^{13}CNMR spectroscopies. The electrochemical study was investigated using cyclic polarization, chronoamperometry, electrochemical impedance techniques and scanning electronic microscopy. The polymeric film was achieved by successive cyclic voltammetry sweep between 0 and 2.2 V at the scan rate of 10 mV s^{-1}. The effect of the scan rate for 10^{-3} M of MTSNH in a basic solution of potassium hydroxide 0.1 M containing methanol shows that the increase of the scan rate is accompanied by the increase of the intensity of the first oxidation peak, indicating the acceleration of the studied process. We have also shown that the monomer oxidation reaction is essentially irreversible and controlled by a diffusion process. The protective effect of the film formed on brass has been studied in a 3% NaCl. The results showed important inhibition efficiency, about 83% for 1 h of testing time.

Keywords: Cyclic voltammetry, Chronoamperometry, Brass alloy, Corrosion, Inhibition, MTSNH

INTRODUCTION

Copper and its alloys have interesting properties such as electrical and thermal conductivity, and especially good resistance to corrosion, enabling these materials to be used in various industrial fields [1-3].

The inhibition of corrosion by triazole-thione compounds on copper and its alloys has been widely studied in recent years [4-6]. The results obtained show that this type of compounds have a good protective effect of these materials against corrosion.

The electrochemical polymerization is widely used [7-9], and several monomers have been used such 3-amino-1,2,4-triazole [10], 2-mercaptobenzimidazole [11], aminophenol [12], benzotriazole [13] and polyaniline [14]. This technique allows a great precision in the control of the reaction and consequently the properties of the polymers obtained.

In the present work, we have studied the film deposition issued from the MTSNH monomer on a brass electrode. The synthesis method of this monomeric compound, carried out in our laboratory by the microwave technique, has the advantage of being an ecological method, respectful of the environment and of reducing reaction times compared to that described in the literature [15] which consists of a reflux reaction of thiocarbohydrazide with acetic acid.

The techniques of cyclic voltammetry and chronoamperometry have facilitated studies of the electrosynthesis of poly 4-amino-3-methyl-1,2,4-triazole-5-thione on brass and the kinetics of electropolymerization.

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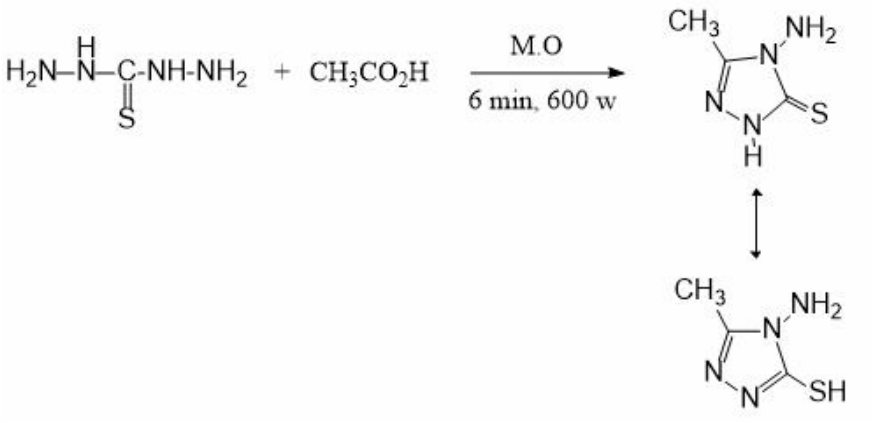

Fig. 1. Synthesis of 4-amino 3-methyl-1,2,4-triazole-5-thione (MTSNH) using microwave.

The corrosion inhibiting effect of this deposit of polymer film on the surface of the brass in a medium containing 3% NaCl was studied using potentiodynamic curves and impedance spectroscopy diagrams. Surface analysis techniques of the polymer film were carried out by SEM/ EDS.

EXPERIMENTAL

Materials

The composition of the brass studied was (wt%): 60.61% Cu, 39.19% Zn, 0.12% Al, and 0.08% Si.

Solutions

The aggressive solution 3% NaCl was prepared by dissolving NaCl (Aldrich) in distilled water.

Inhibitor

M. Aouial reported a simple method for the synthesis of 4-amino-3-methyl-1,2,4-triazole-5-thione consisting of a reflux of thiocarbohydrazide in acetic acid followed by cooling [15]. For our part, we have developed a new and eco-friendly method using accelerated synthesis in the microwave (Fig. 1).

Spectral Characteristics

^{1}H NMR (300 MHz, DMSO-d6) δ: CH_3: 2.22, NH_2: 5.49, NH: 13.38. ^{13}C NMR (75 MHz, DMSO-d6) δ: 10.86 (CH_3), 149.611 (C=N), 165.84 (C=S).

Potentiodynamic Polarization Method

The voltammograms, I-t transient curves and the electrochemical impedance measurements were performed using a potentiostat PGZ101. The electrochemical glass cell performed in all tests contained three electrodes: saturated calomel electrode (SCE) as the reference, platinum as the auxiliary electrode and the working electrode as brass alloy. In this study, we obtained the corrosion current density (i_{corr}), corrosion potentials (E_{corr}), and cathodic Tafel slope (b_c). The inhibiting efficiency (E%) was calculated from corrosion current density by applying the following equation:

$$E\% = \frac{I^0_{corr} - I_{corr}}{I^0_{corr}} \times 100$$

where $I°_{corr}$ and I_{corr} are the corrosion current densities obtained respectively without and with inhibitor.

Electrochemical Impedance Spectroscopy (EIS)

The electrochemical impedance spectroscopy analysis was performed at 20 °C with respect to corrosion potential (Ecorr) over a frequency range of 100 kHz to 10 mHz with a signal amplitude perturbation of 1 mV s^{-1}. Data were presented as Nyquist plots.

Surface Analysis

The specimens used for surface morphology were characterised by scanning electron microscopy SEM

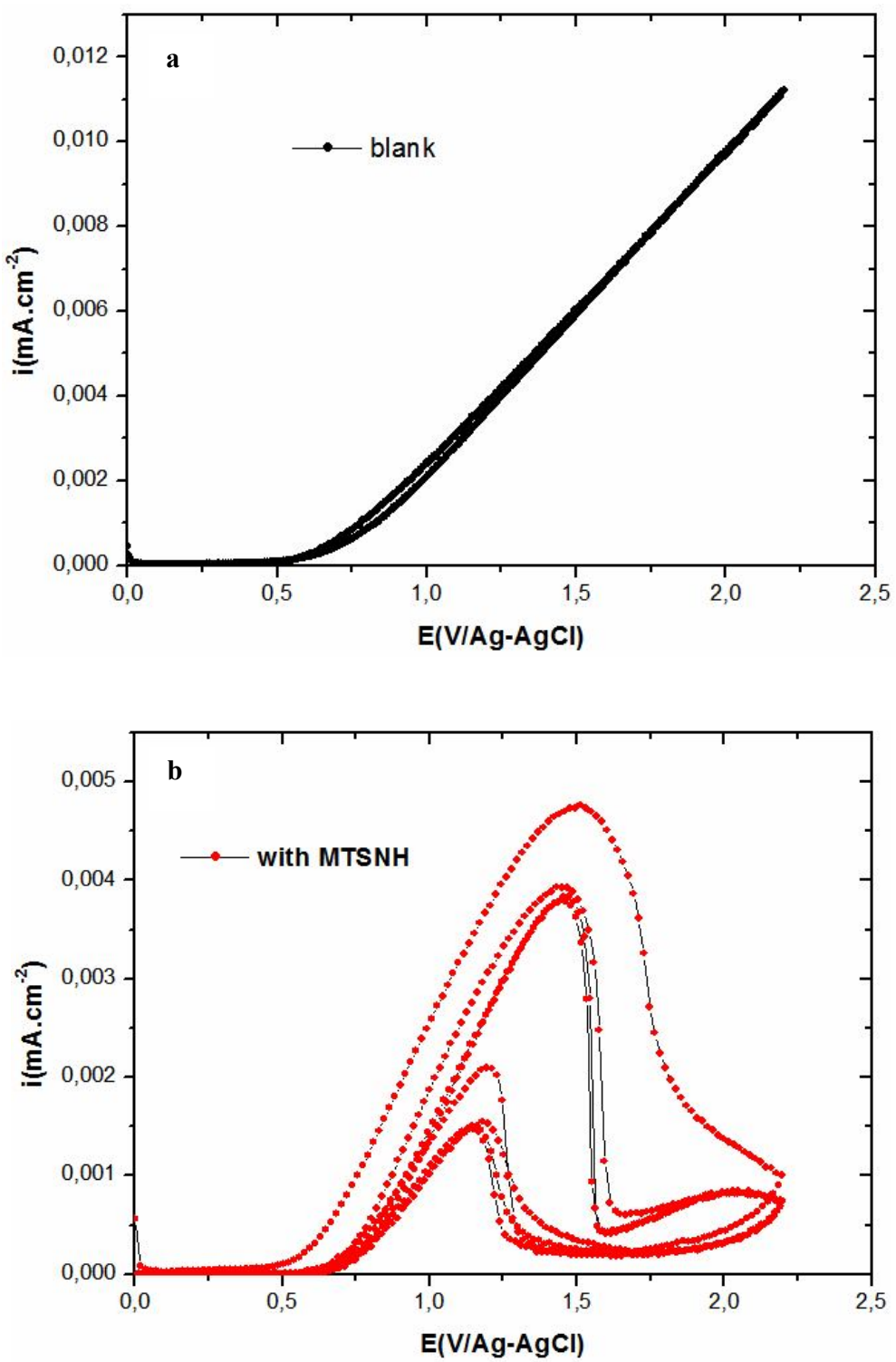

Fig. 2. Cyclic voltammograms obtained in methalonic solution containing 0.1 M of potassium hydroxide without (a) and with (b) 10^{-3} M MTSNH as a monomer with scan rate of 10 mV s^{-1}.

coupled with EDS elemental analysis. The microscope used in this study is a FEI (model quanta FEG 450). The EDS is flash 6130 model X (Bruker).

RESULTS AND DISCUSSION

Electrochemical Properties of 4-Amino-3-methyl-1,2,4-triazole-5-thione

Cyclicvoltammetry. The anodic electroactivity domain is determined by the oxidation of 0.1 M potassium hydroxide as a supporting electrolyte on the brass in the absence of the monomer (Fig. 2a)

Figure 2b shows the cyclic voltammograms obtained during the formation of poly-4-amino-3-methyle-1,2,4-triazole-5-thione (poly-MTSNH) on the brass substrate with scan rate 10 mV s^{-1}. In the absence of MTSNH, the curve shows that the oxidation current increases continuously. This increase is due to the oxidation of the electrolyte. In the presence of MTSNH, there is a current peak during the anode potential scan (go), however, no peak was detected during the cathodic scan (return), the peak of anodic current appears at the potential 1.5 V.

Figure 2b shows a decrease in current intensities with an increase in the number of cycles. It can be observed that the oxidation peak potential was shifted to less anodic potentials. This may indicate that the film formed on the 60Cu-40Zn alloy is more permeable [16]. These results show that 4-amino-3-methyl-1,2,4-triazole-5-thione (MTSNH) acts as a monomer oxidize to form poly-4-amino-3-methyl-1,2,4-triazole -5-thione (p-MTSNH).

Effect of scan rate on the peak current of MTSNH. The effect of scan rate for 10^{-3} M of MTSNH in a basic solution of potassium hydroxide 0.1 M containing methanol was investigated by cyclic voltammetry technique. Figure 3 showed an increase in redox peak currents with increase in the scan rate according to Randles-Sevcik equation [17-18] in the range 10 to 50 mV s^{-1}.

$$IP = 2.69 \times 10^5 n^{\frac{3}{2}} A D^{\frac{1}{2}} C_0 \gamma^{\frac{1}{2}}$$

where Ip is the peak current in A, C_0 is the concentration of the electroactive species (mol cm^{-3}), n is the number of electrons exchanged, D is the diffusion-coefficient (cm^2 s^{-1}), γ is the scan rate (V s^{-1}), and A is the surface area (cm^2). The results relating to the oxidation of MTSNH for different scanning speeds are grouped in Table 1. The increase of the scan rate is accompanied by the increase in the intensity of the first oxidation peak, indicating the acceleration of the studied process. A good linearity with the correlation coefficient (R^2) of 0.99 was observed for the graph of current density of this peak Ip *vs.* $\gamma^{1/2}$ (Fig. 4). Therefore, the result confirms that the electropolymerization process is limited by diffusion through the polymer film formed.

Chronoamperometry. A chronoamperometry study was conducted at different potentials in the range of values before and after the potential of the oxidation peak of the monomer. Figure 5 illustrates the variation of current density versus time for the brass substrate. Figure 5 shows that the current density decreases rapidly as a function of time and stabilizes after about ten seconds, which corresponds to the development of insulating film of poly-4-amino-3-methyl-1,2,4-triazole-5-thione on the brass surface. In all cases, there is a residual current at the end of electrolysis. This could be explained by the presence of porosities in the formed film. Indeed, electrolysis at a high potential ($E \geq 1.7$ V) and at a potential $E \leq 1.3$ V most often leads to the formation of cracked, porous films and low adhesions.

Oxidation mechanism of MTSNH. The oxidation steps of MTSNH were located on mercapto group related to the triazolic ring, which represents after deprotonation of the thiole -SH function in basic medium, a typical redox system with one electron oxidation process as shown in Fig. 6. This type of mechanism has been proposed in earlier reports. [19].

Corrosion Inhibition of Brass by Poly-MTSNH Film in 3% NaCl Medium

The poly-MTSNH film was grown by electrochemical deposition on brass and its corrosion performance was monitored by potentiodynamic curves and impedance spectroscopy. Poly-MTSNH was successfully polymerised on brass electrodes, as shown by cyclic voltammetry, and provided corrosion inhibition in 3% NaCl.

Stationary measurement. Cathodic polarization curves: The cathodic polarization curves of brass in 3% NaCl medium without and with poly-MTSNH are illustrated in Fig. 7. It can be seen that the formation of the

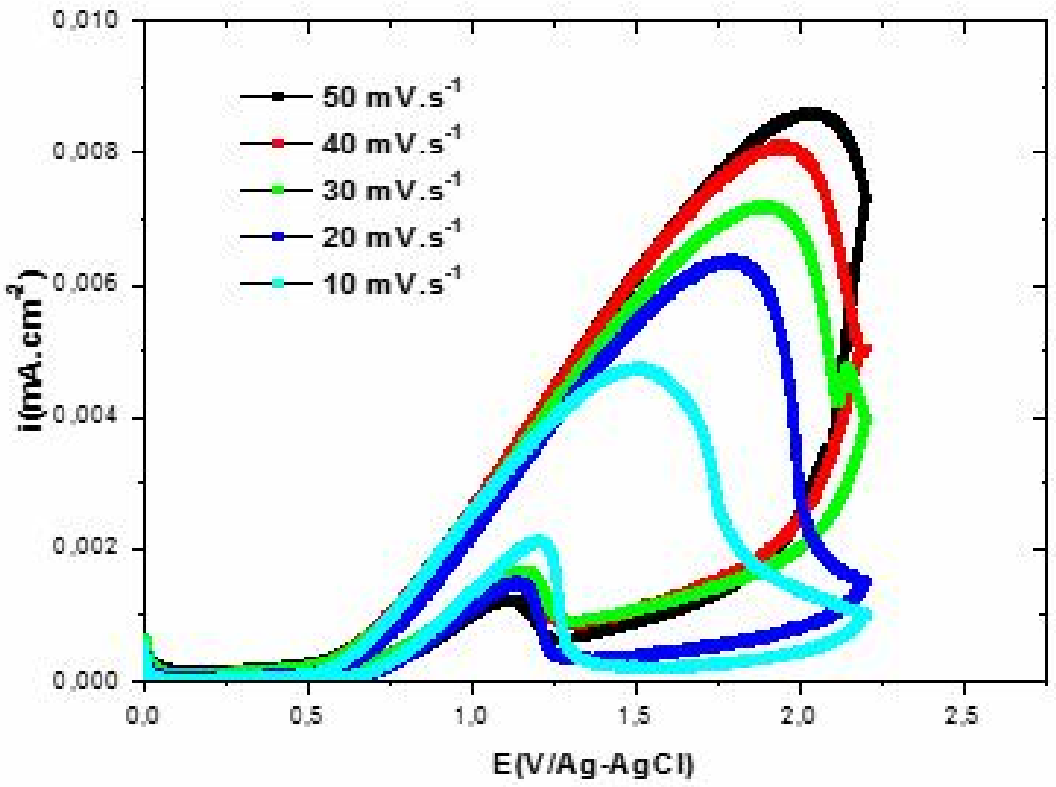

Fig. 3. Cyclic voltammograms of brass in electrodeposition medium at the given scan rates (mV s^{-1}).

Table 1. Characteristics of $I_p = f(E_p)$ Curves Rrecorded at Different Scan Rates

Scan rate γ (mV s^{-1})	I_{pic} (mA cm^{-2})	E_{pic} (V/Ag-AgCl)
10	0.656	1.156
20	0.867	1.213
30	1.192	1.293
40	1.314	1.329
50	1.314	1.329

polymer film (poly-MTSNH) results in a reduction in the density of corrosion current with a displacement of the corrosion potential to positive values. Similarly, there is a change in the shape of the curve which is due to a change in kinetics of the reactions, reflecting the predominance of charge transfer. For more cathodic potentials, E < -0.6 V, this effect decreases and the current reaches a lower value than that when the oxygen diffusion plateau is determined

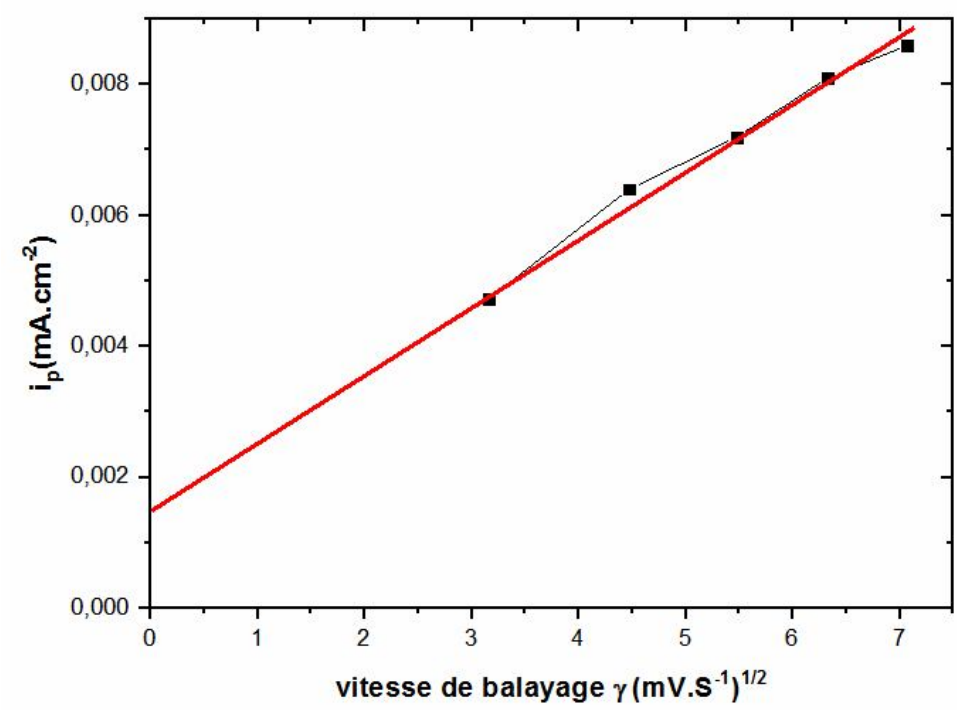

Fig. 4. Variation of peak current density *versus* square root scan rate during electropolymerization of MTSNH on brass.

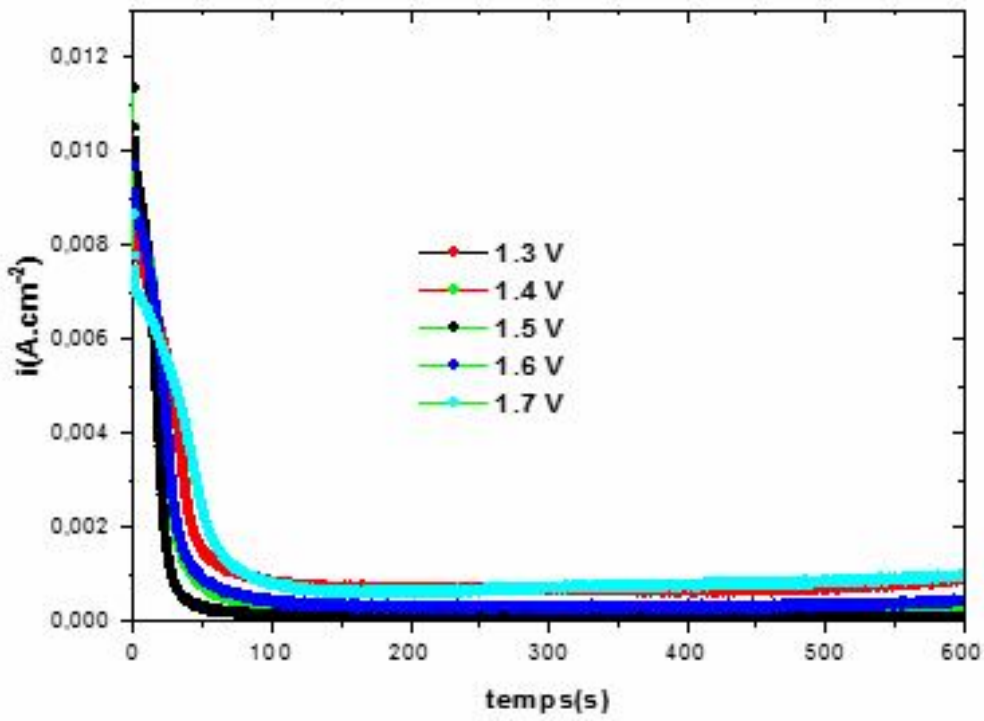

Fig. 5. Chronoamperograms recorded at the brass electrode at different potentials in a methalonic solution containing 1 mM of MTSNH and 0.1 M of KOH.

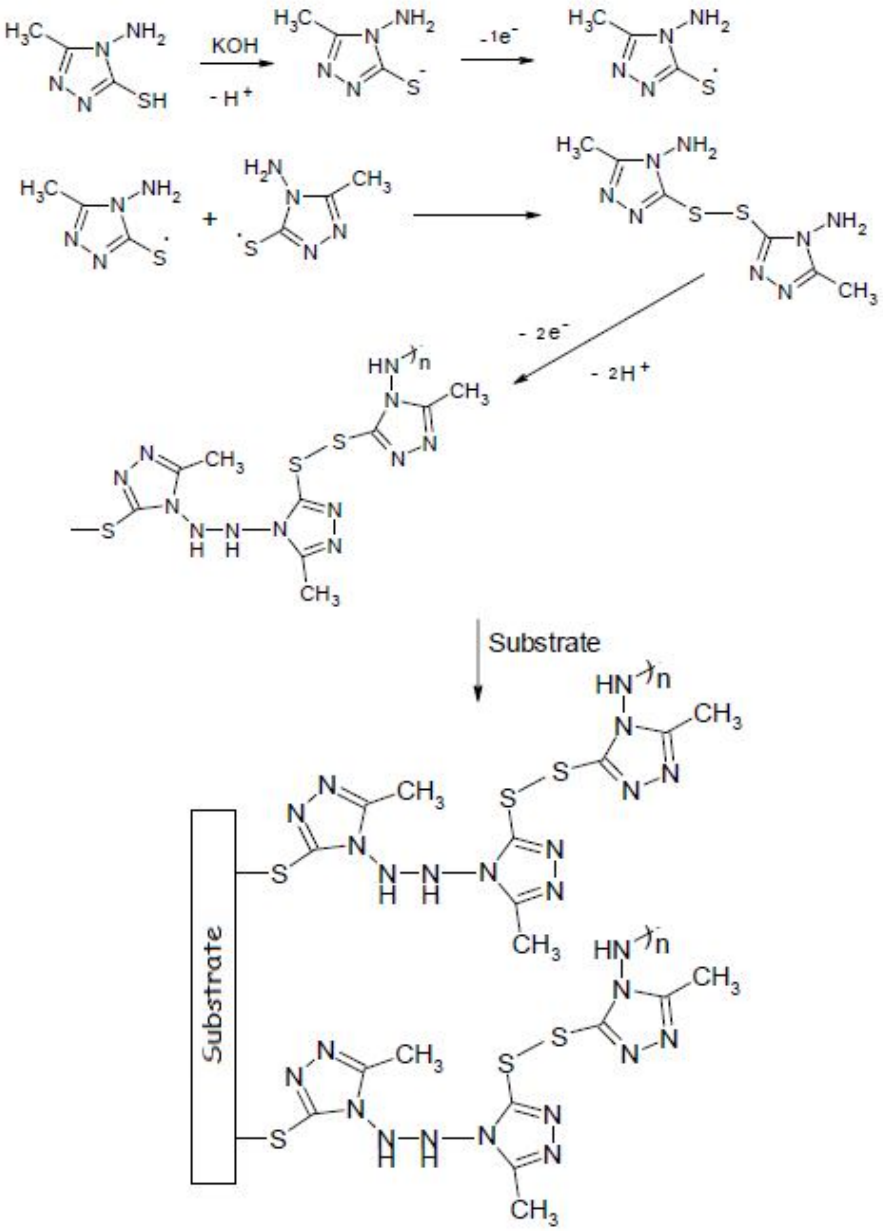

Fig. 6. Oxidation mechanism of MTSNH.

in the case of the brass electrode without inhibitor.

The values of the electrochemical parameters resulting from the cathodic curves, as well as the inhibitory efficiency are grouped in Table 2. The parameters issued from Table 2 showed that there is a noticeable decrease in the density of the corrosion current. Thus, the inhibition efficiency reaches 83%.

Anodic polarization curves: Figure 8 shows the anodic polarization curves for the brass electrode in a 3% NaCl solution with and without poly-MTSNH film, after 1 h immersion of the electrode and a speed of 1000 rpm. These curves show that the presence of poly-MTSNH film on the brass substrate in 3% NaCl medium causes a net decrease in the anodic current density in the immediate vicinity of the

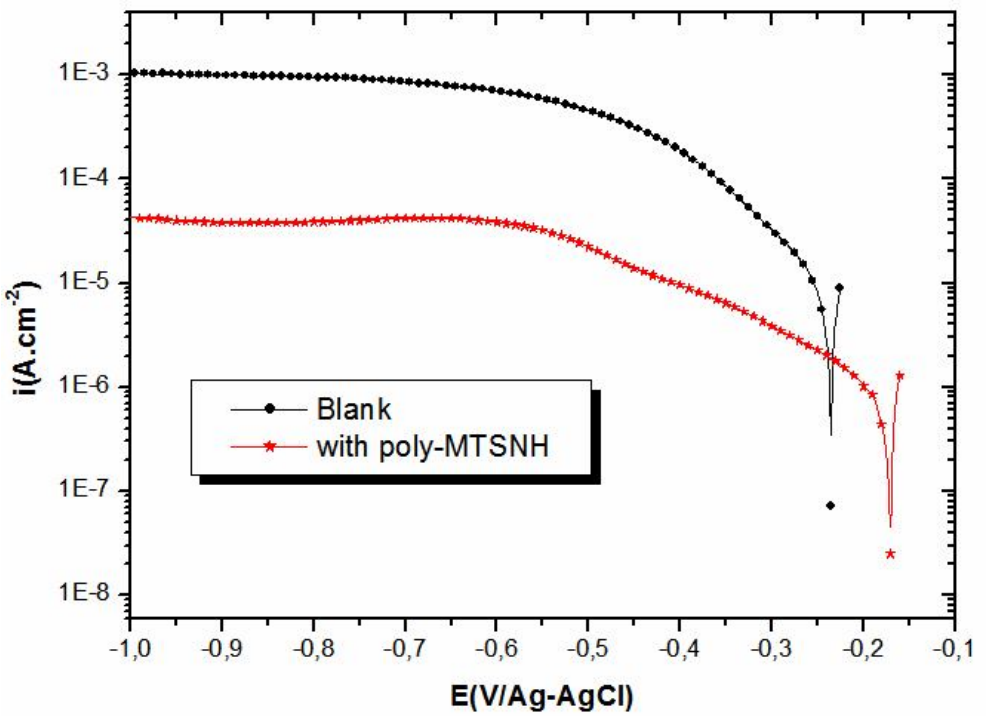

Fig. 7. Cathodic curves of brass in 3% NaCl medium without and with poly-MTSNH.

Table 2. Electrochemical Parameters of the Cathodic Polarization Curves of Brass in 3% NaCl without and with Poly-MTSNH

	E_{corr} (mV)	I_{corr} ($\mu A\ cm^{-2}$)	b_c ($mV\ dec^{-1}$)	E (%)
Blank	-235	10.68	-135	-
With Poly-MTSNH	-172	1.78	-180	83.33

corrosion potential. For more anodic potentials, the current densities increase. This behaviour may be due to the destruction or desorption of the polymer film poly-MTSNH.

Impedance spectroscopy. In order to better characterize the mechanisms involved in the interfacial process of brass in 3% NaCl without and with polymer film, we performed the electrochemical impedance measurements (Fig. 9). The electrochemical parameters issued from the Nyquist impedance diagrams are summarized in Table 3. In the absence of poly-MTSNH, there is a capacitive loop which is attributed to the charge transfer reaction. The characteristics of this loop are [19-21], R_t = 1.41 kΩ cm^2 and C_{dc} = 113 µF cm^{-2}.

In the presence of poly-MTSNH, the impedance diagram recorded in Nyquist mode after 1 h of immersion (Fig. 9) clearly shows the presence of two different contributions. The first is at high frequencies, may be associated with the charge transfer, and the second is at low

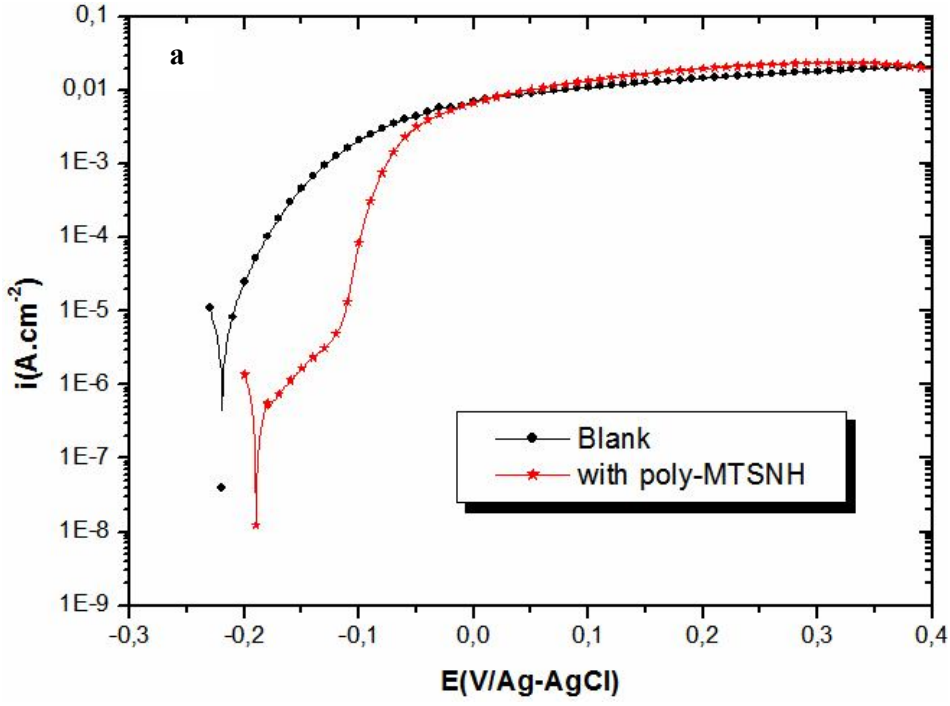

Fig. 8. Anodic potentiodynamic curves of the brass electrode with and without poly-MTSNH film in 3% NaCl.

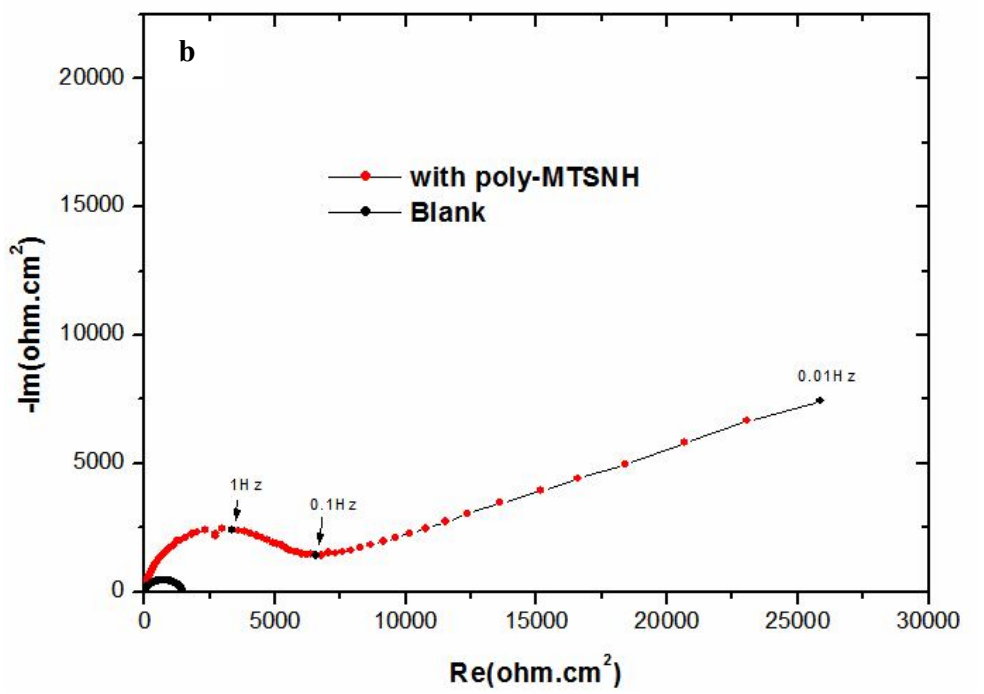

Fig. 9. Electrochemical impedance diagrams obtained for brass at 1 h immersion time in 3% NaCl without and with poly-MTSNH, Ω = 1000 rmp.

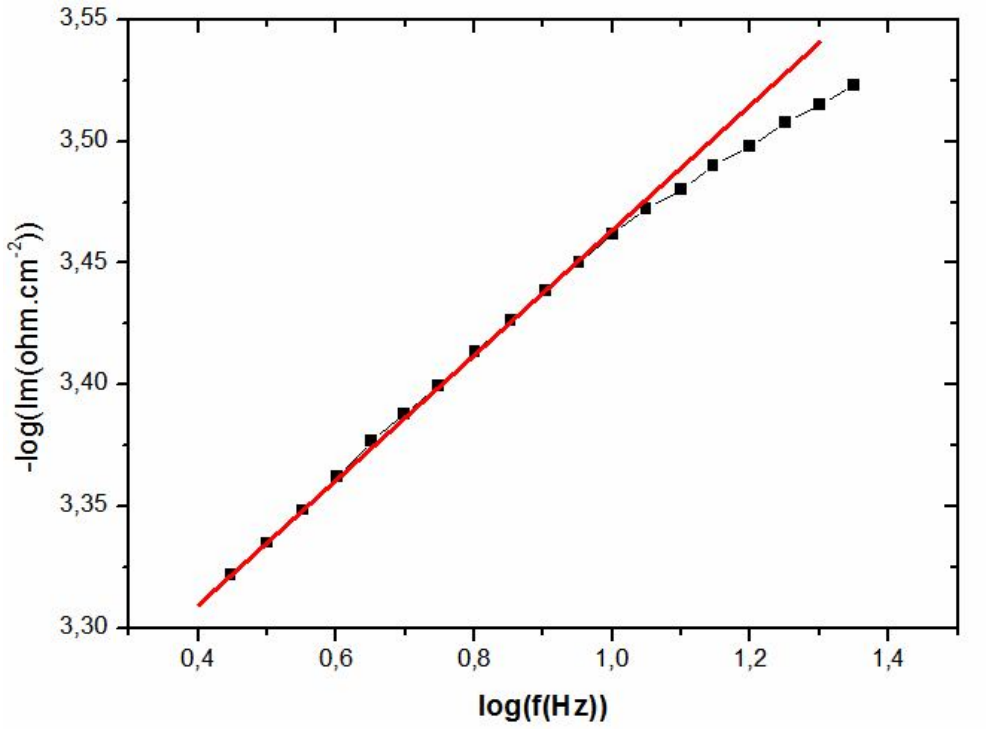

Fig. 10. -log(Im) *versus* log(f) of the 60Cu-40Zn/3% NaCl + poly-MTSNH interface after 1 h immersion.

Table 3. Effect of the Brass Electrode Immersion Time on Characteristic Parameters Evaluated

	R_t (KΩ cm²)	C_t (µF cm^{-2})	E (%)
Blank	1.41	112	-
With Poly-MTSNH	7.20	22	80.42

frequencies, indicating a linear part with respect to the real axis. Such behaviour is typically characteristic of a diffusion process. It reflects the diffusion of corrosion products on the surface of the metal substrate through a porous layer [4,22]. To further support this hypothesis, we have shown in Fig. 10, the variation of the logarithm of the imaginary part as a function of the logarithm of the frequency.

SEM-EDS Analysis

The electrode surface was examined by SEM after 24 h of immersion in 3% NaCl without and with polymer. The micrograph figure shows that in the presence of polymer, the surface is covered by a heterogeneous layer of products. The studies on the corrosion of 60Cu-40Zn alloy showed that for the short immersion times, there is a selective dissolution of Zinc and that this dissolution probably involves complexes such as $CuCl_2^-$ [25]and oxides such as ZnO and Cu_2O [20].

In the presence of polymer, the state of the surface is improved significantly (Fig. 11b), indicating the inhibiting effect of this film. The EDX technique was used to identify

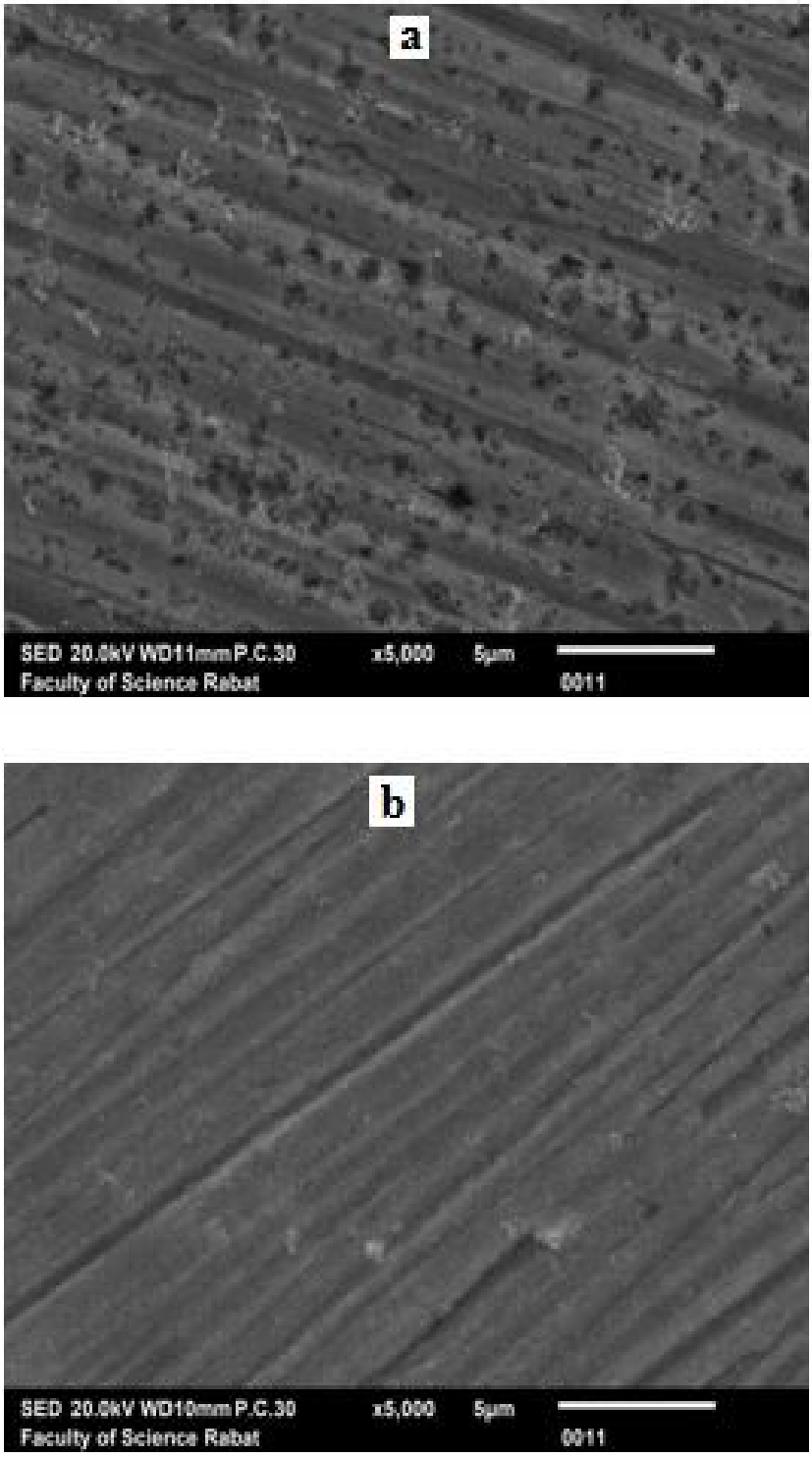

Fig. 11. The SEM images of the brass electrode surface after 24 h immersion in 3% NaCl (a) without polymer coating, and (b) with polymer coating.

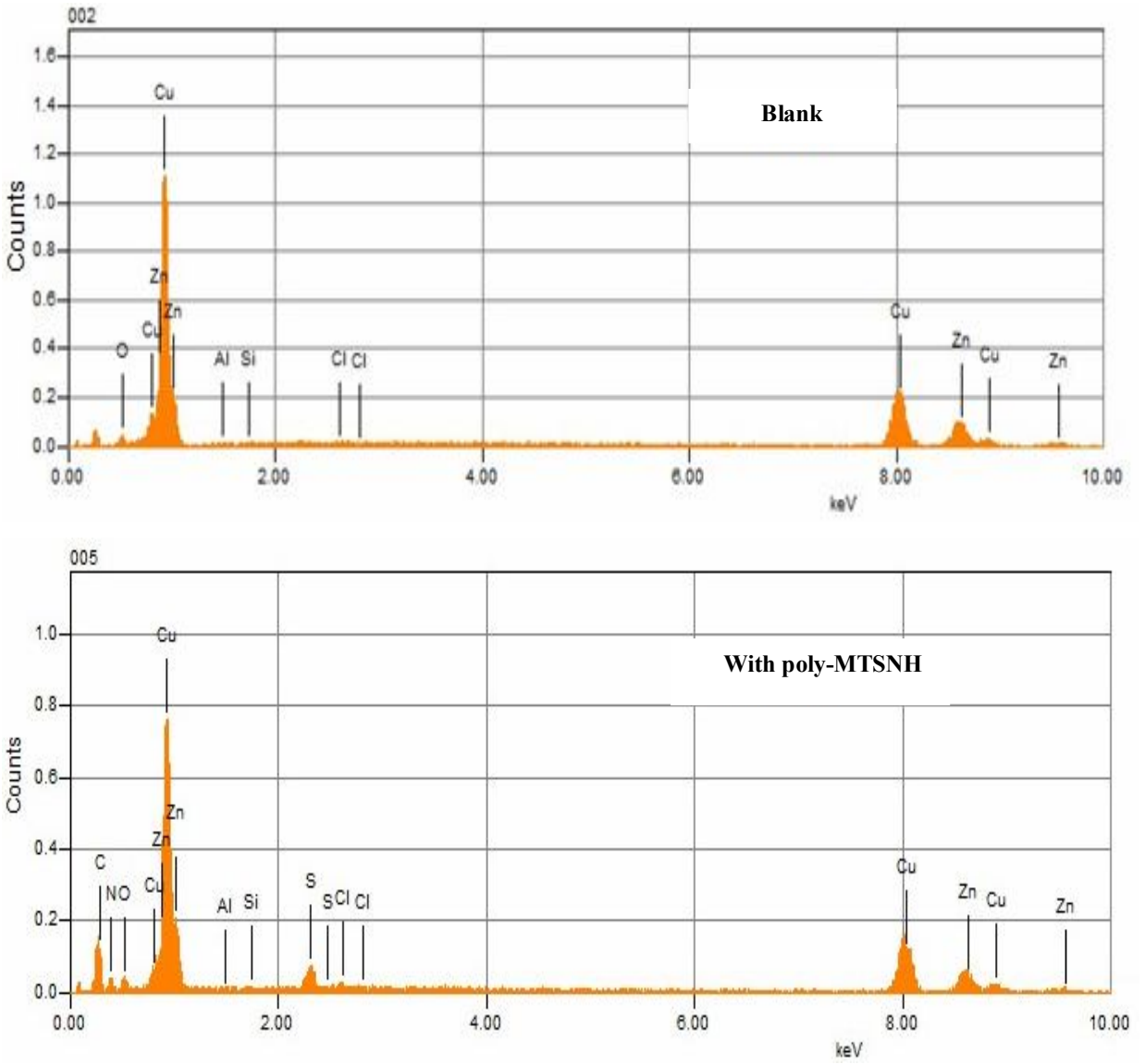

Fig. 12. EDS spectrum of brass 60Cu-40Zn with and without polymer coating.

the chemical composition of the working electrode used in this study and the component adsorbed on the surface of the brass, after and before immersion in solution with and without polymer inhibitor at an optimal concentration.

The EDX spectra shows that in the presence of poly (MTSNH), the appearance of elements like S, C and N indicates the presence of polymer on the brass surface, whereas in the absence of polymer, the EDS spectra (Fig. 12) show the characteristic peaks of the elements from the brass alloy along with carbon and oxygen from contamination. This study provides clear evidence in the formation of polymer on the brass surface.

CONCLUSIONS

This article illustrates the potentiodynamic polymerization of MTSNH on 60Cu-40Zn in methanol in the presence of 0.1 M KOH. The voltammograms I = f (E)

and I = f (t) enabled us to study the properties of the polymeric film as well as the optimal conditions of its formation. The p-MTSNH compound was characterized by cyclic voltammetry, amperometry and electrochemical impedance spectroscopy. The electropolymerization mechanism of MTSNH was proposed on the basis of CV. The protective effect of organic coatings submitted to 3% NaCl solution was evaluated. The results showed that the inhibition efficiency was about 83%. Surface examination studies by SEM confirm the presence of protective p-MTSNH film on the brass surface. Based on the results, we can conclude that p-MTSNH is an excellent candidate for use as an inhibitor of corrosion for 60Cu-40Zn.

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