Inhibition effect of 1,2,4-triazole-5-thione derivative on the Corrosion of Brass in 3% NaCl solution

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3 Sevichim Society SARL Productions of Corrosion Inhibitors, 101rue Maamoura, N° 10,

Abstract

Corrosion inhibition of Cu60Zn40 alloy in aerated 3% NaCl solution using 4-amino-3-methyl -1,2,4-triazole-5-thione (MTSNH) was investigated by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The Surface analysis studies were carried out by scanning electron microscopy (SEM). Effect of immersion time on the efficiency of the corrosion inhibition process was studied. The inhibiting efficiency found to increase with increasing inhibitor concentrations and with increasing immersion time. The polarization curves indicate that MTSNH act as mixed type inhibitor retarding both anodic and cathodic reaction. The impedance results show a change the corrosion mechanism of brass in the presence of inhibitor. Appropriate electric equivalent circuit model was used to calculate the impedance parameters. SEM studies confirm the presence of protective MTSNH film on the alloy surface.

Key words: Corrosion inhibition, NaCl, Cu60Zn40 alloy, 4-amino-3-methyl -1,2,4-triazole-5-thione.

1. Introduction

Copper and its alloys are industrial materials with a wide variety of applications due to electrical, thermal, mechanical and corrosion resistance properties, among others. But, in the presence of oxygen, chlorides, sulphates or nitrates ions they are exposed to localized corrosion [1,2]**.** However, the corrosion resistance of these alloys not only depends on their chemical composition but also depends on the environment medium nature. It is noticed that organic inhibitors containing nitrogen, oxygen and/or sulfur have been widely used for copper and its alloys [3,4]. The corrosion inhibition by heterocyclic compounds containing azole nucleus have been found to be effective inhibitors for copper and its alloys in different corrosive media [5-9].

The aim of this present paper is to study the effect of the addition of 4-amino-3-methyl-1,2,4-triazole-5-thione (MTSNH) on the corrosion resistance of Brass in 3% NaCl solution using different techniques such as potentiodynamic polarization, impedance spectroscopy and surface analysis techniques.

2. Experimental

2.1. Materials

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

2.2. Solutions

The aggressive solution of 3% NaCl was prepared by diluting in distilled water, reagent grade NaCl "Aldrich".

2.3. Inhibitor

The MTSNH is prepared by simple solvolysis of thiocarbohydrazide in refluxed acetic acid, and after cooling to obtain 4-amino-3-methyl-1,2,4-triazole-5-thione [10]. The structure of this compound (Figure 1) was confirmed by NMR analysis.
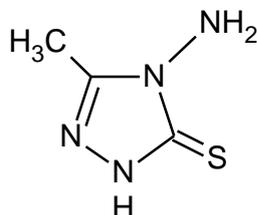
Figure1: Chemical structure of 4-amino-3-methyl-1,2,4-triazole-5-thione (MTSNH)

Spectral characteristics:
^{1}H NMR(75 MHz, DMSO-d6) δ: CH$_3$: 2.22, NH$_2$: 5.49, NH: 13.38
^{13}C NMR(75MHz, DMSO d6) δ: 10.86(CH$_3$), 149.611(C=N), 165.84(C=S)

2.4. Potentiodynamic polarization method

The potentiodynamic polarization curves were recorded using a potentiostat PGZ101. The electrochemical measurements were performed in a conventional three electrodes electrochemical cell: Consisting of platinum electrode as Auxiliary electrode, saturated calomel electrode (SCE) as the reference and Brass alloy as the working electrode the form of a disc of the surface 0,78cm^2.

The samples were first polished with emery paper grade 1200 and rinsed with distilled water.

The working electrode was initially immersed in aerated solution at room temperature, and allowed to stabiles for 1 hour at open circuit potential. Then the cathodic and anodic curves were recorded by potententiokinetic mode with a scan rate of 1mV/s and the rotation speed is 1000 rpm.

From this study we obtained the corrosion current density (i_{corr}), corrosion potentials (E_{corr}), cathodic and anodic Tafel slopes (β_c) and (β_a). The inhibiting efficiency (IE %) was calculated from corrosion current density using the following formula

$$IE\% = \frac{I^0_{corr} - I_{corr}}{I^0_{corr}} X 100 \qquad (1)$$

Where I^0_{corr} and I_{corr} are the corrosion current densities obtained respectively without and with inhibitor.

2-5-Electrochemical impedance spectroscopy (EIS)

The electrochemical impedance spectroscopy (EIS) spectra were carried out at the open-circuit potential E_{corr} using a potentiostat PGZ101. The measuring ranged from 100 kHz down to 10 mHz, were applied in these tests which were performed in the potentiostatic mode at the corrosion potential at 1 hour of immersion time. Data were presented as Nyquist plots. The IE % was calculated using the following equation.

$$IE\% = \frac{R_t^{-1} - R_{t(inh)}^{-1}}{R_t^{-1}} \times 100 \qquad (2)$$

Where $R_{t(inh)}$ and R_t are the charge transfer resistance respectively without and with MTSNH.

2-6-Surface analysis

The surface morphology of the electrode was examined with a scanning electron microscopy (SEM; Leica stereoxam 440). After 24 hours of immersion with and without inhibitor, the sample was cleaned with double distilled water and dried at room temperature. The morphology of Brass surface was examined by SEM technique.

3. Results and discussion

3. 1. Potentiodynamic polarization studies

The cathodic and anodic polarization curves of the brass obtained with a RDE at 1000 rpm in 3%NaCl solution with various MTSNH concentrations are presented in Figures 2 and 3, respectively. All of these curves were obtained after 1h of immersion of the electrode in the electrolytic solution at open-circuit corrosion potential (E_{corr}). Then cathodic and anodic polarization curves were recorded from independent experiments.

It is clear, from these curves, that both anodic metal dissolution and cathodic O_2 reduction reactions were inhibited when investigated MTSNH is added to 3%NaCl. This inhibition was more pronounced with increasing inhibitor concentration. For more cathodic potentials, we note the apparition of current limit corresponds to the reduction of dissolved oxygen observed for all values of MTSNH concentrations, but with a value of current density lower than that obtained without inhibitor. This can be explained by the formation of a protective film on the metal surface. Values of associated electrochemical parameters such as corrosion potential (IE_{corr}), cathodic tafel slop (b_c), corrosion current density value (I_{corr}), inhibition efficiencies (IE %) and degrees of surface coverage (θ) for various concentrations of MTS are given in Table 1.
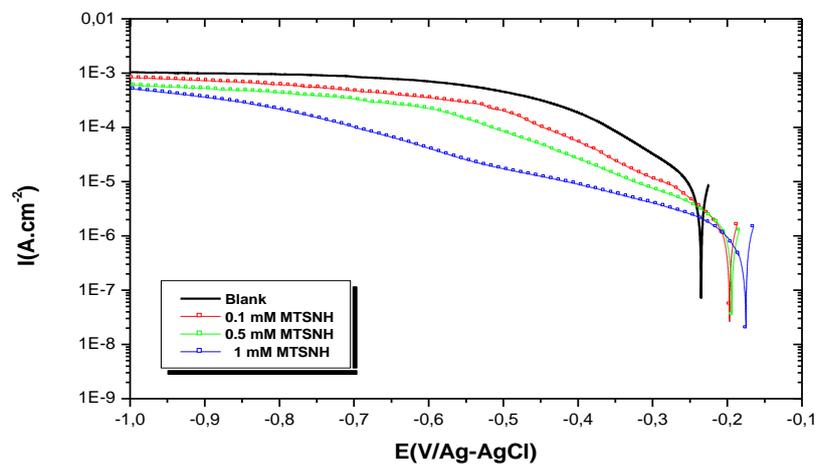
Figure 2: Cathodic polarization curves of brass in aerated 3%NaCl without and with various concentration of MTSNH at 25°C; f=1000 rpm; $/\frac{dE}{dt}/$=1mV/s.
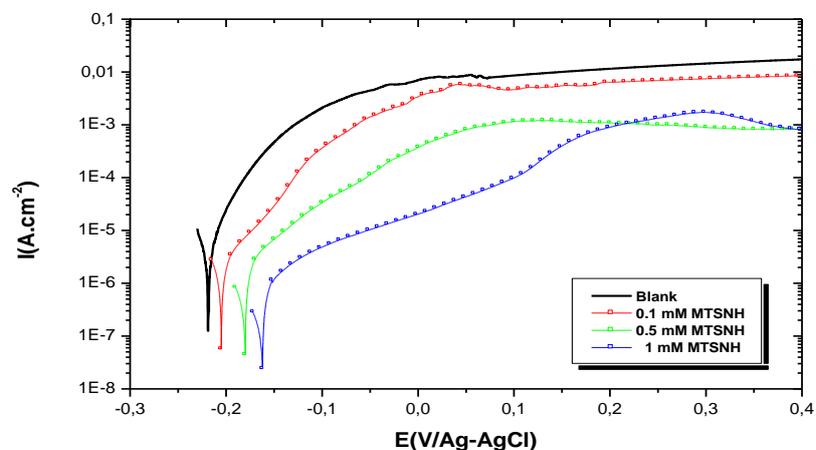
Figure 3: Anodic polarization curves of brass in aerated 3%NaCl without and with various concentration of MTSNH at 25°C; f=1000rpm; $/\frac{dE}{dt}/$=1mV/s

In presence of MTSNH, the anodic polarization curves change considerably. This change is accompanied by a significant decrease of the anodic current density which is more marked near E_{corr}, followed by an apparition of large passive domain. This later is clearly observed for 10^{-3}M of MTSNH.

Table 1: Corrosion inhibition parameters of Brass in aerated 3%NaCl solution without and with addition of MTSNH at various concentrations at 25°C.

[MTSNH]	E_{corr} (mV/Ag-AgCl)	$I_{corr}(\mu A/cm^2)$	b_c(mV/dec)	IE%	θ
Blank	-235	10.68	-135	-	-
10^{-4}M	-202	1.16	-79	89	0.8914
5.10^{-4}M	-196	1.09	-99	90	0.8980
10^{-3}M	-177	0.56	-89	95	0.9480

The inhibitors efficiency increase with increasing inhibitor concentrations. The maximum inhibition efficiency was found to be 95% for 1mM of MTSNH. These effects can be explained by the fact that the product tested acts by adsorption on the metal surface and contributes to an establishment of an inhibiting film relatively compact.

The mechanism of corrosion inhibition may be explained on the basis of adsorption behavior. The degrees of surface coverage (θ=IE%/100) for different inhibitor concentrations were evaluated by polarization data. The ratio C/θ versus C is plotted linearly, showing that the adsorption obeys to Langmuir isotherm

$$C / \theta = 1 / K + C \qquad (3)$$

where *C, k* and *θ* are the concentration of inhibitor, the adsorptive equilibrium constant and the surface coverage, respectively.

The values of linear regression between *C/θ* and *C,* and the parameters of adsorption are determined from Figure 4.

The obtained slope 1.045 indicates that inhibitor adsorption is an ideal one as mentioned by Langmuir hypothesis. The coefficient correlation r^2 is 0.999. The value of adsorption equilibrium constant is equal to 50000. The standard adsorption free energy ($\Delta G°_{ads}$) is obtained according to the following equation:

$$\Delta G°_{ads} = - RT \, Ln(55.5*K) \qquad (4)$$

The calculated value of $\Delta G°ads$ = -36.25 kJ mol^{-1}. The largest negative value of $\Delta G°_{ads}$, indicates that MTSNH are strongly adsorbed on the brass surface. Literature shows that values which are negative than -30 kJ mol^{-1} indicate chimisorption of MTSNH molecules [11].
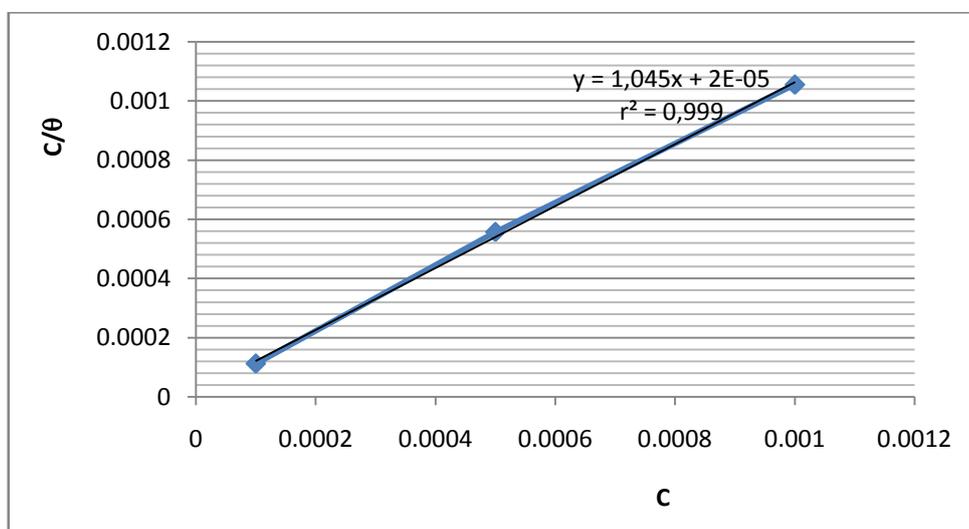
Figure 4: Langmuir isotherm adsorption model of MTSNH on the surface of Brass in 3% NaCl

3-2-Electrochemical impedance spectroscopy (EIS)
3-2-1-Effect of the inhibitor concentrations:

The aim of this study is to obtain more information concerning the electrochemical process which carried at the 60Cu-Zn electrode in corrosive solution in presence of inhibitor.

The effect of inhibitor concentration on the impedance behavior of brass in 3%NaCl solution at 25°C is presented in Figure 5. The electrode was polarized at the free corrosion potential until a steady-state was attained.
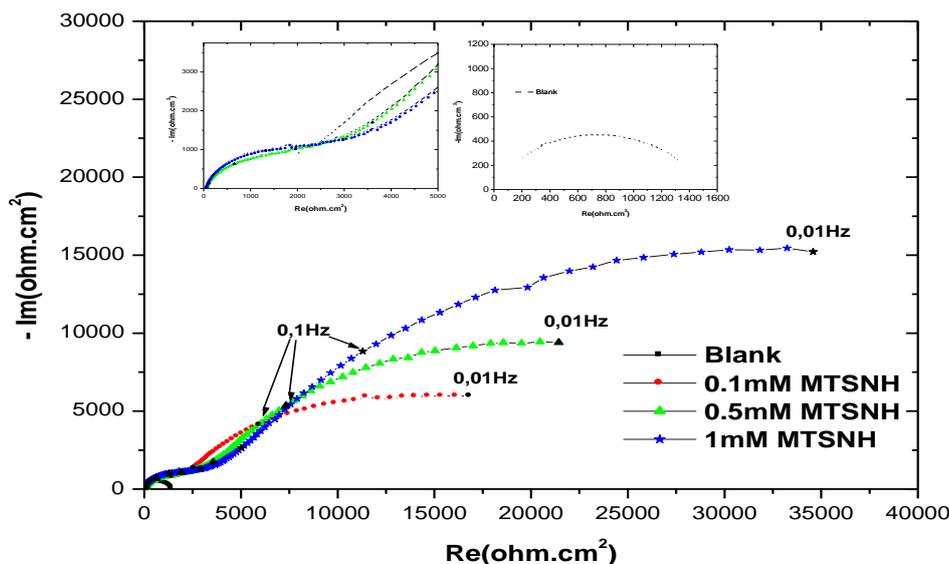
Figure 5: Nyquist plots of brass 60Cu-Zn in 3%NaCl without and with various concentration of inhibitor obtained at free corrosion potential for 1h of immersion times, f=1000rpm.

The impedance spectra in the absence of MTSNH present one capacitive loop. In the context of a detailed study published elsewhere [12,13]. This loop can be attributed to a charge transfer process. The value of associated resistance is about $1.41k\Omega.cm^2$, the capacity is in the order of $112\mu F.cm^{-2}$. In the presence of inhibitor, we note that the impedance spectra changes in shape and size, two capacitive loops are observed. The first located in the high frequencies can be associated with the inhibitor film. The capacity value decrease and reach $0.29\mu F.cm^{-2}$ for 1mM of inhibitor. These values are low compared to that usually attributed to the double layer, which confirms the hypothesis of the presence of a relatively thick film of inhibitor.

The second in the base frequency was attributed to the charge transfer. The resistance value passe from$1.41k\Omega.cm^2$ in the case of 3%NaCl to $64.57k\Omega.cm^2$ in the presence of $10^{-3}M$ of MTSNH. The associate's capacity decrease from$112 \mu F.cm^{-2}$ to $49\mu F.cm^{-2}$. These values attributed to the ability of the double layer.

The impedance parameters such as charge transfer resistance (R_t), double layer capacitance (C_{dl}) and inhibition efficiency (% IE) were calculated and are listed in Table 2.

Table2: Impedance measurements and inhibition efficiency on brass 60Cu-Zn in 3%NaCl solution without and with various concentration of inhibitor.

MTSNH	$R_f(k\Omega.cm^2)$	$C_f(\mu F.cm^{-2})$	$R_t(k\Omega.cm^2)$	$C_{dl} (\mu F.cm^{-2})$	IE%
0mM	-	-	1.41	112	-
0.1mM	3.10	0.46	29.91	76.42	95
0.5mM	3.60	0.39	38.85	65.40	96
1mM	4.80	0.29	64.57	49.29	98

Its protective power is about 98% for the concentration of 10^{-3} M chosen as the best concentration. The inhibition efficiency obtained from impedance measurements are in good agreement with those obtained from potentiodynamic polarization studies.

Impedance data were interpreted using the equivalent electrical circuit of Figure 6, where Cf and Rf represent the inhibitor film properties. C_{dl} is the double layer capacitance, and R_t is the charge transfer resistance.
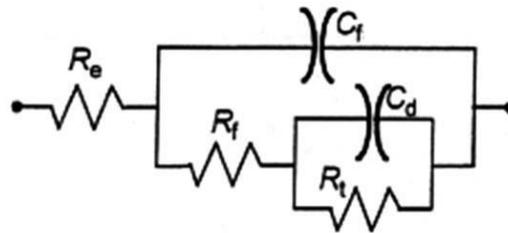
Figure 6: Electric equivalent circuit

R_e: Electrolyte resistance ($\Omega.cm^2$)
R_f: Film resistance due to the ionic conduction through inhibitor layer ($\Omega.cm^2$)
C_f: Film capacitance due to the electronic insulating property ($F.cm^{-2}$)
R_t: Charge transfer resistance ($\Omega.cm^2$)
C_{dl}: Double layer capacitance at the metal electrolyte interface ($F.cm^{-2}$)

3. 2. 2. Effect of immersion time.

The figure 7 shows electrochemical impedance diagrams obtained on the electrode Cu-40Zn in 3% NaCl in the presence of 10^{-3} M of MTSNH for different immersion times.
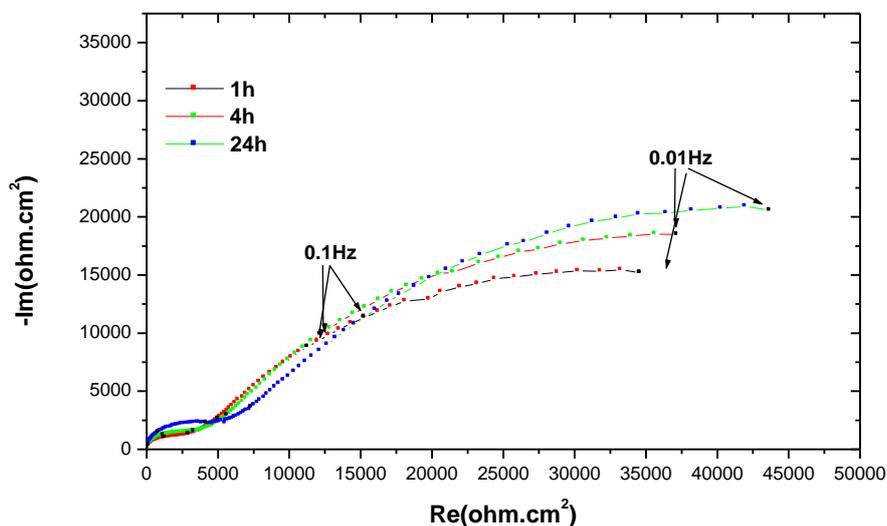
Figure 7: Influence of immersion time on the shape of the impedance diagrams interfaces 60Cu-Zn / 3% NaCl + 10^{-3} M MTSNH. f = 1000 rpm.

These diagrams show a capacitive behavior of the interface in the frequency range examined, with two loops indicating the existence of two time constants.

The first loop at high frequencies is connected to the capacitor C_f of the film in parallel with the resistor R_f of the film.

The impedance parameters obtained from these diagrams are given in Table 3.

Table 3: Parameters determined from electrochemical impedance diagrams of the interface 60Cu-Zn/ 3%NaCl + 10^{-3} M MTSNH for different immersion time. f = 1000 rpm.

Time(h)	$R_f(k\Omega.cm^2)$	$C_f(\mu F.cm^{-2})$	$R_t(k\Omega.cm^2)$	$C_{dl}(\mu F.cm^{-2})$
1	4.80	0.29	64.57	49.29
4	5.65	0.25	75.12	42.37
24	7.40	0.19	87.71	36.29

The evolution of the electrochemical impedance diagram for different immersion times show that after 1hour of immersion, C_f is about $0.29\mu F.cm^{-2}$ then decreases with time to reach a value of $0.19\mu F.cm^{-2}$ after 24hour of immersion. In parallel, R_f increases with the immersion time, she spends from $4.80 k\Omega.cm^2$ to $7.40 k\Omega.cm^2$

The decreased ability of the film over time is attributed to a thickening of the layer formed on the metallic surface. Then the increasing the film strength with time indicates that the protective properties of the film formed on the surface of alloy is reinforced for immersion time. The second loop is connected to the double layer capacitance C_{dl} in parallel with the charge transfer resistance R_t.

4. Scanning electron microscopy

Figures (8a and 8b) show the surface of the alloy studied in the absence and presence of the inhibitor after 24 hours immersion in 3%NaCl.
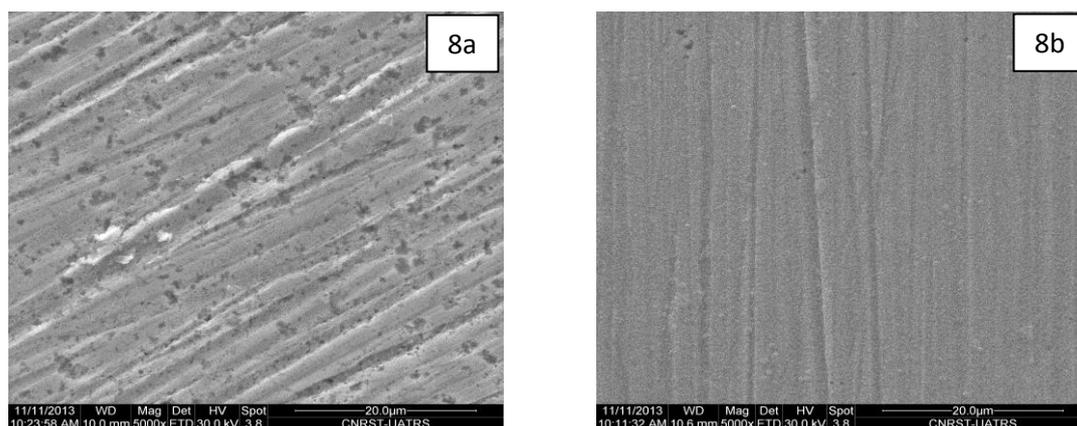
Figure 8: SEM observation after 24h corrosion test at the open circuit, in absence (8a) and presence (8b) of 10^{-3}M (MTSNH).

At the absence of inhibitor (Fig8a), the surface of the electrode is covered by a layer of heterogeneous product with the presence of corrosion pitting. The literature presents some studies involving the corrosion prevention of Cu-40Zn show that this alloy undergoes a selective dissolution of zinc for the long immersion time. And that leads to the formation of $CuCl_2^-$ complex [14].

In the presence of 10^{-3}M MTSNH, the micrograph shows the absence of corrosion, so the brass surface was protected. It can be explicated by the presence of the inhibitor film on the electrode surface.

Conclusion

From the results of this study it was concluded that:

1. The electrochemical methods used reveal that 4-amino 3-methyl-1,2,4-triazole-5-thione is proved to be an excellent inhibitor for 60Cu-Zn.
2. Polarization curves showed that the inhibiting effect of this compound results in a clear decrease of the cathodic and anodic current density value the vicinity of corrosion potential indicate that MTSNH act as mixed-type inhibitor

3. Inhibition efficiency increases with increasing inhibitor concentration to reach the maximum value of 98% at the 10^{-3}M in the MTSNH.
4. Inhibition efficiency values obtained from potentiodynamic polarization curves and EIS measurements were in good agreement.
5. Surface examination studies by SEM confirm the presence of protective MTSNH film on the brass surface.

For all of these raisons, we can conclude that the MTSNH is an excellent candidate for use as inhibitor of corrosion for the 60Cu-Zn.

References

1. Vera R., Bastidas F., Villarroel M., Oliva A., Molinari A., Ramirez D., Rio A. R., *Corros. Sci*. 50 (2008) 729.
2. Alfantazi A. M., Ahmed T. M., Tromans D., *Mater. Des*. 30 (2009) 2425.
3. Benassaoui H., Dermaj A., Chebabe D., Erramli H., Damej M., Hajjaji N., Srhiri A., *Organic Chemistry an Indian Journal*. 11(2015) 433.
4. Otmacic H., Stupnisek-Lisac E., *Electrochem. Acta*. 48 (2003) 985.
5. Chebabe D., Dermaj A., Erramli H., Hajjaji N., Anti-Corros. Method. M. 61 (2014) 281.
6. Dermaj A., Chebabe D., Hajjaji N., Vivier V., *J. Reaserch. Rev. In-Electrochem*. 4 (2013) 147.
7. Chebabe D., Dermaj A., Ait Chikh Z., Hajjaji N., Srhiri A., *Phys. Chem. News*. 19 (2004) 120.
8. Chebabe D., Ait Chikh Z., Dermaj A., Rhattas K., Jazouli T., Hajjaji N., El mdari F., Srhiri A., *Corros. Sci*. 46 (2004) 2701.
9. Dermaj A., Hajjaji N., Joiret S., Rahmouni K., Srhiri A., Takenouti H., Vivier V., *Electrochem. Acta*. 52 (2007) 4654.
10. Aouial M., Thesis. Dr. Sc. (chem. org). Mohamed V. Univ. Rabat. Mar. (1976).
11. Barouni K., Mihit M., Bazzi L., Salghi R., Al-Deyab S. S., Hammouti B., Albourine A., *Open. Corros. J. 3 (*2010) 58.
12. Elbakri M., Touir R., Ebn Tohami M., Srhiri A., Benmessaoud M., *Corros. Sci*. 50 (2008) 1538.
13. Mountassir Z., Srhiri A., *Corros. Sci*. 49 (2007) 1350.
14. Chebabe D., Dermaj A., Ait Chikh Z, Erramli H, Doubi M., Hajjaji N., Srhiri A., Bioanal. A., *Electrochem*. 3 (2011) 279.