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Enhanced 4-amino-5-methyl-4H-1,2,4-triazole-3-thiol Inhibition of Corrosion of Mild Steel in 0.5 M H_2SO_4 by Cu(II)

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The synergistic inhibition effect between Cu^{2+} and 4-amino-5-methyl-4*H*-1,2,4-triazole-3-thiol (AMTT) on the corrosion behavior of mild steel in 0.5 M H_2SO_4, both in the absence and presence of chloride ions, has been investigated by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. The ptentiodynamic polarization and EIS results consistently revealed that Cu^{2+} and AMTT mixture had a synergistic inhibitive effect on the corrosion of mild steel in 0.5 M H_2SO_4 as a result of the cooperative adsorption of the two species on mild steel. AMTT alone and in combination with Cu^{2+} and/or chloride were found to obey Temkin adsorption isotherm. Chemical adsorption is proposed based on obtained values of ΔG^{o}_{ads}.

Keywords: Corrosion inhibitor; A trizaole derivative; Mild steel; Halide ions; Synergism, Cu(II).

1. INTRODUCTION

Corrosion inhibitors have been widely applied in cleaning of industrial equipment and acidisations of oil wells to avoid the acid attack of bulk metal while removing corrosion scales from steel surface [1-4]. Most of efficient acid inhibitors are organic compounds which contain nitrogen, sulphur and/or oxygen atoms in their molecules [5–17]. Among them, N-heterocyclic compounds have been reported as efficient inhibitors in HCl solutions while those containing sulfur atoms are efficient in H_2SO_4 solutions. Inhibitors containing both heteroatoms have a wide inhibition range. Organic inhibitors exert their action via their adsorption on the metal surface via electron-rich centers and thus forming a barrier between the metal and the corrosive media. One of the most important criteria for the selection of a suitable inhibitor is the impact on the environment. Designing of an ecofriendly corrosion inhibitor is one of the ultimate goal for researchers. Also using inhibitors in concentrations as small as possible is another strategy to avoid the toxicity of an inhibitor. Last strategy have been treated in the literature by adding a secondary non-toxic species to the main inhibitor aiming at increasing the inhibition efficiency of the latter at low concentrations in what is the so-called synergistic inhibition [18-21].

In the presence of a secondary species the adsorption of the inhibitor is enhanced by the lateral interaction between the inhibitor molecules and this secondary species. The secondary species could be halide ions [22-30] which pre-adsorb on a positively charged metal and thus enhance the adsorption of an inhibitor as it acts as interconnector between the positively charged inhibitor species and the positively charged metal electrode under the prevailed experimental conditions. Also the secondary species might be a metal ion which could enhance the inhibition efficiency of the organic compound *via* complex formation [31-37]. Also it can be other organic molecules which enhance the adsorption of the primary species [38-43]. The synergistic inhibition using mixture of two inorganic species have been also studied [44].

The present work is devoted for the study of the synergism between methyl aminotriazole thiol (AMTT) and Cu^{2+} on the corrosion of mild steel in 0.5 M H_2SO_4 The inhibition efficiency is studied using Tafel polarization and electrochemical impedance measurements.

2. EXPERIMENTAL

2.1. Mild steel sample

Tests were performed on mild steel of the following composition (wt. %): 0.07% C, 0.29% Mn, 0.07% Si, 0.012% S, 0.021 % P and the remainder iron. Samples of 0.5 cm^2 were used.

2.2. Inhibitor

4-Amino-5-methyl-4*H*-1,2,4-triazole-3-thiol (AMTT) of structure shown in the Figure 1. Sodium chloride and copper sulfate were obtained from Aldrich and used as received. AMTT was synthesized by condensation of thiocarbohydrazide and acetic acid according to the method cited in literature [45] the structure was elucidated using elemental analyses and spectral data.

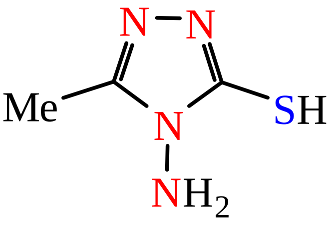

Figure 1. Structure of 4-amino-5-methyl-4*H*-1,2,4-triazole-3-thiol

2.3. Solutions

The solution of 0.5 M H_2SO_4 was prepared by dilution of AR grade 98% H_2SO_4. Stock solutions of AMTT, NaCl and $CuSO_4$ were prepared in 0.5 M H_2SO_4, and the desired concentrations were obtained by appropriate dilution.

2.4. Electrochemical measurements

Electrochemical experiments were carried out in a conventional three-electrode cell with a platinum counter electrode (CE) and a standard calomel electrode (SCE) coupled to a fine Luggin capillary as the reference electrode (RE). In order to minimize the ohmic contribution, the Luggin capillary was kept close enough to the working electrode (WE) which was fitted into a glass tube of proper internal diameter by using epoxy resins. The WE surface area of 0.5 cm^2 was abraded with emery paper down to 2000 on test face, rinsed with distilled water, degreased with acetone, and dried with a cold air stream. Before measurements the electrode was immersed in the test solution at open circuit potential (OCP) for 15 min at 25 ^oC or until the steady state is obtained. All electrochemical measurements were carried out using PGSTAT30 potentiostat/galvanostat. The polarization measurement was carried out from a cathodic potential of -0.25 V to an anodic potential of +0.25 V with respect to the *Ecorr* at a sweep rate of 2 mV/s. Current densities were calculated on the basis of the apparent geometrical surface area of the electrode. The measurements were repeated at least three times to test the reproducibility of the results.

3. RESULTS AND DISCUSSION

3.1. Polarization Measurements

Figure 2 shows Tafel plots obtained at mild steel in 0.5 M H_2SO_4 containing $2.5x10^{-6}$ M AMTT, $1x10^{-5}$ M Cu^{2+}, constant concentration of AMTT and various concentrations of Cu^{2+}. In the presence of either AMTT or Cu^{2+} both Tafel branches are slightly shifted to lower currents. In the presence of the two species, Tafel plots are shifted to current values lower than in the presence of the individual species. Upon increasing the concentration of Cu^{2+}, while keeping AMTT concentration constant, the polarization curves shifted regularly to lower currents. The relevant parameters obtained from this figure are shown in Table 1. Inspection of Fig. 1 and Table 1 reveals several interesting points;

1. Adding Cu^{2+} to AMTT enhances the inhibitive action of the latter; the inhibition efficiency, calculated using Eq. 1;

$$\% \boldsymbol{P} = \left[1 - \frac{i_{cor1}}{i_{cor2}}\right]100 \qquad (1)$$

(where i_{cor1} and i_{cor2} are corrosion current densities in the absence and presence of the inhibitor, respectively) [46] increased more than two folds. For instance, the inhibition efficiency in the presence of individual species, i.e., AMTT and Cu^{2+} equals 26 and 10% (the individual sum equals 36). In the presence of 2.5 x 10^{-6} M AMTT + 1.0 x 10^{-5} M Cu^{2+} the inhibition efficiency equals 33. In this case the protection efficiency in the presence of the two species almost equals the sum of the inhibition efficiencies of the individual species. In the presence of 2.5 x 10^{-6} M AMTT + 1.0 x 10^{-4} M Cu^{2+} the inhibition efficiency equals 65 %, i.e., almost double of the sum of the individual protection efficiencies.

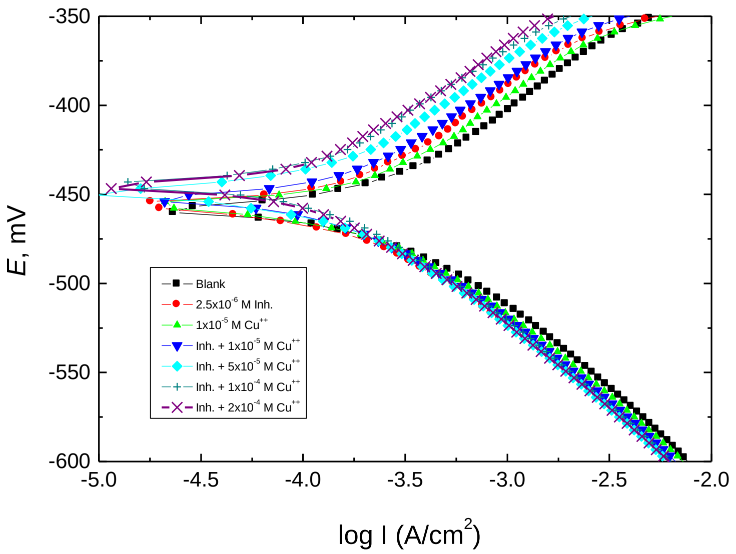

Figure 2. Potentiodynamic polarization curves for mild steel in 0.5 M H_2SO_4 (Blank) in the presence of 2.5x10^{-6} M AMTT and various concentrations of Cu^{2+} at 25 °C.

It is noteworthy to mention that it has been reported that the inhibition efficiency (in the presence of only Cu^{2+}) decreases with the increase in the concentration of Cu^{2+} [47]. This has been attributed to the increase in the rate of the cathodic reaction (hydrogen evolution) which is the controlling reaction in the present case. Thus the inhibition efficiency (65%) in the presence of 2.5 x 10^{-6} M AMTT + 2.0 x 10^{-4} M Cu^{2+} is almost double of the sum (36 %) of those in the presence of the individual species. It means that Cu^{2+} enhance the inhibition of AMTT. The degree of enhancement could be quantified by calculating the so-called synergism factor using Eq. 2 [48].

$$S_\theta = 1-\theta_{1+2} / 1-\theta'_{1+2} \qquad (2)$$

where: $\theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1\theta_2)$; θ_1 and θ_2 are the degrees of surface coverage in presence of the

Cu^{2+} ion and the AMTT, respectively, and θ'_{1+2} is the degree of surface coverage in the presence of both species. The synergism factor was found to equal 1.9. This means the cooperative adsorption of the two species on the mild steel surface.

2. Tafel slopes are constants both in the absence and presence of AMTT and /or Cu^{2+} indicating

that AMTT exerts its action via simple adsorption and does not change the mechanism [49].

Table 1. Polarization data for 2.5 x 10^{-6} M AMTT in the absence and presence of various concentrations of Cu^{2+} on mild steel in 0.5 M H_2SO_4 at 25 °C.

Medium	E_{corr} (mV)	β_c (mV/dec)	B_a (mV/dec)	I_{corr} (µA/cm^2)	% *P*	θ
Blank	-461	102	83	201	--	--
2.5x10^{-6} M AMTT	-458	101	81	149	26	0.26
1x10^{-5} M Cu^{2+}	-453	99	82	161	20	0.20
AMTT + 1x10^{-5} M Cu^{2+}	-452	97	78	134	33	0.33
AMTT + 5x10^{-5} M Cu^{2+}	-447	95	76	107	47	0.47
AMTT + 1x10^{-4} M Cu^{2+}	-445	92	74	91	55	0.55
AMTT + 2x10^{-4} M Cu^{2+}	-452	91	73	71	65	0.65

3. E_{corr} is almost constant, i.e., the inhibitor acts as a mixed type inhibitor as the shift in the corrosion potential is less than 85 mV. According to Riggs [50], the classification of a compound as an anodic or cathodic type inhibitor is based on the E_{corr} displacement; if E_{corr} is at least ±85 mV different to the one measured in the blank solution it can be classified as an anodic or cathodic inhibitor.

The increased inhibition efficiency could be explained based on two possibilities. Either the deposition of copper and the next adsorption of AMTT on previously deposited Cu, or the co-adsorption of the two species via the formation of a complex between AMTT and Cu^{2+}. Regarding the former possibility it can be excluded based on the inhibition of the cathodic branch. Deposition of copper is expected to enhance the hydrogen evolution. Thus, in the present case the inhibition of the hydrogen evolution excludes this possibility. The latter possibility is plausible as triazoles is well reported to form complexes with copper ions [51].

Figure 3 shows the polarization curves obtained at mild steel in 0.5 M H_2SO_4 containing 2.5x10^{-6} M AMTT, 1x10^{-6} M Cl^-, and 2.5x10^{-6} M AMTT + 1x10^{-6} M Cl^- and different concentrations of Cu^{2+}. Electrochemical parameters obtained are summarized in Table 2. The polarization curves are shifted to lower current upon increasing the concentration of Cu^{2+} concentration. Comparing the curve obtained in the presence of 2.5x10^{-6} M AMTT + 2.0x10^{-4} M Cu^{2+} (Fig. 1) and the one in Fig. 2 (2.5x10^{-6} M AMTT + 2.0x10^{-4} M Cu^{2+} + 1x10^{-6} M Cl^-) which were obtained in the presence of the same concentration of AMTT and Cu^{2+} and in presence of chloride, one can see that the inhibition efficiency in the absence of chloride is larger than in its presence. It has been reported that in the presence of chloride of lower concentration copper dissolves according to Eqs. 3-5 [52-54]. In addition the complex formed between AMTT and Cu^{2+} might not be stable.

During the cathodic branch Cu^{2+} is deposited, then during anodic branch Cu dissolution occurs according to Eq. 3. This in turn reacts with chloride according to Eq. 4 which further forms complex with chloride according to Eq. 5.

$$Cu \rightarrow Cu^+ + e^- \qquad (3)$$

$$Cu^+ + Cl^- \rightarrow CuCl \qquad (4)$$

$$CuCl + Cl^- \rightarrow CuCl^- \qquad (5)$$

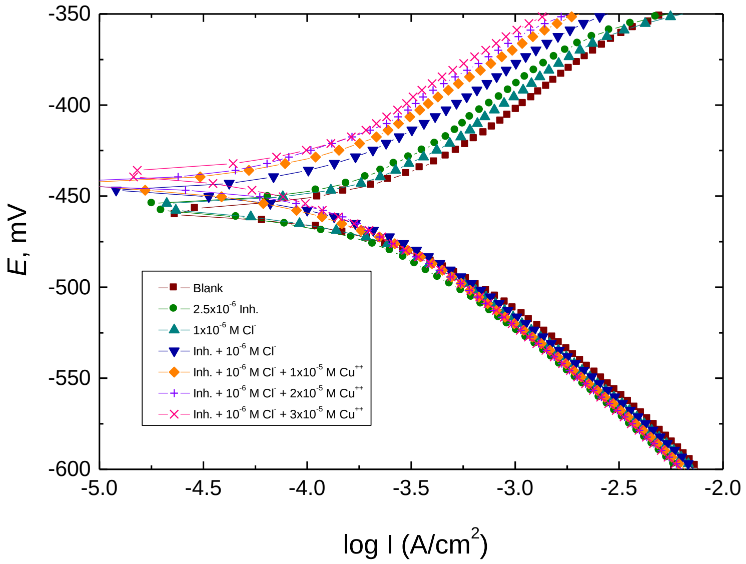

Figure 3. Potentiodynamic polarization curves for mild steel in 0.5 M H_2SO_4 (Blank) in presence of $2.5x10^{-6}$ M methyl aminotriazole thiol and $1x10^{-6}$ M Cl^- and various concentrations of Cu^{2+} at 25 ^{o}C.

Figure 4 shows the polarization curves obtained at mild steel in 0.5 M H_2SO_4 containing $2.5x10^{-6}$ M AMTT, $1x10^{-5}$ M Cu^{2+}, and $2.5x10^{-6}$ M AMTT + $1x10^{-5}$ M Cu^{2+} and different concentrations of Cl^-. Electrochemical parameters obtained are summarized in Table 3. Again the polarization curves are shifted to lower current upon increasing the concentration of Cl^- concentration. Interestingly, by comparing the curve obtained in $2.5x10^{-6}$ M AMTT + $1x10^{-5}$ M Cu^{2+} +$1x10^{-4}$ M Cl^- (Fig.3) and the one obtained in Fig. 1 which was obtained in the presence of the same concentration of AMTT and Cu^{2+} but in absence of chloride, one can see that the inhibition efficiency in the presence of chloride is larger than in its absence, contrary to Fig. 2. In the present case the larger concentration of chloride enhanced the inhibition efficiency of AMTT along with Cu^{2+}. The enhanced inhibition efficiency of organic inhibitors in the presence of halides is well reported [55-63].

Table 2. Polarization data for AMTT on mild steel in 0.5 M H_2SO_4 containing Cl^- and Cu^{2+} at 25°C.

Medium	E_{corr} (mV)	β_c (mV/dec)	B_a (mV/dec)	I_{corr} (μA/cm^2)	% *P*	θ
Blank	-461	102	83	201	--	--
$2.5x10^{-6}$ M AMTT	-458	101	81	149	26	0.26
$1x10^{-6}$ M Cl^-	-454	96	79	173	13	0.13
AMTT + $1x10^{-6}$ M Cl^-	-453	94	76	114	43	0.43
AMTT + $1x10^{-6}$ M Cl^- + $1x10^{-4}$ M Cu^{2+}	-447	95	77	100	50	0.50
AMTT + $1x10^{-6}$ M Cl^- + $2x10^{-4}$ M Cu^{2+}	-441	95	77	88	56	0.56
AMTT + $1x10^{-6}$ M Cl^- + $3x10^{-4}$ M Cu^{2+}	-436	89	74	81	60	0.60

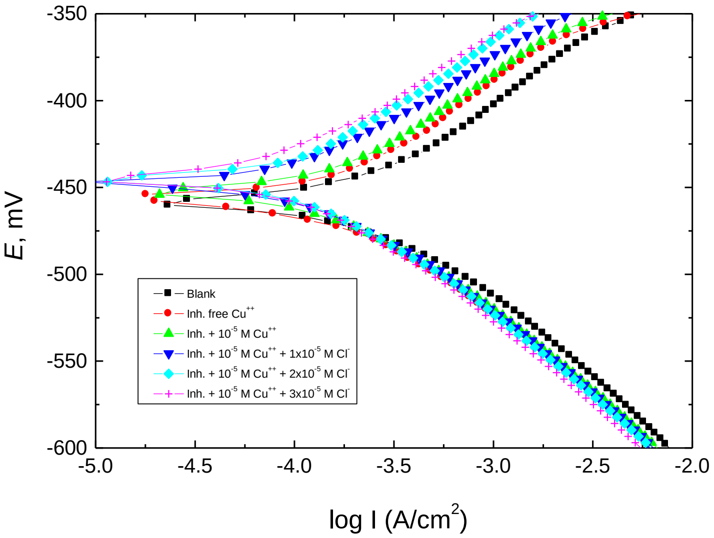

Figure 4. Potentiodynamic polarization curves for mild steel in 0.5 M H_2SO_4 (Blank) in presence of $2.5x10^{-6}$ M methyl aminotriazole thiol and $1x10^{-5}$ M Cu^{2+} and various concentrations of Cl^- at 25 ^oC.

Table 3. Polarization data for AMTT on mild steel in 0.5 M H_2SO_4 containing Cl^- and Cu^{2+} at 25°C.

Medium	E_{corr} (mV)	β_c (mV/dec)	B_a (mV/dec)	I_{corr} (µA/cm^2)	% *P*	θ
Blank	-461	102	83	201	--	--
$2.5x10^{-6}$ M AMTT	-458	101	81	149	26	0.26
AMTT + $1x10^{-5}$ M Cu^{2+}	-453	97	80	126	37	0.37
AMTT + $1x10^{-5}$ M Cu^{2+} + $1x10^{-4}$ M Cl^-	-449	93	79	100	50	0.50
AMTT + $1x10^{-5}$ M Cu^{2+} + $2x10^{-4}$ M Cl^-	-446	95	77	83	59	0.59
AMTT + $1x10^{-5}$ M Cu^{2+} + $3x10^{-4}$ M Cl^-	-442	89	75	67	67	0.67

3.2. Electrochemical impedance spectroscopy measurements

To confirm the above conclusion, extracted from dynamic polarization measurements, regarding enhancing the inhibition efficiency of AMTT in the presence of Cu^{2+} electrochemical impedance spectroscopy (EIS) experiments were carried out and shown in Fig. 5 in which Nyquist plots of mild steel obtained in 0.5 M H_2SO_4 containing $2.5x10^{-6}$ M AMTT, $1x10^{-5}$ M Cu^{2+}, constant concentration of AMTT and various concentrations of Cu^{2+} are shown. Similar results which show the effect of copper ions and chloride ion concentrations on the surface resistance are shown in Figs 6 and 7, respectively. Parameters extracted from those figures including percentage inhibition efficiency calculated using the charge transfer resistance values (Eq. 6) [64] are included in Table 4.

$$\%\ \boldsymbol{P} = \left[\frac{(1/R_{ct})_0 - (1/R_{ct})}{(1/R_{ct})_0}\right]100 \qquad (6)$$

where $(R_{ct})_0$ and (R_{ct}) are the values of charge-transfer resistance in the absence and presence of the inhibitor, respectively. As can be seen the inhibition efficiency increases with increasing the concentration of Cu^{2+} and/or Cl^- confirming the synergism between AMTT and Cu^{2+}. The synergistic action in the presence of Cu^{2+} and Cl^- depends on the concentration of chloride; while the inhibition efficiency in the presence of small concentration of Cl^- along with AMTT + Cu^{2+} is lower than in the absence of chloride, the reverse is obtained when a larger concentration of Cl^- is obtained, consistently with the dynamic polarization results presented above.

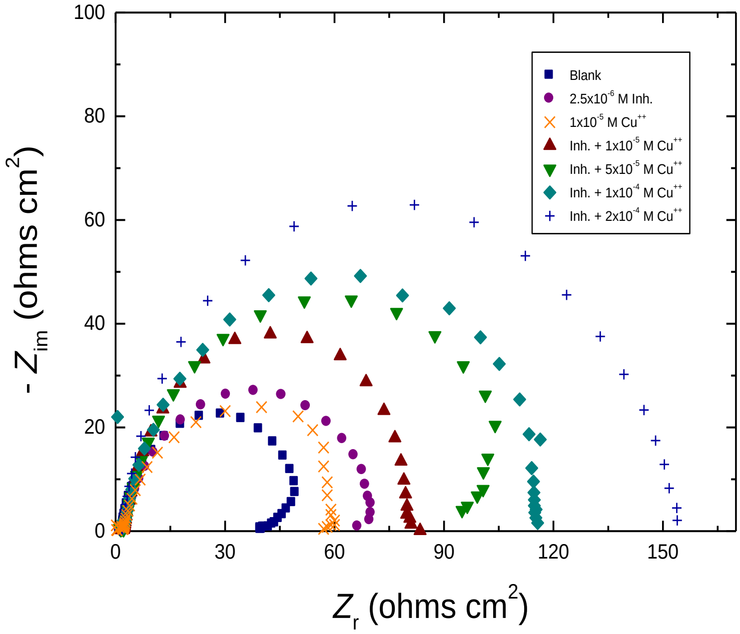

Figure 5. Nyquist plot of mild steel in 0.5 M H_2SO_4 containing AMTT in the absence and presence of Cu^{2+} at 25 °C

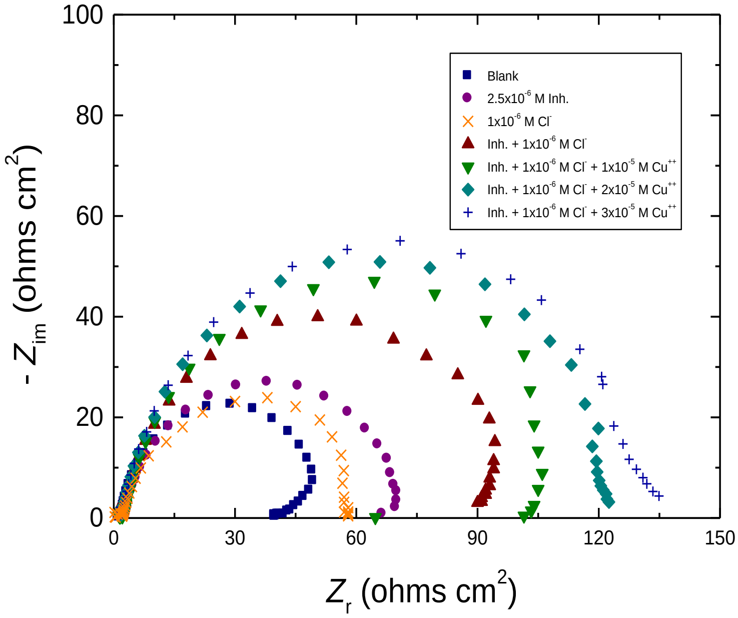

Figure 6. Nyquist plots of mild steel in 0.5 M H_2SO_4 for AMTT and Cl^- in the absence and presence of Cu^{2+} at 25 °C.

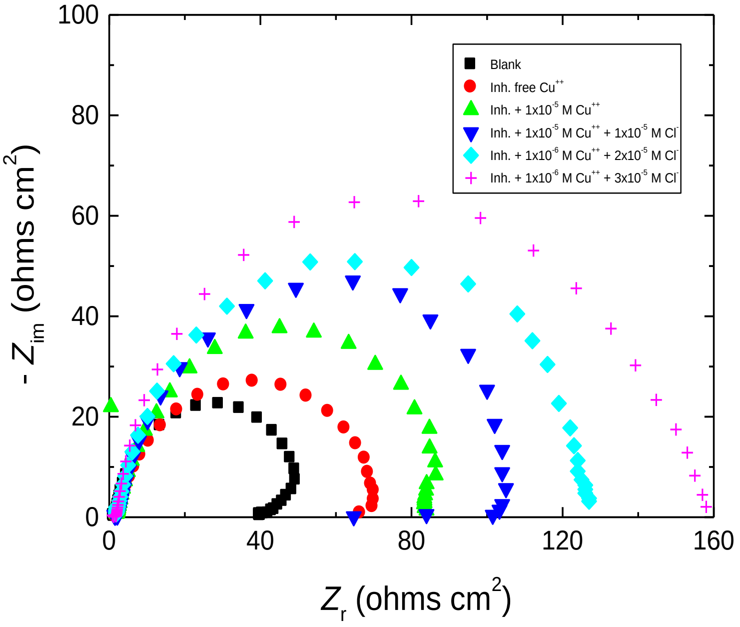

Figure 7. Nyquist plots of mild steel in 0.5 M H_2SO_4 containing AMTT and Cu^{2+} in the absence and presence of Cl^- at 25 °C.

Table 4. Impedance data for AMTT on mild steel in 0.5 M H_2SO_4 containing Cu^{2+} and/or Cl^- at 25 °C.

Medium	R_{ct}	% *P*	Medium	R_{ct}	% *P*	Medium	R_{ct}	% *P*
Blank	52	--	Blank	52	--	Blank	52	--
$2.5x10^{-6}$ M AMTT	70	26	$2.5x10^{-6}$ M AMTT	70	26	$2.5x10^{-6}$ M AMTT	70	26
$1x10^{-5}$ M Cu^{2+}	58	10	$1x10^{-6}$ M Cl^-	60	13			
AMTT + $1x10^{-5}$ M Cu^{2+}	78	33	AMTT + $1x10^{-6}$ M Cl^-	93	43	AMTT + $1x10^{-5}$ M Cu^{2+}	84	37
AMTT + $5x10^{-5}$ M Cu^{2+}	99	47	AMTT + $1x10^{-6}$ M Cl^- + $1x10^{-4}$ M Cu^{2+}	105	50	AMTT + $1x10^{-5}$ M Cu^{2+} + $1x10^{-4}$ M Cl^-	105	50
AMTT + $1x10^{-4}$ M Cu^{2+}	115	55	AMTT + $1x10^{-6}$ M Cl^- + $2x10^{-4}$ M Cu^{2+}	120	56	AMTT + $1x10^{-5}$ M Cu^{2+} + $2x10^{-4}$ M Cl^-	127	59
AMTT + $2x10^{-4}$ M Cu^{2+}	150	65	AMTT + $1x10^{-6}$ M Cl^- + $3x10^{-4}$ M Cu^{2+}	130	60	AMTT + $1x10^{-5}$ M Cu^{2+} + $3x10^{-4}$ M Cl^-	158	67

3.3. Adsorption isotherm

The adsorption of an inhibitor is a substitutional reaction [65]; the adsorbed water molecule is replaced by the inhibitor molecules according to the following equation;

$$Org_{(sol)}+nH_2O(ads) \rightarrow Org_{(ads)}+nH_2O_{(sol)} \qquad (7)$$

where Org(sol) and Org(ads) are the organic molecules in the aqueous solution and the adsorbed one, respectively, $H_2O(ads)$ is adsorbed water molecules and *n* is the number of water molecules replaced by one inhibitor molecule. Adsorption isotherms can provide the interaction between the inhibitor and the mild steel surface. Several isotherms including Langmuir, Temkin, and Flory–Huggins isotherms have been applied to fit the experimental results and Temkin was the best one to accord with experimental results. Temkin adsorption isotherm gives an explanation about the heterogeneity formed on the metal surface. Chemisorption is attributed to Temkin isotherm [37]. The free energy of adsorption (ΔG^{o}_{ads}) equals *ca*. 47 kJ/mol confirming the chemisorption nature of the adsorbed inhibitor molecule [66].

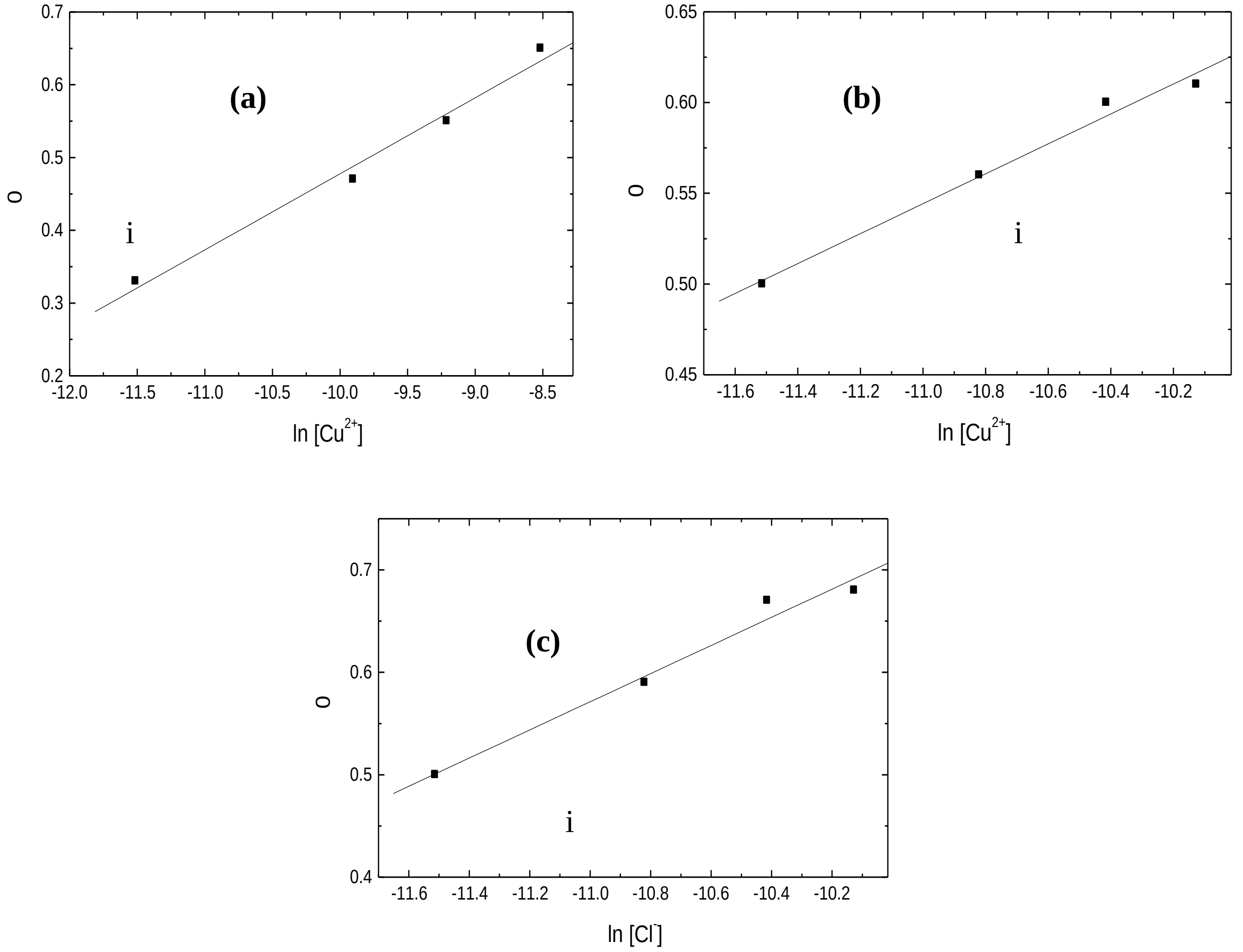

Figure 8. Temkin adsorption isotherms of: (a) Effect of [Cu^{2+}], (b) Effect of [Cu^{2+}] in the presence of 1x10^{-6} M Cl^{-} and (c) Effect of [Cl^{-}] in the presence of 1x10^{-5} M Cu^{2+} for AMTT adsorption on mild steel in 0.5 M H_2SO_4 at 25 ^{o}C.

4. CONCLUSIONS

The corrosion inhibition of steel by AMTT and Cu^{2+} has been studied using potentiodynamic polarization and electrochemical impedance spectroscopy. The following points can be emphasized:

1. Copper ions enhance the inhibition action of AMTT.
2. The synergistic action depends on the concentration of chloride.

3. The adsorption of AMTT follows Temkin adsorption isotherm pointing to the chemical nature of the adsorption of AMTT.

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