

Electrochemical and Gravimetric Study on the Corrosion and Corrosion Inhibition of Pure Copper in Sodium Chloride Solutions by Two Azole Derivatives

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The objective of this work was to investigate the corrosion and corrosion inhibition of 99.999% purity copper in sodium chloride (3.5% NaCl) solutions by 3-amino-5-mercapto-1,2,4-triazole (AMTA) and 5-(3-Aminophenyl)-tetrazole (APTA). Corrosion inhibition was studied using a variety of electrochemical tests and gravimetric and pH measurements. The polarization curves showed that the presence of either AMTA or APTA successfully reduced the corrosion of copper and this effect increased with increasing the compounds' concentration. Chronoamperometric experiments indicated that the highest currents for copper were recorded in 3.5% NaCl alone, while the presence of inhibitors highly decreased the dissolution currents. Electrochemical impedance spectroscopy revealed that the presence of inhibitors remarkably increased the impedance of copper over the whole studied frequency range. Gravimetric experiments showed that the dissolution rate and pH of the solution decreased to a minimum after 24 days of copper immersion due to the presence of the organic compounds. Both electrochemical and gravimetric data confirmed that the presence of inhibitors decreases the corrosion rate and increases corrosion resistance for copper in 3.5% NaCl solutions.

Keywords: chronoamperometry; copper corrosion; corrosion inhibitors; EIS; weight-loss; polarization; sodium chloride solution

1. INTRODUCTION

Copper and copper alloys are widely used in pipelines for domestic and industrial water utilities, shipboard condensers, power plant condensers, heat conductors, heat exchangers, etc. This is because these alloys offer a particularly beneficial combination of electrical and thermal conductivity, corrosion resistance, strength, and wear resistance [1-5]. In spite of a relatively noble potential of copper, its corrosion takes place in a significant rate in chloride containing environments [1-12].

Corrosion Inhibitors are widely used in the protection of copper against corrosion in different corrosive media [13-17]. Azole compounds have nitrogen atoms, which coordinate with Cu(0), Cu(I) or Cu(II) via their nitrogen atoms through lone pair electrons to form complexes [17-22]. These complexes are believed to be polymeric in nature and form an adherent protective film on the copper surface, which acts as a barrier to aggressive ions such as chloride [21-26].

We have been studying the corrosion and corrosion inhibition of metals [12,27-34] and alloys [35-44] in different corrosive environments using different electrochemical and gravimetric techniques, along with surface characterization tools such as SEM, EDX, FT-IR, XPS, AES, UV-visible and Raman spectroscopy. The present work aims to report the results obtained in studying the corrosion and corrosion inhibition of copper in 3.5% NaCl solutions by 3-amino-5-mercapto-1,2,4-triazole (AMTA) and 5-(3-aminophenyl)-tetrazole (APTA). The chemical structures of these two compounds are depicted in Fig. 1a and Fig. 1b, respectively. It is clearly seen from Fig. 1 that AMTA and APTA are heterocyclic compounds contain different donor groups (azole, amino, and mercapto), which is why these compounds were expected to be good inhibitors for copper corrosion in the solution under investigation. In order to achieve the objectives of this study we used a combination of conventional electrochemical methods such as potentiodynamic polarization and chronoamperometric current-time at constant potential along with electrochemical impedance spectroscopy. The work was also complemented by performing a long exposure weight-loss experiments.

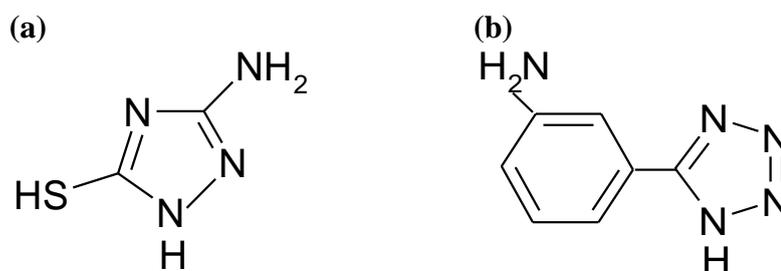


Figure 1. Molecular structures of (a) 3-amino-5-mercapto-1,2,4-triazole (AMTA) and (b) 5-(3-Aminophenyl)-tetrazole (APTA).

2. EXPERIMENTAL DETAILS

Sodium chloride (NaCl, Merck, 99%), 3-amino-5-mercapto-1,2,4-triazole (AMTA, Sigma–Aldrich, 95%), 5-(3-Aminophenyl)-tetrazole (APTA, Alfa-Aesar, 96%), and absolute ethanol (C₂H₅OH, Merck, 99.9%) were used as received. An electrochemical cell with a three-electrode configuration was used; a copper rod (Cu, Goodfellow, 99.999%, 0.5 cm in diameter), a platinum foil, and an Ag/AgCl electrode (in saturated KCl) were used as a working, counter, and reference electrodes, respectively.

The copper rods for electrochemical measurements were first polished successively with metallographic emery paper of increasing fineness of up to 800 grits, washed with distilled water,

degreased with acetone, washed with distilled water again, and finally dried using tissue paper. All electrochemical techniques were performed by using a PARC Parstat-2273 Advanced Electrochemical System. For potentiodynamic polarization experiments the potential was scanned from -600 to +600 mV, Ag/AgCl, at a scan rate of 1 mV/s. Chronoamperometric current-time experiments were carried out by stepping the potential at 250 mV for 120 min. Electrochemical impedance spectroscopy (EIS) tests were performed at corrosion potentials (E_{Corr}) over a frequency range of 100 kHz – 0.05 Hz, with an ac wave of ± 5 mV peak-to-peak overlaid on a dc bias potential, and the impedance data were collected using Powersine software at a rate of 10 points per decade change in frequency.

Gravimetric experiments in NaCl solutions without and with AMTA and APTA molecules were carried out using rectangular copper coupons having the same purity as for copper rods. The dimensions of the coupons were 3.0 cm length, 1.0 cm width, and 0.20 cm thickness. The coupons were polished and dried as for copper rods, weighted (initial weight, m_{int}), and then suspended in a 200 cm³ of the test solutions for exposure periods between 6 days and 24 days. After the designated exposure to the test solution, the specimens were rinsed with distilled water, washed with acetone to remove a film possibly formed due to the inhibitor, dried between two tissue papers, and weighted again (final weight, m_{fin}). Weight-loss measurements were made in triplicate and the loss of weight was calculated by taking an average of these values. The maximum standard deviation in the observed weight loss was calculated to be $\pm 1.0\%$. The weight loss (Δm , mg.cm⁻²), the corrosion rate (K_{Corr} , mg.cm⁻².h⁻¹), and the inhibition efficiency (IE%) over the exposure time were calculated as follows [7-9]:

$$\Delta m = \frac{m_{\text{int}} - m_{\text{fin}}}{A} \quad (1)$$

$$K_{\text{Corr}} = \frac{m_{\text{int}} - m_{\text{fin}}}{A t} \quad (2)$$

$$IE\% = 100 \frac{K_{\text{Corr}}^{\text{Un}} - K_{\text{Corr}}^{\text{In}}}{K_{\text{Corr}}^{\text{Un}}} \quad (3)$$

Where, A is the total surface area in cm², t is the time of exposure in hours, and $K_{\text{Corr}}^{\text{un}}$ and $K_{\text{Corr}}^{\text{in}}$ are the corrosion rates without and with the inhibitor, respectively.

3. RESULTS AND DISCUSSION

3.1. Potentiodynamic polarization measurements

The potentiodynamic polarization curves recorded for copper electrode in 3.5% NaCl solutions containing (1) 0.0, (2) 5.0×10^{-4} and (3) 1.0×10^{-3} M of (a) AMTA and (b) APTA, respectively are

shown in Fig. 2. It is generally believed that the cathodic reaction of copper in aerated sodium chloride solutions is the oxygen reduction according the following equation [45,46]:



On the other side, the anodic reaction at the same condition goes through the dissolution of copper to release cuprous cations as follows [11,12]:



This reaction leads to a rapid increase of current after which the copper cations react with chloride ions from the solution to form cuprous chloride on the metal surface as follows:



The formation of CuCl provides partial protection for copper and leads to decreasing the anodic current till the formation of cuprous chloride complex, CuCl_2^- , due to the reaction of CuCl with further chloride ions [2-7],



The formation of CuCl_2^- on the copper surface has been reported to be the responsible for further copper corrosion through its dissolution either to the solution or its oxidation to cupric cations [2-7].

The presence of 5.0×10^{-4} M AMTA with the chloride solutions, Fig. 2a (curve 2), remarkably decreased the cathodic, corrosion (j_{Corr}), and anodic currents, with the corrosion potential (E_{Corr}) values slightly shifted in the negative direction.

Addition of 1.0×10^{-3} M AMTA, Fig. 2a (curve 3), provided more decreases in the corrosion reactions on the copper surface. This was clear from the calculated values of j_{Corr} , E_{Corr} , cathodic Tafel (β_c) and anodic Tafel (β_a) slopes, polarization resistance (R_p), corrosion rate (K_{Corr}), and the percentage of inhibition efficiency (IE%), which are listed in Table 1. The values of these parameters were obtained as has been reported in our previous work [2-5].

Addition of 5.0×10^{-4} M APTA to the NaCl solution, Fig. 2b (curve 2), also decreased the corrosion of copper and this effect increased when the concentration of APTA was increased to 1.0×10^{-3} M as shown by curve 3 of Fig. 2b.

It is clearly seen from Fig. 2 and Table 1 that AMTA and APTA molecules highly inhibit the corrosion of copper through decreasing the values of j_{Corr} and K_{Corr} and increasing the values of β_c , β_a , R_p , and IE%. The presence of these compounds also shifted the values of E_{Corr} towards the more negative potentials values, especially in the case of APTA molecules.

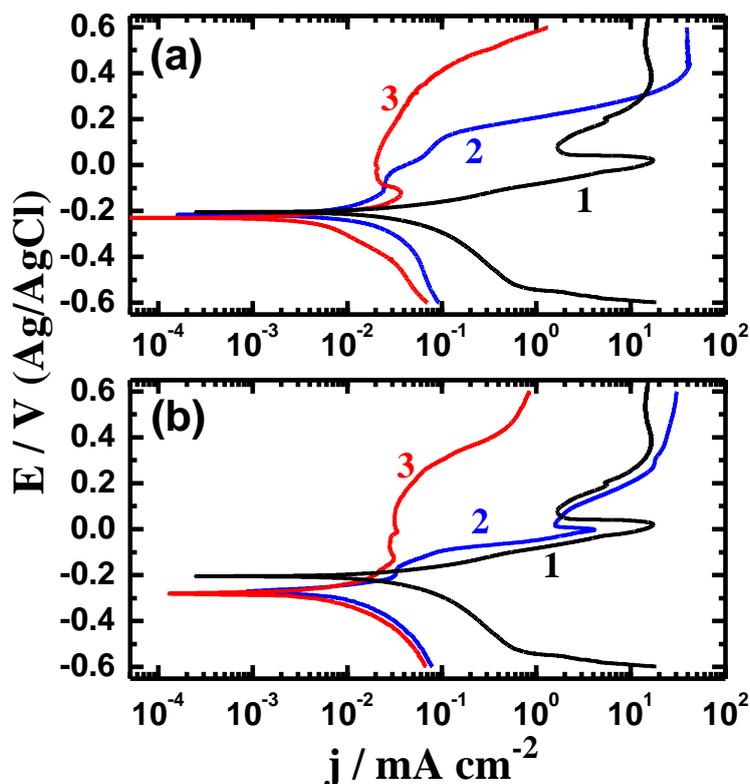


Figure 2. Potentiodynamic polarization curves for copper in 3.5% NaCl solutions containing (1) 0.0 M, (2) 5.0×10^{-4} M and (3) 1.0×10^{-3} M of (a) AMTA and (b) APTA, respectively.

Table 1. Parameters obtained from potentiodynamic polarization curves shown in Fig. 2 for copper electrode in 3.5% NaCl solutions in absence and presence of 5.0×10^{-4} M and 1.0×10^{-3} M AMTA and APTA, respectively.

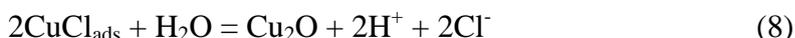
Solution	Parameter						
	$E_{\text{Corr}}/$ mV	$j_{\text{Corr}}/$ μAcm^{-2}	$-\beta_c/$ mVdec^{-1}	$\beta_a/$ mVdec^{-1}	$R_p/$ Ωcm^2	$K_{\text{Corr}}/$ mmy^{-1}	IE/ %
3.5% NaCl alone	-212	38.0	120	90	588	0.443	—
+ 5.0×10^{-4} M AMTA	-220	10.0	130	145	2980	0.116	73.8
+ 1.0×10^{-3} M AMTA	-250	7.0	135	155	4482	0.081	81.7
+ 5.0×10^{-4} M APTA	-260	8.0	155	150	4143	0.093	79.0
+ 1.0×10^{-3} M APTA	-270	4.5	165	165	7971	0.052	88.3

It has been reported that [15-17,20,22] the decreases in the values of j_{Corr} and K_{Corr} for copper in near neutral chloride solutions containing azole compounds are due to the decrease of copper dissolution as a result of the adsorption of the azole molecules, which leads to isolating the metal surface and therefore reducing the chloride ions attack. The adsorbed layers in turn preclude the dissolution of copper and increase its surface resistance against corrosion. This occurs by repairing the flawed areas, blocking the active sites, and also preventing the formation of chloride and oxychloride complexes on the copper surface. The increase in β_c and β_a values is related to the decrease in the

cathodic and anodic currents, respectively. The increase of R_p and IE% in the presence of AMTA and APTA and the increase of their concentrations as seen from Table 1, also confirm that those organic compounds are good inhibitors for copper corrosion in 3.5% sodium chloride solution and their inhibition efficiency increase in the order APTA > AMTA.

3.2. Chronoamperometric current-time (CT) investigations

The chronoamperometric current-time experiments were carried out in order to identify the type of corrosion of copper in chloride solution in absence and presence of AMTA and APTA more anodic potential value. The CT curves measured at 300 mV vs. Ag/AgCl for the copper electrode in 3.5% NaCl solutions containing (1) 0.0 M, (2) 5.0×10^{-4} M, and (3) 1.0×10^{-3} M of (a) AMTA and (b) APTA, respectively are shown in Fig. 3. It is obvious that the copper in NaCl solution alone, curves 1, recorded the highest absolute current values due to the dissolution of copper by the corrosive attack of Cl^- ions. The initial increase of current occurs because copper dissolves at first to cuprous cations that react in turn with Cl^- ions from the solution to form CuCl and further CuCl_2^- . The current then decreases with time due to the formation of a porous oxide layer (Cu_2O) as follows [5],



The formation of such layer provides partial protection and does not allow the current to increase.

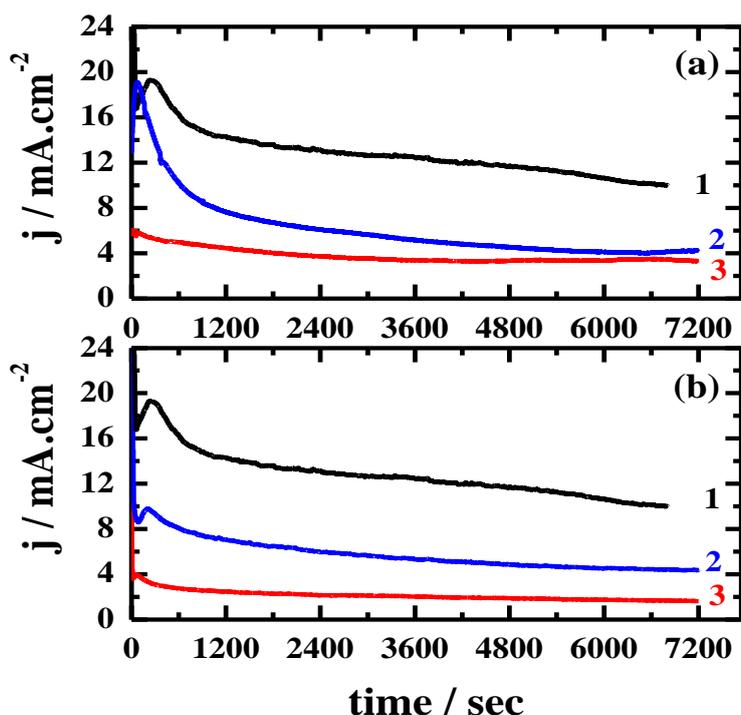
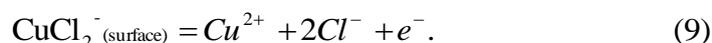
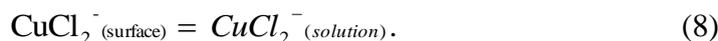


Figure 3. Chronoamperometric current-time curves collected at 300 mV vs. Ag/AgCl for copper in 3.5% NaCl solutions containing (1) 0.0, (2) 5.0×10^{-4} and (3) 1.0×10^{-3} M of (a) AMTA and (b) APTA, respectively.

Addition of 5.0×10^{-4} M AMTA (Figure 3a curve 2) provided great decreases in the current values, which is probably due to the adsorption of AMTA molecules on the copper surface. Increasing the concentration of AMTA to 1.0×10^{-3} M as seen by curve 3 of Fig. 3 led to decreasing the absolute current values from the first moment of Cu immersion up to the end of the run. This is due to the formation of a protective layer on the copper surface blocked the active sites on copper and prevented its dissolution. The presence of 5.0×10^{-4} M and 1.0×10^{-3} M of APTA (Fig. 3b, curves 2 and 3) showed similar behavior to that obtained for copper in the case of AMTA at the same concentrations but with lower current values. The CT results thus agree with the polarization data we have seen in Fig. 2 and Table 1; both confirm that AMTA and APTA molecules have the ability to inhibit copper corrosion and their inhibition efficiency increases in the order APTA > AMTA.

3.3. Electrochemical Impedance Spectroscopy (EIS) measurements

The EIS technique has been extensively used with other electrochemical methods to interpret the corrosion and corrosion inhibition of metals and alloys including copper in severe environments such as chloride media [32-44]. Typical Bode plots of EIS spectra of the copper electrode in 3.5% M NaCl solutions containing (1) 0.0 M, (2) 5.0×10^{-4} M, and (3) 1.0×10^{-3} M of (a) AMTA and (b) APTA respectively are shown in Fig. 4. It is clearly seen from Fig. 4 that the impedance ($|Z|$) of the copper in chloride solution alone, curves 1, recorded lower values at the high frequency range and then increased with decreasing the frequency. The increase of $|Z|$ values at the lower frequency area in the chloride solution alone can be attributed to the dissolution of CuCl_2^- from the copper surface or due to the diffusion of copper cations into the solution as indicated as follows,



At this condition the corrosion of copper is under mixed control by the dissolution of copper and the diffusion of soluble CuCl_2^- from the Helmholtz plane into the bulk solution [47].

Addition of 5.0×10^{-4} M AMTA, Fig. 4a (curve 2) significantly increased the values of $|Z|$ across the whole frequency values of the run. This effect was further increased with increasing the concentration of AMTA to 1.0×10^{-3} M, Fig. 4a, curve 3. This increase in the values of $|Z|$ at high frequency range is attributed to the time constant of charge transfer and double-layer capacitance [48,49]. This effect also increases with increasing the concentration of the molecules of the inhibitor and makes the charge-transfer resistance became dominant in the corrosion process as a result of the formation of AMTA film on the copper surface [50]. The increase of $|Z|$ at low frequency area in the presence of AMTA is probably due to the adsorption then polymerization of AMTA molecules on copper followed by the formation of AMTA-Cu complex on the electrode surface as follows,



Moreover, the presence of 1.0×10^{-3} M and 5.0×10^{-3} M APTA, Fig. 4b (curves 2, 3) recorded the highest $|Z|$ values over the whole frequency range compared to chloride alone or containing AMTA. The adsorption of APTA on the copper surface would be also represented by the following reactions;

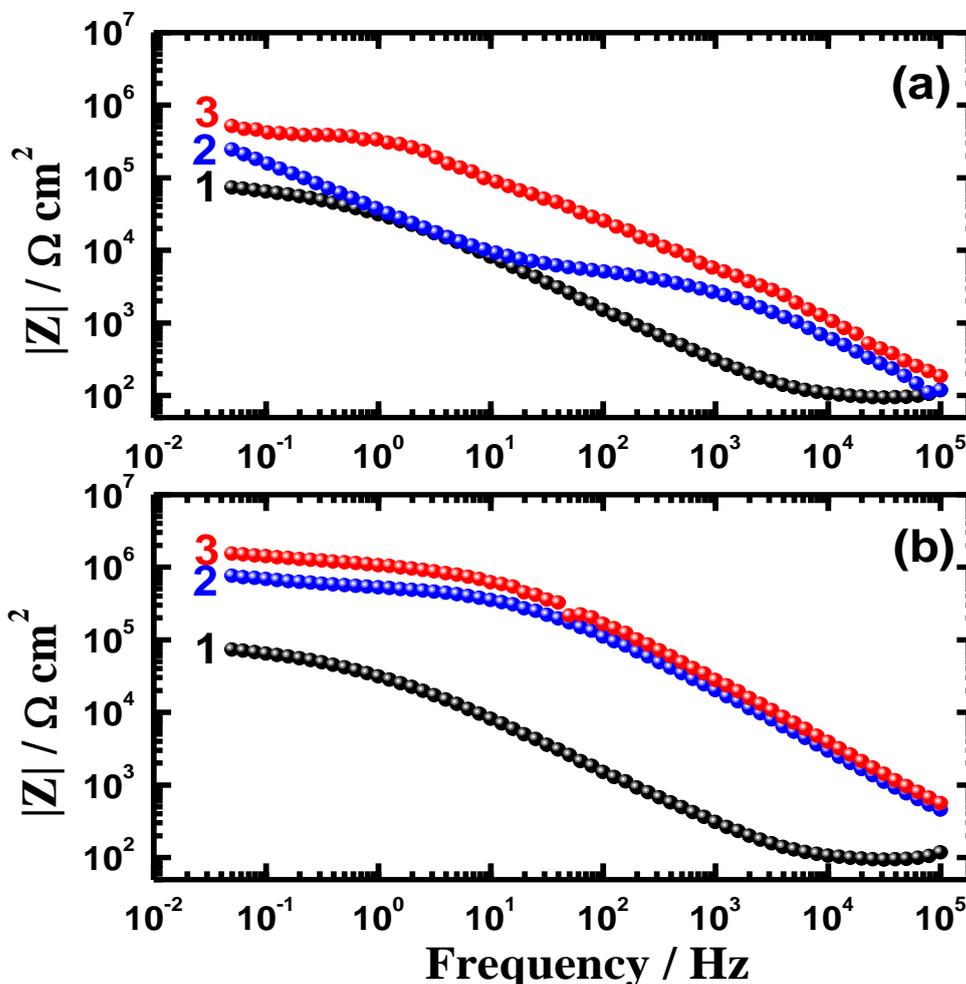
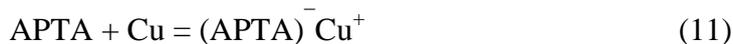


Figure 4. Bode impedance plots obtained at open-circuit potential for copper in 3.5% NaCl solutions containing (1) 0.0, (2) 5.0×10^{-4} and (3) 1.0×10^{-3} M of (a) AMTA and (b) APTA, respectively.

The impedance data represented in Fig. 4 were fitted to an equivalent circuit shown in Fig. 5. The components of this circuit are: R_s the solution resistance; Q_1 and Q_2 the constant phase elements (CPEs); and R_{p1} and R_{p2} two polarization resistances. It clearly seen from Fig. 5 that there are two routes for electron transfer, which are connected in parallel and competing with each other. Both of the routes are similarly affected by the presence of the organic molecules (AMTA and APTA) in the solution. The values of R_s , R_{p1} and R_{p2} have been reported to increase, while the CPEs decrease in the presence of the inhibitors' molecules and up on the increase of their concentrations [11,20]. The impedance of a CPE may be defined as follows [50]:

$$Z_{CPE} = (1/Y\omega) (j\omega)^{-n} \quad (12)$$

Where, $Y\omega$ is the modulus, ω is the angular frequency, and n is the phase. The EIS data thus agree with the ones obtained by polarization and chronoamperometric experiments and provide further confirmation of the ability of AMTA and APTA as good inhibitors for copper corrosion in 3.5% NaCl solutions with the efficiency increases in the order APTA > AMTA.

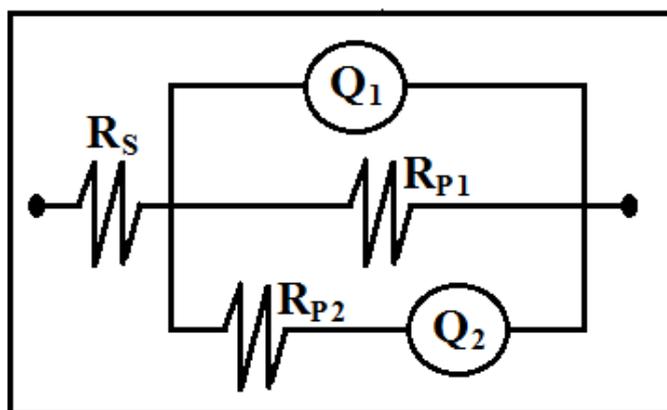


Figure 5. The equivalent circuit used to fit the impedance data shown in figure 4.

3.4. Gravimetric and pH measurements

The loss in weight experiments for copper electrode in the test solutions without and with the desired concentrations of AMTA or APTA concentrations after varied exposure periods were carried out to confirm the electrochemical measurements. The change of the dissolution rate as a function of time for the copper coupons in 3.5% solutions without (1), with (2) 5.0×10^{-4} M and (3) 1.0×10^{-3} M of (a) AMTA and (b) APTA present, respectively are shown in Fig. 6; the corresponding change of the pH values for the same solutions at the same conditions are shown in Fig. 7.

The dissolution rate and the pH increase remarkably with time in chloride solutions in absence of any inhibitor molecules. The increase of the dissolution rate can be explained on the fact that the formed CuCl_2^- on copper surface as shown in Eq. (7) dissolves via diffusion into the bulk solution, Eq. (8) and Eq. (9).

The increase of dissolution rate of CuCl_2^- led to increasing the rate of generate of OH^- ions by the cathodic reaction shown in Eq. (4), which in turn led to raising the corresponding pH values. While, the presence of AMTA and the increase of its concentration dramatically decreased both the dissolution rate and pH values even after the longest immersion time, 24 days.

The dissolution rate and pH values were further decreased by the presence of APTA and upon the increase of its content.

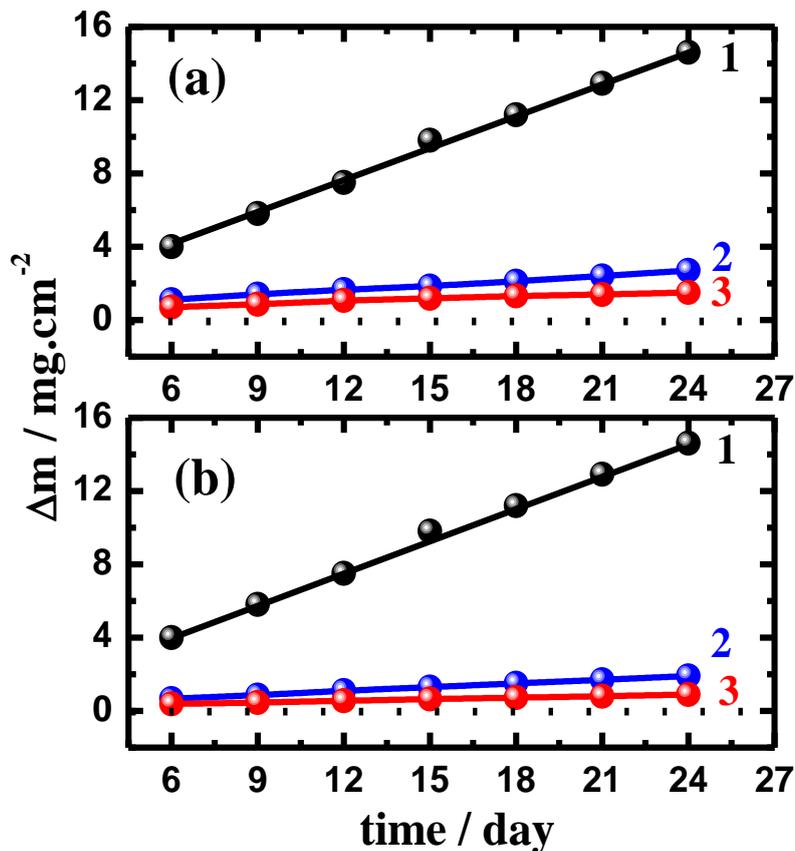


Figure 6. Variations of the weight-loss (Δm , $\text{mg}\cdot\text{cm}^{-2}$) as a function of time for copper coupons in 3.5% NaCl solutions without (1), with (2) 5.0×10^{-4} M and (3) 1.0×10^{-3} M of (a) AMTA and (b) APTA present, respectively.

In order to fully understand the corrosion of copper and the effect of AMTA and APTA on the inhibition of this corrosion, the values of the corrosion rate (K_{Corr}) were calculated using Eq. (2). The variation of K_{Corr} with time for copper in chloride solutions in the absence (1) and presence of 5.0×10^{-4} M (2) and 1.0×10^{-3} M (3) of (a) AMTA and (b) APTA respectively, is shown in Fig. 8. It is clearly seen that the corrosion rate for copper in chloride solution without inhibitors, curves 1, recorded the highest values that decrease with increasing the exposure time. This decrease in K_{Corr} with time is due to the formation of Cu_2O and the accumulation of other corrosion products on the copper surface. It has been reported that [15] increasing the immersion of copper in the chloride solution alone leads to the hydrolyzes of the formed oxide layer (Eq. 8) in the presence of Cl^- to form a top layer of atacamite ($\text{Cu}_2(\text{OH})_3\text{Cl}$) as follows,



The formed atacamite is not fully protective and not compact enough to stop the chloride ion attacks, which is why although the K_{Corr} decreases with time, its values still high. The presence of AMTA or APTA molecules greatly decreased the values of K_{Corr} at all exposure periods, which is most

probably due to the adsorption of these compounds on the surface to prevent the formation of atacamite and cuprous chloride complexes protecting the copper from being corroded.

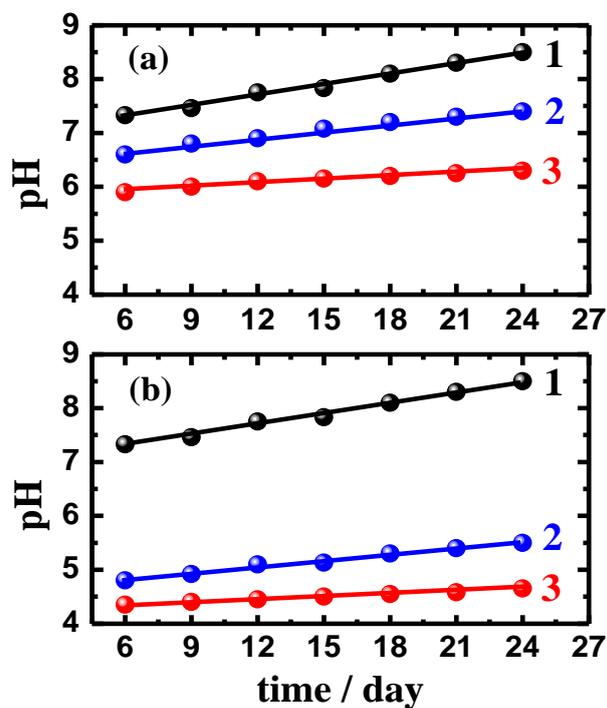


Figure 7. Changes of the pH as a function of time for copper coupons in 3.5% NaCl solutions without (1), with (2) 5.0×10^{-4} M and (3) 1.0×10^{-3} M of (a) AMTA and (b) APTA present, respectively.

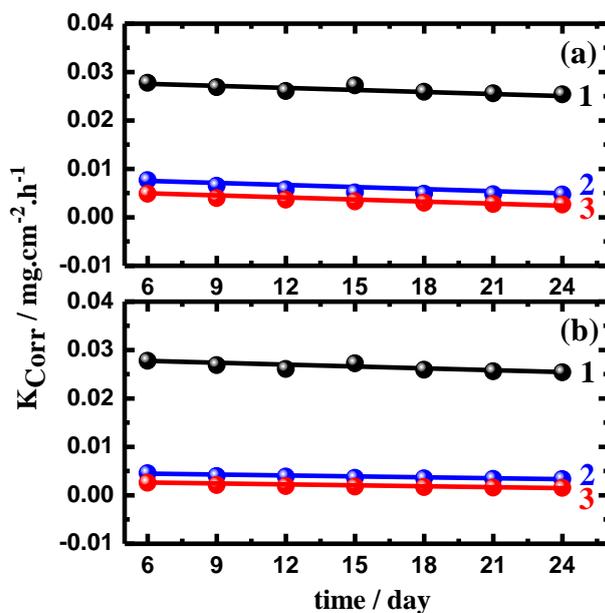


Figure 8. Variations of the corrosion rate (K_{Corr} , $\text{mg}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$) with time for copper coupons in 3.5% NaCl solutions without (1), with (2) 5.0×10^{-4} M and (3) 1.0×10^{-3} M of (a) AMTA and (b) APTA present, respectively.

The gravimetric results were also complemented by plotting the values of the inhibition efficiency (IE%) obtained from weight-loss experiments using Eq. (3) as a function of time for copper in chloride solutions containing (1) 5.0×10^{-4} M and (2) 1.0×10^{-3} M (a) AMTA and (b) APTA, respectively and the curves are shown in Fig. 9. The minimum IE% value obtained for 5.0×10^{-4} M AMTA after 6 days recorded 86.5% increased to 90% in 24 days; these values were increased to 90% and 92%, respectively when the concentration of AMTA was increased to 1.0×10^{-3} M. On the other hand the values of IE% in the presence of APTA, Fig. 9b, recorded 90% with 5.0×10^{-4} M after 6 days immersion in the test solution; this value did not change much with increasing the exposure time to 24 days. The presence of 1.0×10^{-3} M APTA raised the values of IE% to 95% over the different exposure periods for copper. The results of the dissolution rate, pH, KCorr, and IE% are thus confirm those obtained from the polarization, chronoamperometry, and impedance and stating that AMTA and APTA are good corrosion inhibitors for copper in 3.5% NaCl solutions and their efficiency increases in the order APTA > AMTA.

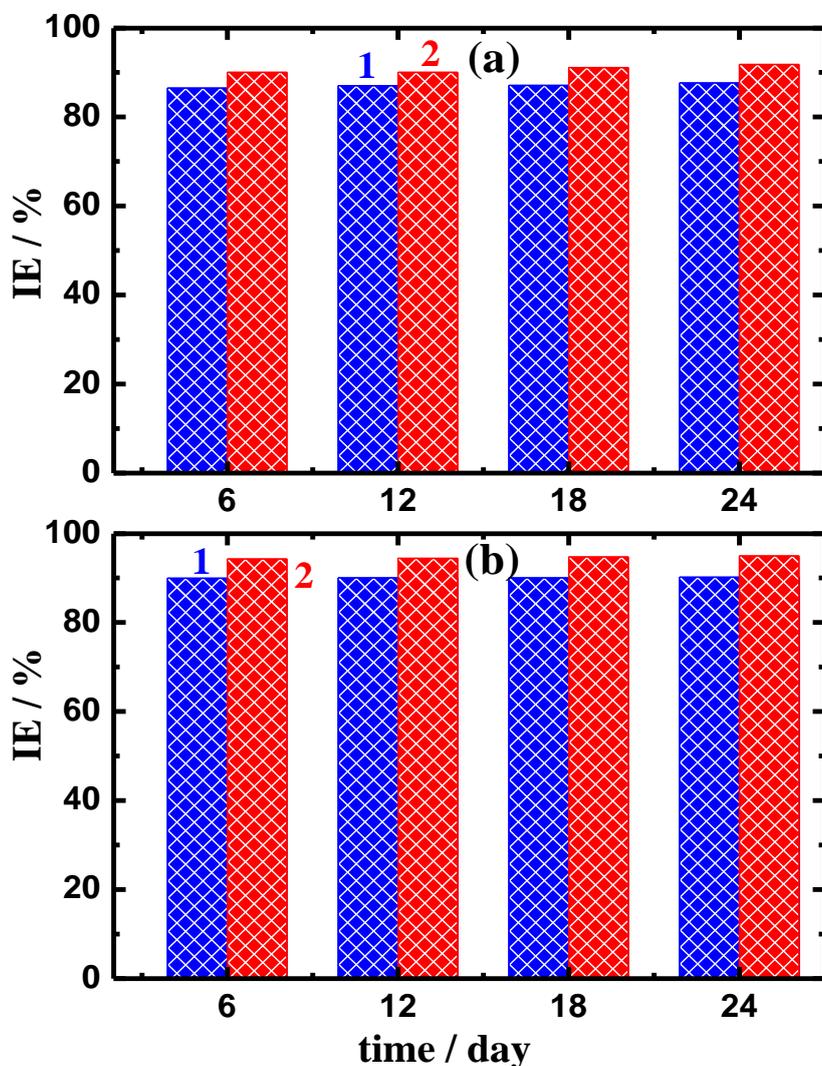


Figure 9. The inhibition efficiency (IE%) obtained for copper coupons in 3.5% NaCl containing (1) 5.0×10^{-4} M and (2) 1.0×10^{-3} M (a) AMTA and (b) APTA, respectively.

4. CONCLUSIONS

In this work, the corrosion and corrosion inhibition of spec pure copper in 3.5% NaCl solutions by two organic compounds, namely 3-amino-5-mercapto-1,2,4-triazole (AMTA) and 5-(3-Aminophenyl)-tetrazole (APTA) have been reported. The values of the corrosion current density and corrosion rate of copper in chloride solutions containing AMTA or APTA decrease to a minimum as indicated by polarization data. The absolute dissolution currents of copper in chloride solution recorded the highest values; these greatly decrease by the presence and the increase of AMTA or APTA concentrations as shown by the chronoamperometric current-time experiments at 300 mV vs. Ag/AgCl. Electrochemical impedance spectroscopy revealed that the presence of inhibitors remarkably increased the corrosion resistance of copper. Gravimetric and pH measurements indicated that the dissolution rate (K_{Corr}) of copper in chloride solutions alone, and conjunctly the solution pH values increase with increasing the immersion time from 6 days to 24 days. On the other hand, the presence of AMTA or APTA and the increase of their concentrations highly decrease the values of K_{Corr} and pH. The values of IE% obtained from weight-loss data recorded circa 88% for 5.0×10^{-4} M AMTA after 24 days increased to ~ 92% when the concentration of AMTA was increased to 1.0×10^{-3} M; these values further increased to 90% and 95% respectively in the presence of APTA molecules at the same concentrations. The results from the combined measurements agree well with one another and prove beyond doubt that AMTA and APTA are powerful corrosion inhibitors for copper in 3.5% NaCl solutions and their efficiency increases in the order APTA > AMTA.

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