Inhibition of Copper Corrosion Reactions in Neutral and Acidic Chloride Solutions by 5-Ethyl-1,3,4-thiadiazol-2-amine as a Corrosion Inhibitor

El-Sayed M. Sherif

Center of Excellence for Research in Engineering Materials (CEREM), College of Engineering, King Saud University, P. O. Box 800, Riyadh 11421, Kingdom of Saudi Arabia
*E-mail: esherif@ksu.edu.sa

In this study, the inhibition of corrosion reactions on copper surface in open to air solutions of 0.5 M NaCl and 0.5 M of HCl by 5-ethyl-1,3,4-thiadiazol-2-amine (ETDA) was investigated. The study was carried out by using a combination of electrochemical techniques, such as potentiodynamic polarization, chronoamperometry; in addition to electrochemical impedance spectroscopy (EIS) and weight-loss (WtL) measurements. Polarization curves showed that the presence of ETDA and the increase of its concentration in chloride media decrease the corrosion current density and corrosion rate and enhance the polarization resistance for copper. Chronoamperometric and EIS investigations revealed that ETDA molecules decrease the pitting and uniform corrosion of copper through decreasing the absolute currents and increasing the surface and polarization resistances of copper in both NaCl and HCl solutions. This effect was found to remarkably increase with increasing the concentration of ETDA from 1.0 mM to 5.0 mM. WtL results depicted that NaCl and HCl molecules aggressively attack copper causing its fast dissolution with time. WtL data proved also that the presence of ETDA and the increase of its concentration highly preclude the dissolution of copper. The calculated inhibition efficiency of ETDA recorded higher values for copper in NaCl solutions than HCl ones.

1. INTRODUCTION

Copper and its alloys have been widely used in many industrial applications owing to their excellent electrical and thermal conductivities, good mechanical workability and high corrosion resistance. Some of these applications are in electronic industries and communications as a conductor

in electrical power lines, pipelines for domestic and industrial water utilities including sea water, heat conductors, and heat exchangers [1-7]. In spite of a relatively noble potential of copper, its corrosion takes place in a significant rate in chloride containing environments. The formed scale and corrosion products have negative effects on heat transfer and cause a decrease in the heating efficiency of the equipment, which requires periodic de-scaling and cleaning in hydrochloric acid solution. Therefore, the corrosion of copper and its inhibition in a wide variety of media, particularly when they contain chloride ions, have attracted attention of a number of investigators [8-16].

Heterocyclic compounds, especially nitrogen-based ones such as azole derivatives, are effective inhibitors, being coordinate with Cu^0, Cu^+ or Cu^{2+} via their nitrogen atoms through lone pair electrons to form polymeric complexes with copper [15-20]. These form an adsorbed protective film on the copper surface, providing inhibition of corrosion by acting as a barrier to aggressive ions such as chloride [18–21]. It is generally believed that polar functional groups such as nitrogen, sulfur, and oxygen as well as conjugated double bonds are considered reaction centers in establishing the adsorption process [16-23].
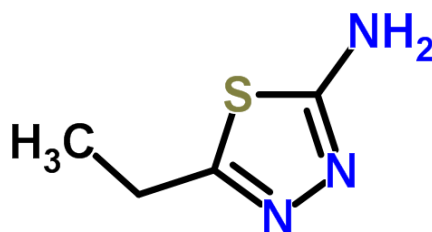

Figure 1. 5-ethyl-1,3,4-thiadiazol-2-amine (ETDA).

The objective of the present work was to report the corrosion and corrosion inhibition of copper corrosion reactions in 0.5 M NaCl and 0.5 M HCl solutions by the heterocyclic azole compound 5-ethyl-1,3,4-thiadiazol-2-amine (ETDA) whose chemical structure is shown in Fig. 1. It was anticipated that ETDA would be effective in the present case since it is a heterocyclic compound containing a variety of donor atoms; typically three nitrogen groups, a sulphur group, and an ethyl group whose presence increases the ability of the nitrogen and sulphur groups to be adsorbed onto the copper surface. Moreover, ETDA is nontoxic and inexpensive azole derivative compound. Several techniques including conventional electrochemical, impedance spectroscopy and weight-loss were used in this study.

2. EXPERIMENTAL DETAILS

Sodium chloride (NaCl, 99.99%), hydrochloric acid (HCl, 35-37%), 5-ethyl-1,3,4-thiadiazol-2-amine (ETDA, 97%), and absolute ethanol (C_2H_5OH, 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), a platinum foil, and an Ag/AgCl electrode (in saturated KCl) were used as working, counter, and reference electrodes, respectively. The copper electrodes were polished successively with emery paper of increasing fineness of up to 600 grits, and further with 5 through 0.3 µm alumina slurries. The electrode was then washed with doubly distilled water, degreased with acetone, washed using doubly distilled water again and finally dried with pure nitrogen.

Electrochemical experiments were collected by using the Potentiostat / Galvanostat EG&G Model 273A, Princeton Applied Research (PAR). For potentiodynamic polarization experiments, the potential was scanned from -0.55 to 0.55 V versus Ag/AgCl at a scan rate of 0.001 V/s. Chronoamperometric current-time experiments were carried out by stepping the potential at 0.3 V for 60 min. Electrochemical impedance spectroscopy (EIS) measurements were performed by using a Solatron SI 1255 HF frequency response analyzer along with the PAR Potentiostat / Galvanostat EG&G model 273A. The instruments were controlled by the EG&G M398 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. The EIS measurements were carried out at an open circuit potential after 60 min immersion of the copper electrode in the NaCl and HCl solutions free and containing the desired concentrations of ETDA.

The weight loss experiments were carried out using cylindrical copper coupons (Goodfellow, 99.999%) having a dimension of 5.10 cm diameter, 0.20 cm height, and the exposed total area of 42.4 cm^2. The coupons were polished and dried as for the case of copper rods, weighted, and then suspended in a 200 cm^3 solution of 0.5 M NaCl and 0.5 M HCl with and without the desired concentrations of ETDA for different exposure periods varied from 2 hours to 240 hours. The corrosion rate (K_{Corr}, mg cm^{-2} h^{-1}) of copper coupons was calculated from the weight-loss data as follows [24-30];

$$K_{Corr} = \left(\frac{m_i - m_f}{At} \right) \qquad (1)$$

Where, m_i and m_f are the weighs of the copper coupon per gram before and after its immersion in the test solution, respectively; A is the area of the copper coupon per cm^2; and t is the immersion time per hour. The percentages of the inhibition efficiency (IE %) for copper in the chloride solutions containing ETDA were calculated also according to the following equation [20,31,32];

$$IE \% = 100 \left(\frac{K_{Corr}^i - K_{Corr}^f}{K_{Corr}^i} \right) \qquad (2)$$

Here, K_{Corr}^i and K_{Corr}^f are the corrosion rates of copper coupons in the chloride solutions without and with ETDA molecules present, respectively.

All solutions were prepared using doubly distilled water (99.0% vol.) and ethanol (1.0% vol.) and all measurements were carried out at room temperature.

3. RESULTS AND DISCUSSION

3.1. Potentiodynamic polarization data

The potentiodynamic polarization curves for copper electrode in (a) 0.5% M NaCl and (b) 0.5 M HCl solutions containing (1) 0.0 mM, (2) 1.0 mM and (3) 5.0 mM ETDA, respectively are shown in Fig. 2. It is clearly seen from Fig. 2 (curves 1) that the highest cathodic and anodic currents are recorded for copper in NaCl and HCl solutions in the absence of ETDA. The cathodic reaction for metals and alloys including copper in open to air near neutral solutions has been reported [33-38] to be either the water or the oxygen reduction depending on the percentage of oxygen in the solution according to the following equations, respectively;

$$2H_2O + 2e^- = H_2 + 2OH^- \tag{3}$$

$$O_2 + 2H_2O + 4e^- = 4OH^- \tag{4}$$

It is well known also [3,4,39] that the cathodic reaction for copper in open to air 0.50 M HCl solutions is the oxygen reduction as follows;

$$O_2 + 4H^+ + 4\,e^- = 2H_2O \tag{5}$$

This is because Cu is nobler than H^+ in the electromotive series, a cathodic reaction other than the displacement of H^+ must account for metal dissolution. This is readily available in terms of O_2 reduction from solution [39].

On the other hand, the anodic reaction of pure copper in 0.5 M NaCl and 0.5 M HCl solutions is the dissolution of Cu to Cu^+ as follows [3,4,31,32];

$$Cu = Cu^+ + e^- \quad (fast) \tag{6}$$

$$Cu^+ = Cu^{2+} + e^- \quad (slow) \tag{7}$$

The resulted cuprous cation, Cu^+, reacts in a fast reaction than Cu^{2+} does with Cl^- from the solution to form a partially protective layer of CuCl on the copper electrode surface as follows [10,40,41],

$$Cu^+ + Cl^- = CuCl \tag{8}$$
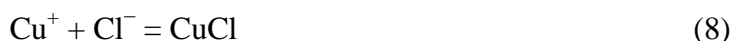
The formed CuCl transforms to the soluble cuprous chloride complex, $CuCl_2^-$ [31,32],

$$CuCl + Cl^- = CuCl_2^- \tag{9}$$

Once $CuCl_2^-$ is formed at the surface of copper electrode, it will diffuse into the bulk solution or will dissolve by oxidation causing the copper dissolution,
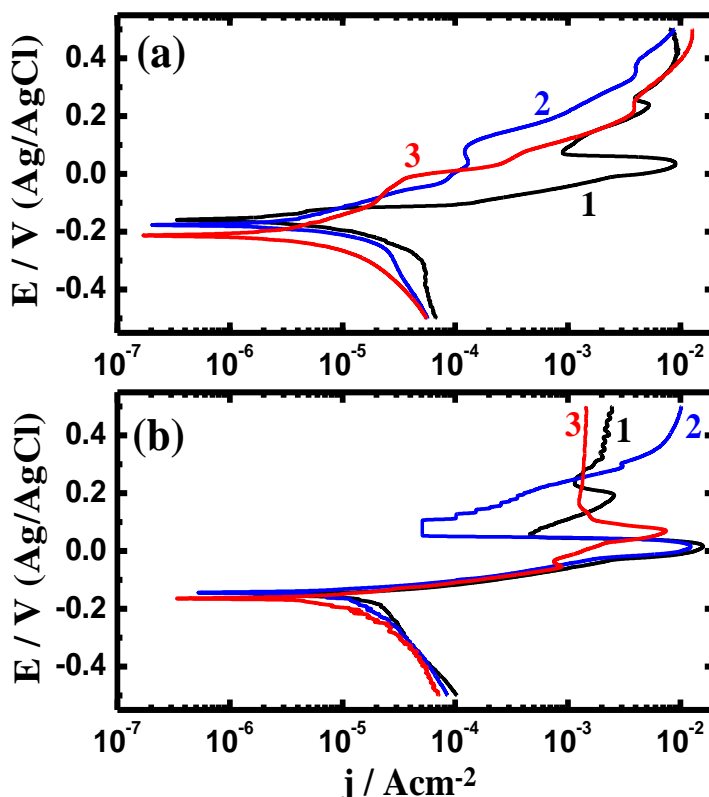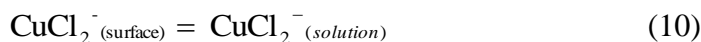
$$CuCl_2^-{}_{(surface)} = CuCl_2^-{}_{(solution)} \qquad (10)$$

$$CuCl_2^-{}_{(surface)} = Cu^{2+} + 2Cl^- + e^- \qquad (11)$$

Figure 2. Potentiodynamic polarization curves for the copper electrode in aerated solutions of (a) 0.5 M NaCl and (b) 0.5 M HCl, (1) in the absence and (2) presence of 1.0 mM and (3) 5 mM ETDA, respectively.

The presence of 1.0 mM ETDA in the chloride solutions as shown in Fig. 2 (curves 2) shifted the corrosion potential (E_{Corr}) values slightly in the more negative direction and remarkably reduced the cathodic, corrosion current density (j_{Corr}), and anodic currents. This effect was greatly increased with increasing the ETDA concentration to 5.0 mM. The values of the corrosion parameters obtained from the curves of Fig. 2, E_{Corr}, j_{Corr}, cathodic (β_c) and anodic (β_a) Tafel slopes, corrosion rate (K_{Corr}), polarization resistance (R_P), and the percentage of the inhibition efficiency (IE%) for copper by the different concentrations of ETDA, are listed in Table 1. The calculations of all these parameters were made according to the previous work [42-49]. The results together from Fig. 2 and Table 1 indicated that the presence of ETDA molecules and the increase of its concentration decrease the values of K_{Corr} and raise the values of R_P and IE%. The data also showed that ETDA is a better corrosion inhibitor for

copper in NaCl than HCl solutions at the same concentration and this is because the corrosivity of HCl is higher than that for NaCl.

Table 1. Corrosion parameters obtained from polarization curves shown in Fig. 2 for copper in 0.5 M NaCl and 0.5 M HCl solutions in absence and presence of ETDA molecules.

Solution	Parameter						
	$\beta_c/$ mVdec^{-1}	$E_{Corr}/$ mV	$\beta_a/$ mVdec^{-1}	$j_{Corr}/$ μAcm^{-2}	Rp/ kΩcm^2	$K_{Corr}/$ mmpy	IE/ %
0.5 M NaCl alone	60	-160	25	3.5	2.19	0.041	−
+1.0 mM ETDA	65	-183	100	1.4	12.23	0.016	60.0
+ 5.0 mM ETDA	69	-215	112	1.0	18.56	0.012	71.4
0.5 M HCl alone	130	-153	35	18	0.666	0.210	−
+1.0 mM ETDA	160	-156	39	10.5	1.298	0.122	44.5
+ 5.0 mM ETDA	190	-162	50	7.8	2.206	0.091	56.7

3.2. Chronoamperometric current-time measurements

The change of the current versus time for the copper electrode at 0.3 V (against Ag/AgCl) in open to air solutions of (a) 0.5 M NaCl and (b) 0.5 M HCl without ETDA (1) and with 1.0 mM ETDA (2) 5.0 mM ETDA (3) present, respectively is depicted in Fig. 3. The current of copper electrode in 0.5 M NaCl solution without inhibitor present, curve 1, started from very high values and decreased before increasing again in the first few moments. This behavior is due to the sudden shift of potential for copper from the negative corrosion potential to 0.3 V and the aggressive action of the chloride ions. After about 180 sec, the current decreased rapidly at first then slightly continue decreasing till the end of the experiment. The current of copper in HCl solution alone, Fig. 3b (curve 1) shows almost similar behavior. In this case, the copper recorded the highest absolute current values as a result of its dissolution by the corrosive attack of Cl¯ ions. The initial increase of current occurs because copper dissolves at first to cuprous cations, Eq. (6), that react in turn with Cl¯ ions from the solution to form CuCl and further CuCl$_2$¯as seen in Eq. (7) and Eq. (8), respectively. The final decreases for current with time are due to the formation of a porous oxide layer (Cu$_2$O) as follows [7,9],

$$2CuCl_{ads} + H_2O = Cu_2O + 2H^+ + 2Cl^- \qquad (12)$$
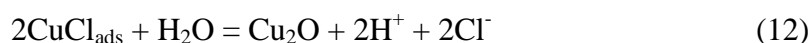
The formation of the oxide layer provides partial protection and does not allow the current to increase. The overall reaction for copper corrosion in an acidic chloride solution can be represented as follows [50];
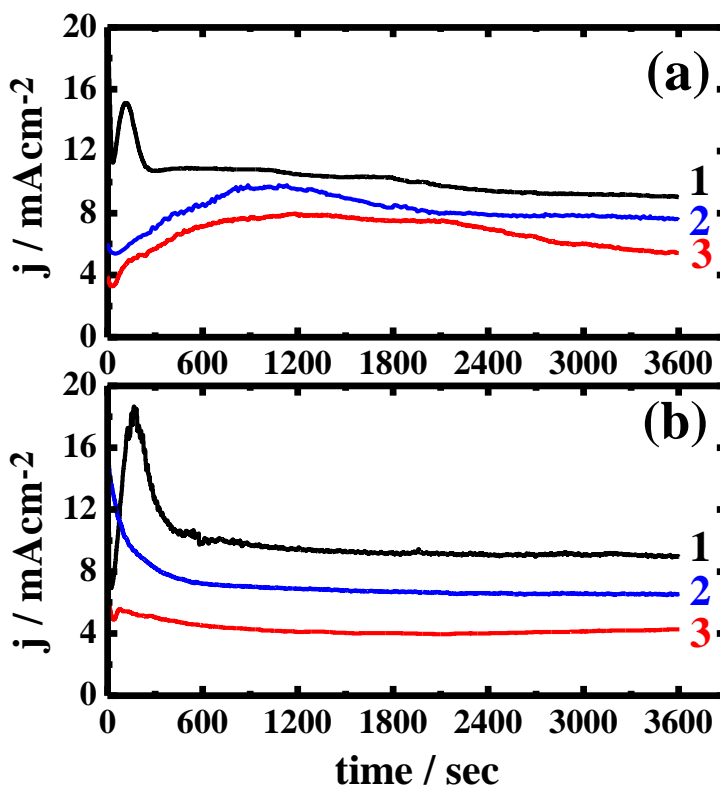
$$2Cu + 4HCl + O_2 = Cu^{2+} + 4Cl^- + 2H_2O \qquad (13)$$
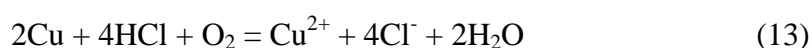
Figure 3. Chronoamperometric current-time curves obtained for the copper rod in aerated solutions of (a) 0.5 M NaCl and (b) 0.5 M HCl, (1) in the absence and (2) presence of 1.0 mM and (3) 5 mM ETDA, respectively.

The release of cupric cations, Cu^{2+} (Eq. 13), increases the dissolution of copper and explains the reason why the absolute current values for copper in HCl solution are higher than those for copper in NaCl solution at the same condition. This is also because and in the presence of metallic copper, Cu^{2+} ions are subject to dismutation, which is competitive with the corrosion reaction,

$$Cu^{2+} + Cu^0 = 2Cu^+ \qquad\qquad (14)$$

It is clearly seen that the addition 1.0 mM ETDA to the neutral and acidic chloride solutions, curves 2 of Fig. 3, reduced the absolute current values along the whole time of the experiment. This effect was greatly increased when the concentration of ETDA was increased to 5.0 mM as can be seen from Fig. 3 (curves 3). This behavior confirms the data obtained from polarization curves shown in Fig. 2 that the ETDA molecules adsorb on the copper to preclude its surface from being attacked by the chloride ions.

3.3. Electrochemical impedance spectroscopy (EIS) measurements

The EIS Nyquist plots obtained for the copper electrode at an open circuit potential after 60 min immersion in (a) 0.5 M NaCl and (b) 0.5 M HCl solutions, (1) in the absence and (2) presence of

1.0 mM ETDA and (3) 5.0 mM ETDA, respectively are shown in Fig. 4. It is clearly seen from Fig. 4a that only once semicircle is shown for copper in NaCl solution. The diameter of the semicircle increases in the presence of ETDA and with the increase of its content. The Nyquist plot for copper in HCl solution, Fig. 4b (curve 1), showed a single semicircle followed by a segment; the diameter of the semicircle also increases with ETDA concentration. The semicircles at high frequencies in Fig. 4 are generally associated with the relaxation of electrical double layer capacitors and the diameters of the high frequency semicircles can be considered as the charge transfer resistance. This indicates that ETDA increases the resistance of copper surface against corrosion in chloride solutions.

In order to understand the mechanistic and kinetic information for electrochemical systems under investigation, the spectra shown in Fig. 4a and Fig. 4b were analyzed by fitting it to the equivalent circuit models shown in Fig. 5a and Fig. 5b, respectively. The parameters obtained by fitting the equivalent circuits along with the values of the percentage of the efficiency (IE%) are listed in Table 2 and Table 3, respectively. The parameters of the circuits shown in Fig. 5 can be defined according to usual convention as, R_s represents the solution resistance, R_{p1} the polarization resistance, Q_1, Q_2 and Q the constant phase elements (CPEs), R_{p2} another polarization resistance, W the Warburg impedance, and C_{dl} the double layer capacitance. It is seen from Fig. 5, Table 2 and Table 3 that the R_s, R_{p1}, and R_{p2} values recorded for copper in Cl^- solutions increase in the presence of ETDA and further with increasing its concentration.
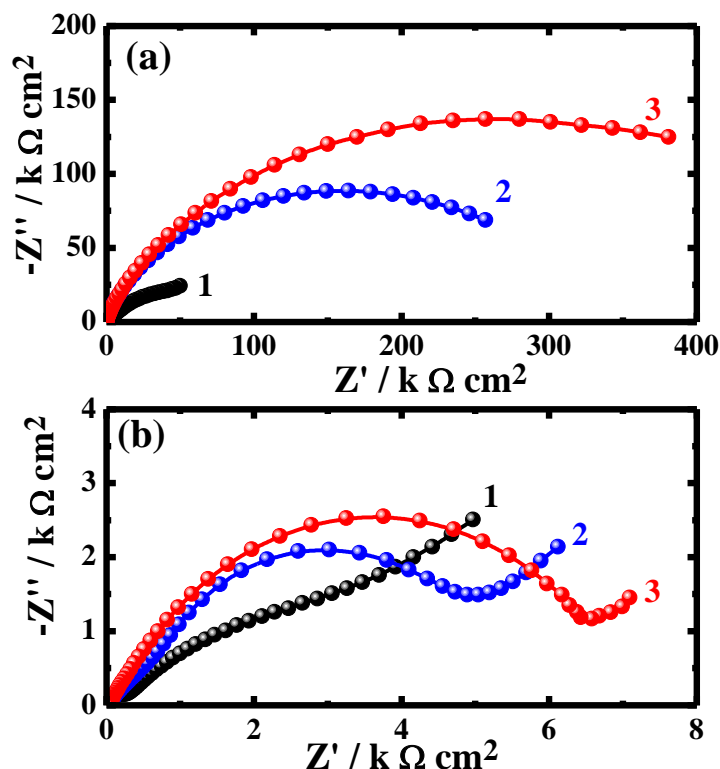

Figure 4. EIS Nyquist plots obtained for the copper rod in aerated solutions of (a) 0.5 M NaCl and (b) 0.5 M HCl, (1) in the absence and (2) presence of 1.0 mM and (3) 5 mM ETDA, respectively.

The constant phase elements (CPEs, Q1) with their n values close to 1.0 represent double layer capacitors with some pores; the CPEs (Q2 in Table 2 and Q in Table 3) are almost like Warburg impedance when their n values close to 0.5; and the Cdl. All these parameters decrease in the presence of ETDA and upon the increase of its concentration in both NaCl and HCl solutions. This was expected to cover the charged copper surfaces, which lead to reducing the capacitive effects. The presence of the Warburg (W) impedance indicates that the mass transport is limited by the surface adsorbed layer on the Cu surface. The values of IE% were also calculated from EIS data as reported in our previous work [24-26]; these values confirm that ETDA has good inhibition efficiency for copper in chloride media and its ability increases with increasing its content in the solution.
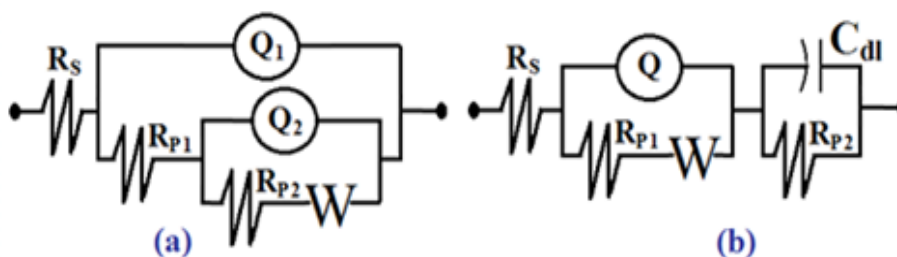

Figure 5. The equivalent circuit models (a) and (b) used to fit the experimental data presented in Fig. 4a and Fig. 4b, respectively.

Table 2. EIS parameters obtained by fitting the plots shown in Fig. 4a with the equivalent circuit model shown in Fig. 5a for copper in 0.5 M NaCl solutions in absence and presence of ETDA molecules.

Solutions	Parameters								
	Rs Ωcm^2	Q1		$Rp1$ $k\Omega cm^2$	Q2		$Rp2$ $k\Omega cm^2$	W/ $\Omega S^{-1/2}$	IE %
		Y_{Q1} μFcm^{-2}	n		Y_{Q2} μFcm^{-2}	n			
0.5 M NaCl alone	111	0.91	0.91	81	9.31	0.01	2.82	1.69E-5	-
+1.0 mM ETDA	114	0.458	0.93	672	2.07	0.50	3558	3.1E-6	87.9
+ 5.0 mM ETDA	139	0.244	0.93	8948	1.478	0.54	5078	4.13E-5	99

Table 3. EIS parameters obtained by fitting the plots shown in Fig. 4b with the equivalent circuit model shown in Fig. 5b for copper in 0.5 M HCl solutions without and with of ETDA molecules.

Solutions	Parameters							
	Rs Ωcm^2	Q		$Rp1$ $k\Omega cm^2$	W/ $\Omega S^{-1/2}$	C_{dl} $\mu F/cm^{-2}$	$Rp2$ $k\Omega cm^2$	IE %
		Y_Q $\mu F/cm^{-2}$	n					
0.5 M HCl alone	31.5	0.96	0.57	4.28	5.29 E-5	96.8	0.165	-
+1.0 mM ETDA	33.58	0.427	0.65	11.11	6.1E-5	0.35	3.18	61.5
+5.0 mM ETDA	41.4	0.326	0.70	21.05	9.78E-5	0.25	3.86	79.7

3.4. Weight-loss measurements

The variation of the corrosion rat (K_{Corr}, mg cm^{-2} h^{-1}, calculated using Eq. (1)) as a function of time (t, h) for the copper coupons in open to air solutions containing (a) 0.5 M NaCl and (b) 0.5 M HCl in the absence of ETDA (1) and presence of 1.0 mM ETDA (2) and 5.0 mM ETDA (3), respectively is shown in Fig. 6. For copper in 0.5 M NaCl solution containing no ETDA molecules, curves 1, the corrosion rate recorded the highest value at the shorter immersion period, 48 h; this is because the fresh copper surface dissolves fast till it develops a layer of corrosion products and/or oxide film.
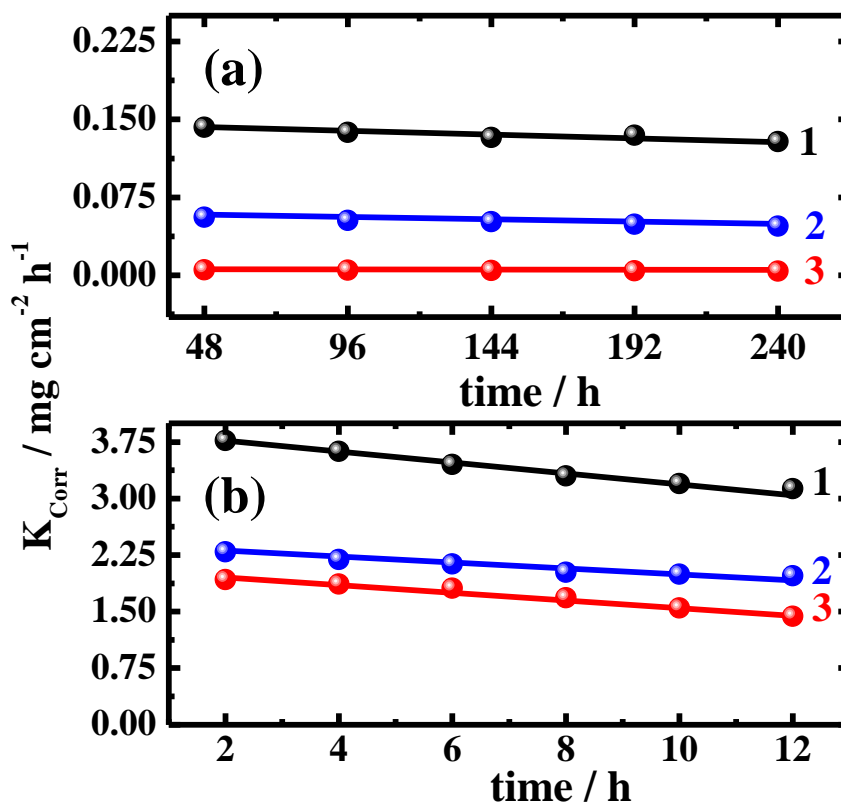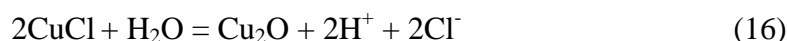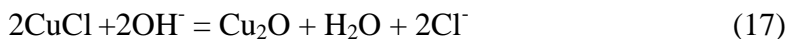

Figure 6. The corrosion rate - time relationship for copper coupons in (a) 0.5 M NaCl and (b) 0.5 M HCl solutions containing (1) 0.0 mM (2) 1.0 mM and (3) 5.0 mM ETDA, respectively.

The values of K_{Corr} decreased after that with increasing the exposure time due to the thickening of the formed oxide film, Cu_2O, and the accumulation of other corrosion products on the copper surface. The oxide film on the copper surface may be formed as shown in Eq. (12) and/or as a result of other reactions as follows;

$$2Cu + \tfrac{1}{2} O_2 = Cu_2O \qquad\qquad (15)$$

$$2CuCl + H_2O = Cu_2O + 2H^+ + 2Cl^- \qquad\qquad (16)$$

$$2CuCl + 2OH^- = Cu_2O + H_2O + 2Cl^- \qquad (17)$$

In this case and in the absence of ETDA, the hydrolysis of the oxide layer in the presence of Cl$^-$ occurs to form a top layer of atacamite according the following reaction,

$$Cu_2O + Cl^- + 2H_2O = Cu_2(OH)_3Cl + H^+ + 2e^- \qquad (18)$$

The formation of atacamite layer, $Cu_2(OH)_3Cl$, partially protects the copper surface and leads to the decrease of K_{Corr} with time. On the other hand, the copper corrodes faster in HCl solution, Fig. 6b (curve 1) and the K_{Corr} of copper in this case recorded more than 10 times higher than its value for copper in NaCl solutions. This confirms the data obtained by electrochemical experiments that HCl is more aggressive solution than NaCl at similar concentration. The addition of 1.0 mM ETDA to the chloride solutions Fig. 6 (curves 2) led to great decreases of K_{Corr} value with increasing the immersion time and this effect increased with increasing ETDA concentration to 5.0 mM. This is attributed to the ability of ETDA molecules to be adsorbed strongly by forming a protective layer on the copper surface preventing it from being corroded easily.
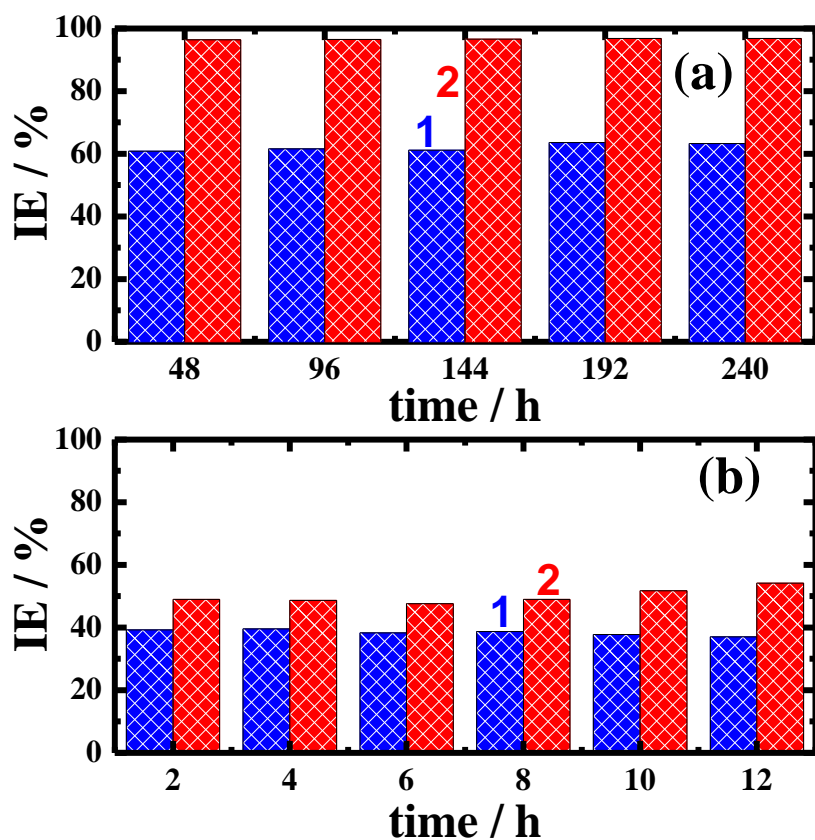

Figure 7. The percentage of the inhibition efficiency (IE%) versus time for copper coupons in (a) 0.5 M NaCl and (b) 0.5 M HCl solutions containing (1) 1.0 mM and (2) 5.0 mM ETDA, respectively.

In order to confirm the ability of ETDA molecules on the inhibition of copper surface in chloride solutions under investigation, the percentage of the inhibition efficiency (IE%) values were calculated according to Eq. (2). The changes of the IE% values versus time for copper coupons in (a) 0.5 M NaCl and (b) 0.5 M HCl solutions containing (1) 1.0 mM and (2) 5.0 mM ETDA, respectively are shown in Fig. 7. It is clearly seen that 1.0 mM ETDA, Fig. 7a (column 1) recorded circa 60% efficiency for copper in NaCl solution after 48 h immersion time and increased to ~ 63% in 240 h. Increasing the concentration of ETDA to 5.0 mM, Fig. 7a (column 2) raises the value of IE% to about 97% at all exposure periods. On the other hand and for the copper coupons in HCl solutions, Fig. 7b, the value of IE% at 1.0 mM ETDA recorded almost 40% increased to 55% when the concentration of ETDA was increased to 5.0 mM. The gravimetric experiments thus confirmed the results obtained by polarization, chronoamperometry and EIS that EDTA is a good corrosion inhibitor for copper in NaCl and HCl solutions and its ability increases with the increase of its concentration.

4. CONCLUSIONS

The corrosion and corrosion inhibition of copper in freely aerated neutral and acidic chloride solutions, namely 0.5 M NaCl and 0.5 M HCl, by 5-ethyl-1,3,4-thiadiazol-2-amine (ETDA) were reported using potentiodynamic polarization, chronoamperometry, electrochemical impedance spectroscopy and weight-loss measurements. It was found that the corrosion of copper in HCl solutions proceeds faster than in NaCl ones. The presence of ETDA and the increase of its concentration decrease the corrosion current and connectively the corrosion rate of copper through increasing its corrosion resistance. The inhibition efficiency of ETDA increases with the increase of its concentration from 1.0 mM to 5.0 mM and its value on the copper surface in NaCl solutions was higher than that obtained in HCl solutions. The gravimetric weight-loss experiments confirmed the data obtained by polarization, chronoamperometric current-time at 0.3 V vs. Ag/AgCl, and impedance spectroscopy. All these results proved that ETDA is a good corrosion inhibitor for copper in 0.5 M NaCl and 0.50 M HCl solutions by increasing the corrosion resistance of copper and preventing its surface from being attacked by preventing the formation of cuprous chloride and cuprous chloride complex.

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