

Surface protection of copper in aerated 3.5% sodium chloride solutions by 3-amino-5-mercapto-1,2,4-triazole as a copper corrosion inhibitor

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Abstract Surface protection of copper in aerated 3.5% NaCl solutions by 3-amino-5-mercapto-1,2,4-triazole (AMTA) has been reported. The study has been carried out using weight loss, pH, potentiodynamic polarization (PDP), electrochemical impedance spectroscopy (EIS), and chronoamperometric (CA) measurements along with scanning electron microscopy (SEM) and energy dispersive X-ray (EDS) investigations. Weight-loss data indicated that the dissolution rate and the pH of the solution decreased to a minimum after 24 days of copper immersion due to the inhibitive action of AMTA. PDP, CA, and EIS measurements showed that AMTA decreased the corrosion rates and increased the polarization resistance and inhibition efficiency. This effect was increased with increasing AMTA concentration as well as the immersion time of the copper electrode to 50 h before measurements. SEM micrograph and EDS analysis proved that the inhibition of copper corrosion takes place due to adsorption of AMTA onto the surface. These results together confirmed that AMTA is a

good mixed-type inhibitor and the inhibition of copper corrosion is achieved by strong adsorption of AMTA molecules.

Keywords 3-Amino-5-mercapto-1,2,4-triazole · Copper corrosion · Corrosion inhibitors · Electrochemical and gravimetric techniques · Sodium chloride solutions

1 Introduction

Copper has been commonly used in a wide range of applications such as heat conductors, heat exchangers because of its excellent thermal conductivity, mechanical workability, and corrosion resistance [1–5]. Copper is considered a great resistant against atmospheric corrosion and other forms of corrosion caused by many chemicals. However, copper becomes very susceptible to corrosion in a significant rate in media that contain chloride ions [6–16].

Prevention of corrosion in copper has attracted many researchers and many possible techniques have been used. Organic inhibitors are one of the most important methods used in the protection of copper against corrosion and many possible compounds have been investigated. It has been reported that azole derivatives contain nitrogen atoms, which coordinate with Cu(0), Cu(I), or Cu(II) through lone pair electrons to form complex compounds, are good corrosion inhibitors for copper [10–16]. These complexes are generally 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. It is believed that the presence of hetero atoms such as nitrogen, sulphur, and phosphors in the organic compound

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improves its inhibition efficiency as a corrosion inhibitor for copper. This is explained by the presence of vacant *d* orbital in copper atoms that forms coordinative bonds with atoms that are able to donate electrons [3–6, 8–10, 15–19]. Interaction with rings containing conjugated bonds, π electrons, is also present [15–23].

We have been studying corrosion and corrosion inhibition of copper [2–6, 8–10, 16–20], aluminum [24, 25], and iron [26] as well as stainless steel alloys [27–29] in a variety of media. These studies have been carried out using different electrochemical, gravimetric, spectroscopic, and surface analyses investigations under different experimental conditions. In the earlier study [2], pitting corrosion of copper at different concentrations of sodium chloride has been reported. The XPS study of the copper surface showed that the predominant species in the surface film at lower chloride concentrations (≤ 1.0 mM) is Cu_2O , while it is CuCl at higher concentrations (≥ 100 mM), and the copper dissolution occurs via the formation of the soluble complex, CuCl_2^- . More recently [19], the inhibition of corrosion processes on copper in aerated 3.5% NaCl solutions by 5-(3-aminophenyl)-tetrazole (APT) has been investigated. It was concluded that the adsorption of APT blocks the active sites on the copper surface preventing the formation of cuprous chloride and oxychloride complexes, which are responsible for corrosion in copper.

The present study focuses on the corrosion behavior and corrosion inhibition of copper in 3.5% sodium chloride solutions by 3-amino-5-mercapto-1,2,4-triazole (AMTA). This organic compound was expected to show powerful inhibition effectiveness versus the corrosion of copper in the reported concentration of the chloride solution because it is a heterocyclic compound containing a variety of donor atoms.

2 Experimental

2.1 Materials and electrochemical cell

3-Amino-5-mercapto-1,2,4-triazole (Sigma–Aldrich, 95%), sodium chloride (NaCl, Merck, 99%), and absolute ethanol ($\text{C}_2\text{H}_5\text{OH}$, Merck, 99.9%) were used as received. An electrochemical cell with a three electrode configuration was used; a copper rod (Cu, Goodfellow, 99.999%, 5.0 mm in diameter), platinum foil, and an Ag/AgCl electrode (in saturated KCl) were used as working, counter, and reference electrodes, respectively. The copper electrode was polished successively with emery paper with increased fineness for up to 800 grits. The electrode was then washed with doubly distilled water, degreased with acetone, re-washed using doubly distilled water again and finally dried with tissue paper.

2.2 Weight loss, inhibition efficiency, scanning electron microscopy (SEM), and energy dispersive X-ray (EDS) investigations

The weight-loss experiments were carried out using rectangular copper coupons (Goodfellow, 99.999%) having dimensions of length 3.0 cm, width 1.0 cm, and thickness 0.20 cm with an exposed total area of 7.6 cm^2 . The coupons were polished and dried as for copper rods, weighed (W_1), and then suspended in a 100 cm^3 solution of 3.5% NaCl with and without the desired concentrations of AMTA for different exposure periods (6–24 days). After exposure to test solution, the specimens were rinsed with distilled water, washed with acetone to remove any film possibly formed due to the inhibitor, dried with tissue papers, and weighed (W_2). 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 (ΔW , mgcm^{-2}), the corrosion rate (K_{Corr} , $\text{mgcm}^{-2}\text{h}^{-1}$), and the inhibition efficiency (IE%) over the exposure time were calculated as follows [4–6]:

$$\Delta W = \frac{W_1 - W_2}{A} \quad (1)$$

$$K_{\text{Corr}} = \frac{\Delta W}{t} \quad (2)$$

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

where A is the area of copper coupon (cm^2); t is the exposure time (h); $K_{\text{Corr}}^{\text{Un}}$ and $K_{\text{Corr}}^{\text{In}}$ the corrosion rates ($\text{mg cm}^{-2} \text{h}^{-1}$) in the absence and presence of AMTA molecules, respectively.

The morphology of the formed layers on the copper surface after its immersion in 3.5% NaCl solution in the presence of 1.0 mM AMTA for 24 days was investigated using ASEM 6360A, JOEL scanning electron microscope (SEM). The elemental analysis of the copper surface was detected using an energy dispersive X-ray (EDS) analyzer unit attached to the SEM machine.

All solutions were prepared using doubly distilled water and ethanol (99:1, vol:vol) and all measurements were carried out at room temperature.

2.3 Electrochemical techniques

Electrochemical experiments were performed using a Schlumberger SI 1286 electrochemical interface potentiostat–galvanostat. For potentiodynamic polarization experiments, the potential was scanned from -600 to 700 mV at a scan rate of 1 mV s^{-1} . Chronoamperometric measurements were carried out by applying a constant potential of

350 mV vs. Ag/AgCl for 120 min. EIS measurements were made using a Solatron SI 1255 HF frequency response analyzer along with the potentiostat–galvanostat. The instruments were controlled by the FRA-3.5 software program between 100 kHz and 0.05 Hz with an ac wave of ±5 mV peak to peak overlaid on a dc bias potential, and the impedance data were obtained at a rate of 10 points per decade change in frequency.

3 Results and discussion

3.1 Weight loss, inhibition efficiency, SEM, and EDS investigations

The dissolution rate (ΔW) versus time for the copper coupons in 3.5% sodium chloride solutions is presented in Fig. 1a. Three cases of AMTA concentration were investigated; (1) 0.0 mM; (2) 0.5 mM, and (3) 1.0 mM, respectively. The corresponding change in pH is also shown in Fig. 1b. It is clear that the weight loss and the accompanying pH, curves 1, increased rapidly in the NaCl

solutions even after 24 days. The dissolution of copper at this condition occurs through oxidation of Cu(0) to Cu⁺ first [2, 16, 30],



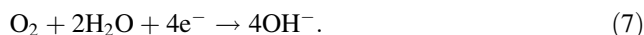
This Cu⁺ reacts with chloride ion from the solution and forms CuCl,



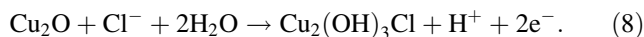
This CuCl does not produce enough protection to the copper surface and transforms to the soluble cuprous chloride complex, CuCl₂⁻ [11],



Under this condition, CuCl₂⁻ was the main species formed at the surface of copper and then diffused into the bulk. Since there was no blocking film or layer of corrosion products covering the surface, the weight loss of copper in 3.5% NaCl solution increased linearly with time. The accompanying increase in pH indicates that the amount of dissolution products is more than that accounted for by the dissociation of Cu(OH)₂ (pK_{sp} = 19.32) or Cu₂O (pK_{sp} = 29.4) and significant amounts of copper must be in the form of CuCl₂⁻. Because the cathodic couple of the corrosion reaction of copper in aerated solutions is the reduction of oxygen, the rate of generation of OH⁻ ions according to reaction (7) would be the same as that of CuCl₂⁻ ions produced in reaction (6).



Thus, the corrosion process is accompanied by a surface alkalization as reported before [16]. At the same time, the reaction between the hydroxide group and the cuprous chloride complex could lead to a top layer of sparingly soluble atacamite (Cu₂(OH)₃Cl) [31],



In comparison, the addition of AMTA decreased both the dissolution rate and the corresponding pH values to a minimum even after the longest exposure period, 24 days. This effect increased with increasing AMTA concentration and bestowed the protection ability to its maximum at 1.0 mM. The increase in the surface protection was due to the adsorption of a thin layer of AMTA molecules onto the copper (see below, SEM/EDS).

Figure 2a shows the variation of the calculated corrosion rate (K_{Corr} , mg cm⁻² h⁻¹) as a function of time for copper in 3.5% NaCl solutions with different AMTA concentrations (1) 0.0 mM, (2) 0.5 mM, and (3) 1.0 mM, respectively. It is clear from Fig. 2a that the corrosion rate of copper in chloride solution alone, column 1, increased remarkably with time. In contrast, the presence of 0.5 mM AMTA highly reduced the K_{Corr} and further reductions of

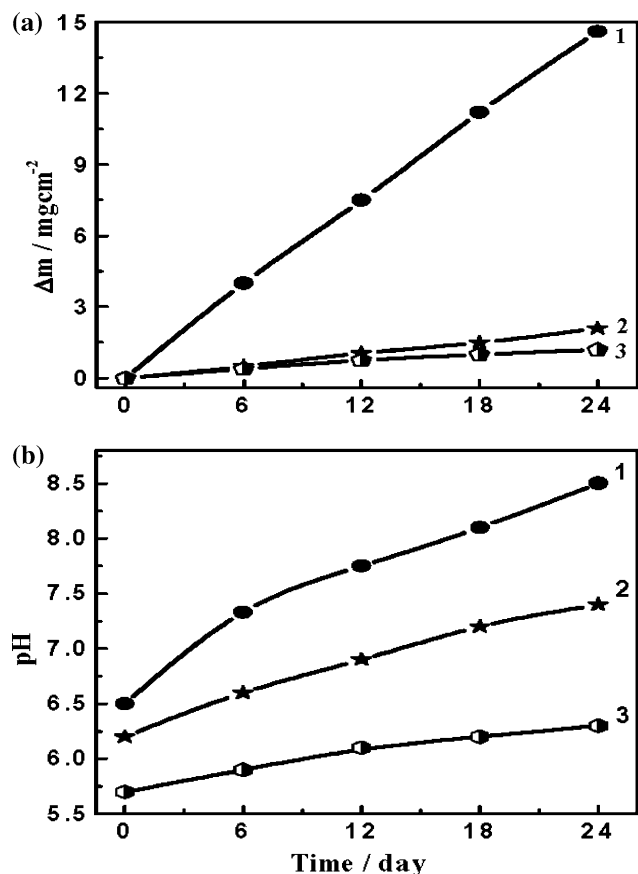


Fig. 1 Variations of the weight loss, Δm (a) and pH (b) with time for copper coupons in aerated solution of 3.5% NaCl containing (1) 0.0 mM, (2) 0.5 mM and (3) 1.0 mM AMTA, respectively

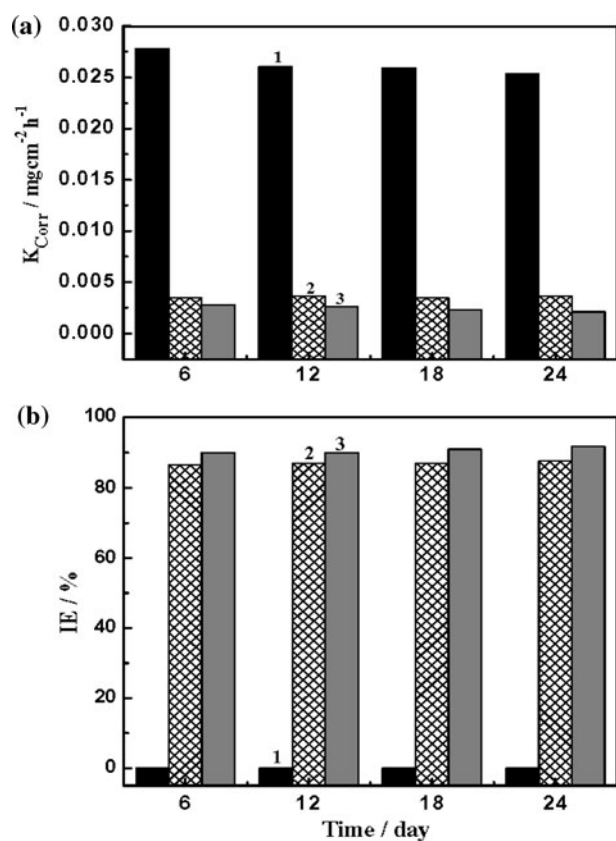


Fig. 2 Change of the corrosion rate (a) and inhibition efficiency (b) with time for copper coupons in aerated 3.5% NaCl solution containing (1) 0.0 mM, (2) 0.5 mM, and (3) 1.0 mM AMTA, respectively

K_{Corr} were recorded when the concentration of AMTA was increased to 1.0 mM. The ability of AMTA to inhibit copper corrosion in the tested chloride solution was also confirmed by plotting the change of the inhibition efficiency (IE%, calculated from weight loss) against time in chloride solution containing (1) 0.0 mM, (2) 0.5 mM, and (3) 1.0 mM as shown in Fig. 2b. The maximum IE% obtained for 0.5 mM AMTA was recorded 88% after 24 days, this value was increased to 92% for 1.0 mM AMTA.

In order to see whether the AMTA molecules are indeed adsorbed on the copper surface, SEM and EDS analyses were carried out. The SEM micrograph obtained for the copper surface after 24 days immersion in 3.5% NaCl containing 1.0 mM AMTA is shown in Fig. 3a. The corresponding EDS profile analysis of the area shown in the SEM micrograph is shown in Fig. 3b. It is obvious from SEM micrograph that the AMTA molecules completely cover the copper surface. The atomic percent of the elements found on the sample surface obtained by EDS was 12.02% carbon, 30.01% nitrogen, 9.72% sulphur, 5.40% oxygen, 5.47% chlorine, and 37.38% copper. The detection of C, N, and S on the surface indicates that the AMTA

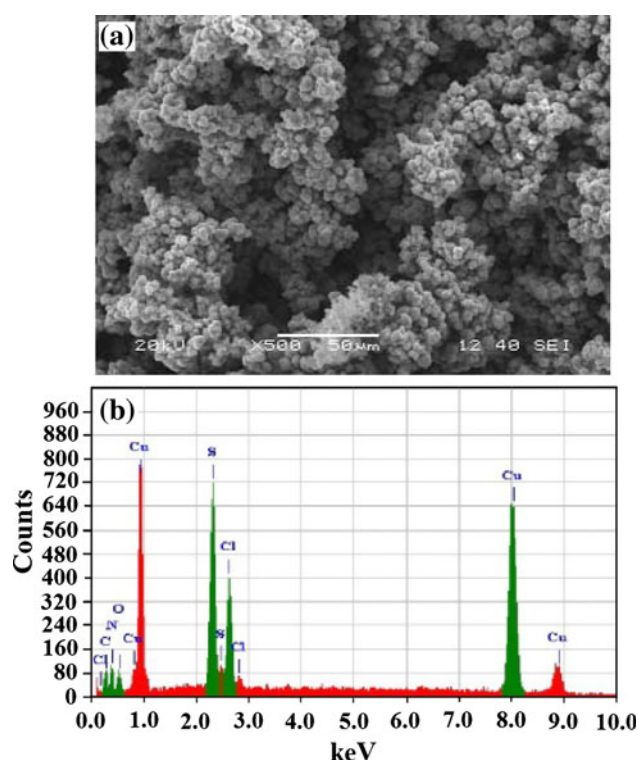


Fig. 3 (a) SEM image of the copper surface obtained after 24 days immersion in 3.5% NaCl containing 1.0 mM AMTA; and (b) EDS profile analysis of the copper surface shown in the micrograph

molecules are indeed strongly adsorbed on the surface, which led to the minimum corrosion rate of copper as well as the high inhibition efficiency of AMTA against corrosion. The presence of oxygen might have resulted from an adherent oxide film due to the presence of oxygen in the solution and/or hydrolysis of CuCl [2, 16, 17] as follows,



The detection of low content of chlorine also reveals that the adsorption of AMTA molecules prevented the formation of cuprous chloride and oxychloride complexes resulted from Eqs. 6 and 8, respectively.

3.2 Potentiodynamic polarization measurements

The potentiodynamic polarization (PDP) curves of the copper electrode in 3.5% NaCl solutions after (a) 0.0 h and (b) 50.0 h of electrode immersion, for different AMTA concentrations; (1) 0.0 mM, (2) 0.5 mM, and (3) 1.0 mM are shown in Fig. 4. It is well known that the cathodic reaction of copper in aerated sodium chloride solutions is the oxygen reduction as represented by Eq. 7 [32, 33]. On the other hand, the anodic reaction at the same condition is the dissolution of copper as has been reported in our

previous study [16–18]. The increase of the immersion time of Cu to 50 h in NaCl solution without inhibitor, Fig. 4b, curve 1, greatly decreased the cathodic current and to some extent the anodic current. This may be due to the accumulation of the corrosion products on the surface with time before obtaining the PDP curves, which led to decreasing the cathodic reaction, Eq. 7, and partially protected the copper surface from further dissolution.

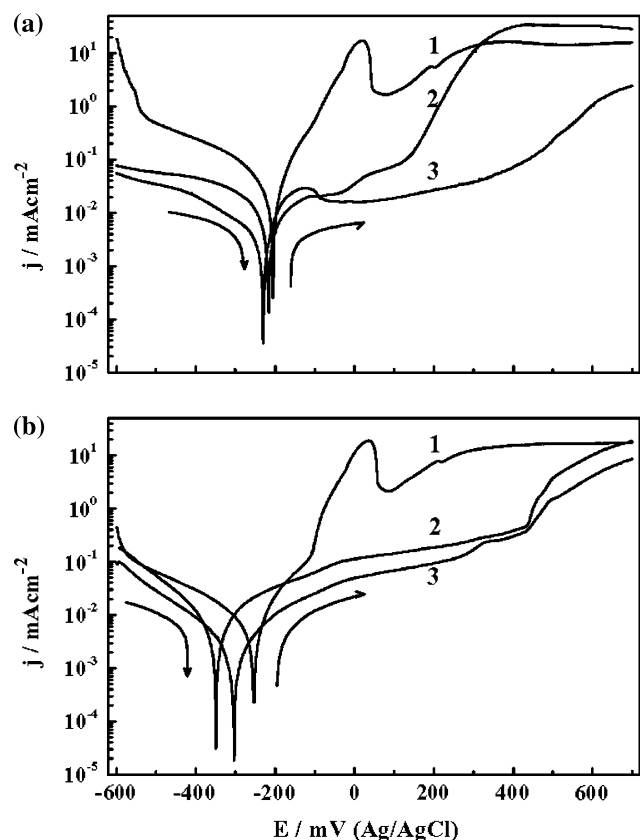


Fig. 4 Potentiodynamic polarization curves for copper electrode in aerated 3.5% NaCl containing (1) 0.0 mM, (2) 0.5 mM, and (3) 1.0 mM AMTA after (a) 0 h and (b) 50 h, respectively. The Potential scan rate was 1 mV s⁻¹

Addition of 0.5 mM AMTA to the chloride solutions for 0 and 50 h of copper immersion significantly decreased the cathodic, corrosion (j_{CORR}), and anodic currents, with the corrosion potential (E_{CORR}) values slightly shifted to the negative direction. This effect increased with increasing the concentration of AMTA to 1.0 mM as well as increasing the immersion time of copper to 50 h before measurements. The j_{CORR} and E_{CORR} values were obtained from the extrapolation of anodic and cathodic Tafel lines located next to the linearized current regions. Other corrosion parameters such as cathodic (β_c) and anodic Tafel (β_a) slopes, polarization resistance (R_p), corrosion rate (K_{CORR}), and the inhibition efficiency (IE%) obtained from Fig. 4 were calculated according to the previous studies [17, 18]; the values of these parameters are listed in Table 1. It is shown in Table 1 that the values of j_{CORR} and K_{CORR} decrease with slight negative shifts in E_{CORR} , while β_c , β_a , R_p , and IE% increase in the presence of AMTA molecules. The decreases in j_{CORR} and K_{CORR} values were mainly due to the adsorption of AMTA molecules on the copper surface for which both the chloride ions attack and Cu dissolution decreased. Furthermore, the increase in the values of β_c and β_a is related to the decrease in the cathodic and anodic currents, respectively. This reveals that the presence of AMTA molecules and the increase of its content in the test solution precluded the electro-dissolution of copper. This effect was remarkably increased with the increase of the immersion time of copper in the solution.

3.3 Chronoamperometric measurements

In order to shed more light on the dissolution of copper and whether pitting corrosion occurs, as well as the effect of AMTA on copper corrosion at a more positive potential value, we measured the variation of current with time at constant potential, 350 mV vs. Ag/AgCl. The current–time curves recorded for copper electrode that was immersed for (a) 0 h and (b) 50 h in 3.5% NaCl containing different AMTA concentrations (1) 0.0 mM, (2) 0.5 mM, and (3)

Table 1 Corrosion parameters obtained from potentiodynamic polarization curves shown in Fig. 4 for copper electrode in 3.5% NaCl solutions in the absence and presence of 0.50 and 1.0 mM AMTA after 0 and 50 h, respectively

Solution	Parameter								
	$\beta_c/\text{mV dec}^{-1}$	$E_{\text{CORR}}/\text{mV}$	$\beta_a/\text{mV dec}^{-1}$	$j_{\text{CORR}}/\mu\text{A cm}^{-2}$	$j_{\text{peak}}/\mu\text{A cm}^{-2}$	$j_{\text{min}}/\mu\text{A cm}^{-2}$	$R_p/\text{k}\Omega \text{ cm}^2$	$K_{\text{CORR}}/\text{mpy}$	IE/%
3.5% NaCl (0 h)	100	-210	48	16	17,000	1,700	0.87	7.33	-
0.5 mM ATT (0 h)	125	-215	59	3.5	60	60	4.73	1.6	78
1.0 mM ATT (0 h)	140	-230	70	1.8	40	15	11.5	0.82	89
3.5% NaCl (50 h)	110	-255	52	3.8	19,000	2,300	4.04	1.74	-
0.5 mM ATT (50 h)	130	-335	85	0.8	100	100	29	0.37	85
1.0 mM ATT (50 h)	145	-305	120	0.3	35	35	95.2	0.14	94

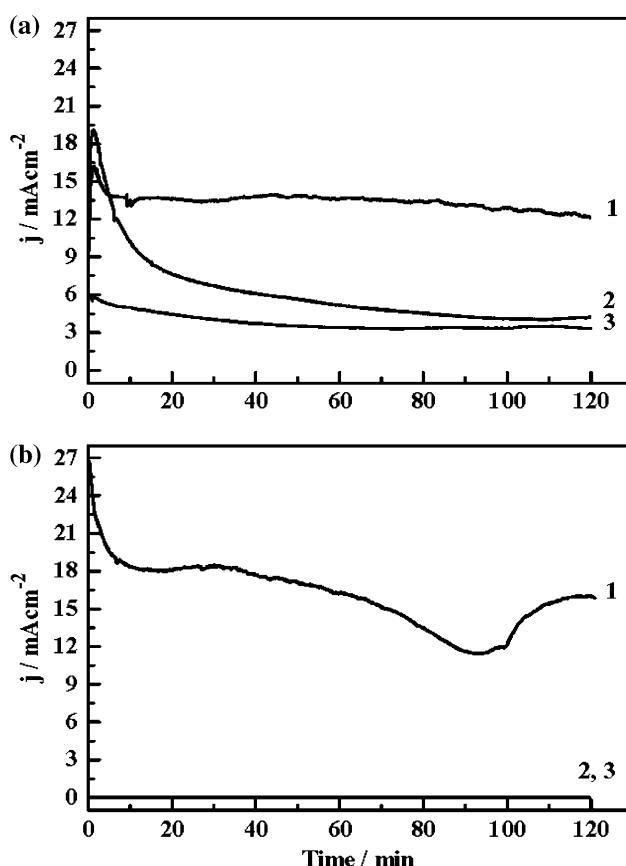


Fig. 5 Chronoamperometric curves of copper electrode that had been immersed in the aerated solution of 3.5% NaCl containing (1) 0.0 mM, (2) 0.5 mM, and (3) 1.0 mM AMTA for (a) 0 h and (b) 50 h, respectively, before the potential was stepped to 350 mV vs. Ag/AgCl

1.0 mM before the potential was stepped to 350 mV (Ag/AgCl) are shown in Fig. 5a and b, respectively. It is seen from Fig. 5a that high currents were recorded for Cu in the chloride solution in the absence of AMTA, curve 1, which was due to the aggressiveness of Cl^- ions toward copper surface. It is noticed that the measured current after 50 h of Cu immersion in 3.5% NaCl solution containing 0.0 mM AMTA, Fig. 5b (curve 1), showed higher values compared to those obtained after 0 h. This was due to the long immersion period of copper in the chloride solution could allow its surface to form a porous layer of Cu_2O , Eq. 10. This porous oxide in turn was hydrolyzed to form a top layer of atacamite as represented by Eq. 8 [31]. The formed atacamite was not protective and not compact enough to decrease the chloride ion attacks. Moreover, the increase of current values with increasing time (Fig. 5b, curve 1) indicated that the occurrence of pitting corrosion was due to further formation of atacamite; the pits could be seen with the naked eye after corrosion products were removed from the copper surface.

Table 2 Change of pH values before and after potentiodynamic polarization and chronoamperometric measurements for copper electrode in aerated 3.5% NaCl solutions in the absence and presence of 0.50 and 1.0 mM AMTA after 0 and 50 h, respectively

Solution	pH		
	Before measurements	After polarization	After chronoamperometric
3.5% NaCl (0 h)	6.50	10.42	10.37
0.5 mM AMTA (0 h)	6.05	7.81	7.84
1.0 mM AMTA (0 h)	5.50	6.90	6.95
3.5% NaCl (50 h)	7.25	9.83	9.13
0.5 mM AMTA (50 h)	6.42	7.12	7.12
1.0 mM AMTA (50 h)	5.79	6.01	6.20

The addition of 0.5 mM AMTA (Fig. 5a, curve 2) showed large decreases in the absolute current. The effect of AMTA was more significant with increasing the time of the experiment. In the presence of 1.0 mM AMTA (Fig. 5a, curve 3), the absolute current values decreased from the first moment of Cu immersion up to the end of the run. This was attributed to the fact that the AMTA molecules at this concentration not only block the corrosion sites but also form a protective layer on the copper surface and hence prevent copper pitting and general corrosions. This effect was clear with increasing the immersion time to 50 h (Fig. 5b, curve 2 and curve 3), where the recorded current values were minimum with no evidence for the occurrence of pitting corrosion.

It is worth mentioning that the increase of the obtained pH values by the loss in weight (Fig. 1b), was also recorded for the test solutions in the absence and presence of AMTA after the polarization and chronoamperometric measurements. Table 2 presents the change of pH values pre and post PDP and CA measurements for copper electrode in aerated 3.5% NaCl solutions in the presence of different AMTA concentrations (1) 0.0 mM, (2) 0.5 mM, and (3) 1.0 mM for 0 and 50 h, respectively. Table 2 shows that the values of pH increased dramatically for the sodium chloride solutions that did not contain AMTA molecules after carrying out both the PDP and CA. On the other hand, the presence of ATMA in the chloride solution highly reduced the values of pH and that effect increased with increasing ATMA concentration to 1.0 mM. This proves that the dissolution of copper was accompanied by an increase in the solution alkalinity and the presence of ATMA protected the copper surface and reduced its dissolution.

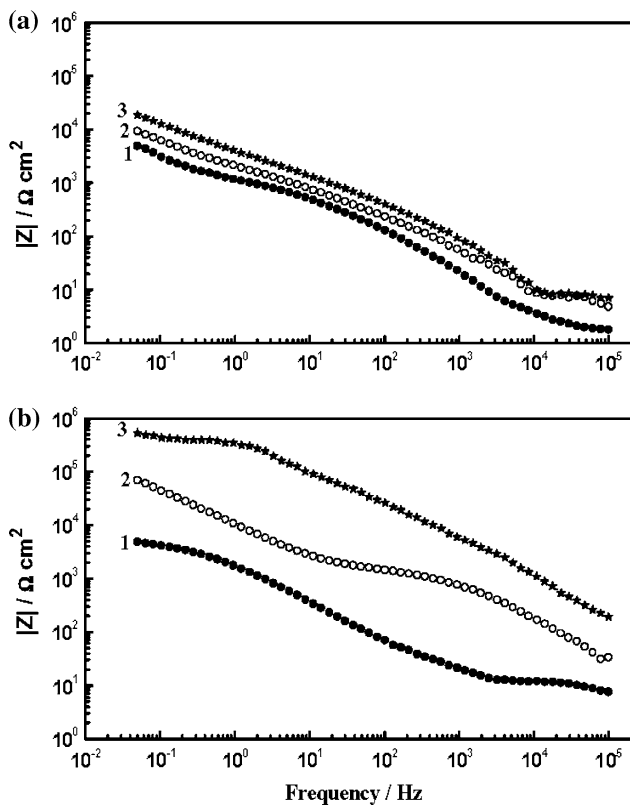


Fig. 6 Bode plots for the copper electrode that was immersed for (a) 0 h and (b) 50 h in 3.5% NaCl solutions containing (1) 0.0 mM, (2) 0.5 mM, and (3) 1.0 mM AMTA

3.4 Electrochemical impedance spectroscopy (EIS) measurements

In order to confirm the data obtained by dynamic polarization and static current–time, we carried out EIS experiments. EIS provides important mechanistic and kinetic information for an electrochemical system under investigation and the method was successfully employed to explain the corrosion and corrosion inhibition on Cu in chloride media [3–6, 8–10, 16, 17, 19]. Typical Bode EIS plots obtained for the Cu electrode at open circuit potential after (a) 0 and (b) 50 h immersion in 3.5% sodium chloride solutions without (1) and with 0.5 (2) and 1.0 mM AMTA (3) are shown in Fig. 6. The impedance of Cu in 3.5% NaCl solution alone, Fig. 6a, curve 1, recorded lower values, especially at high frequency, then increased with decreasing frequency, and finally measured a slight increase at the lowest frequency. After 50 h immersion, Fig. 6b, curve 1, the impedance of Cu in the absence of AMTA attained higher values in comparison to that obtained from the first moment of immersion at the same Cl⁻ concentration. This indicates that the copper was more passivated after 50 h immersion due to the accumulated corrosion products on its surface.

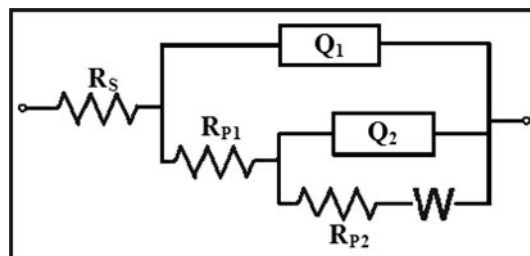


Fig. 7 The equivalent circuit model used to fit the EIS experimental data. The symbols used in the circuit are defined in the text

In the presence of 0.5 mM AMTA, the impedance values of the Cu electrode increased, especially at low frequencies; this effect was increased as the immersion time increased to 50 h and the concentration of AMTA to 1.0 mM. According to Mansfeld et.al [34], the higher the impedance values at low frequencies, the higher the passivation of the metal surface against corrosion. However, our impedance data were analysed by fitting to the equivalent circuit model shown in Fig. 7. This circuit model was also reported in many studies for copper/chloride solution interface [3, 16, 17, 19]. The elements of this model are; R_S the solution resistance, Q_1 and Q_2 constant phase elements (CPEs), R_{P1} polarization resistance, R_{P2} another polarization resistance and can be defined also as the charge transfer resistance, and W the Warburg impedance. R_S , R_{P1} , and R_{P2} have been reported to increase, while the CPEs decrease in the presence of the organic inhibitor and up on the increase of its concentration [3, 16, 17, 19]. The admittance and impedance of a CPE are defined as follows, respectively [35]:

$$Y_{CPE} = Y_0(j\omega)^n \tag{11}$$

$$Z_{CPE} = (1/Y_0)(j\omega)^{-n} \tag{12}$$

where, Y_0 is the modulus, ω is the angular frequency, and n is the phase. The presence of the Warburg impedance (W) characters in the circuit confirms that the mass transport was limited by the surface adsorbed film. In general, EIS results agree with the data obtained by polarization and chronoamperometric measurements and provide further confirmation of the ability of AMTA as a good mixed-type inhibitor for copper corrosion in 3.5% NaCl solutions.

4 Conclusions

Corrosion of copper in 3.5% NaCl solutions and its inhibition by AMTA have been investigated using gravimetric, surface analysis, and electrochemical techniques. Weight loss and pH measurements indicated that the corrosion rate of copper and the corresponding change of pH of the solution highly decreased in the presence of AMTA and

with the increase of its concentration from 0.5 to 1.0 mM. The inhibition efficiency of AMTA rose from 86 to 92% when the concentration increased from 0.5 to 1.0 mM after 24 days of copper immersion. The inhibition of copper corrosion was achieved by the adsorption of AMTA molecules onto its surface as was confirmed by SEM/EDS investigations. Potentiodynamic polarization, chronoamperometric, and EIS experiments revealed that the presence of AMTA and the increase of its content greatly decreased the corrosion parameters. This effect also increased by increasing the immersion time of copper in the test solution from 0 to 50 h. The results are collectively in good agreement and show clearly that AMTA is a good mixed-type inhibitor for copper corrosion in 3.5% NaCl solution.

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