

Inhibition of 90Cu10Ni Alloy with 1-phenyl 1-H-tetrazole 5-thiol in Chloride Solution in Absence and Presence of Sulfide

Mohammad H. BinSabt^{*}, Faizah M. Al-Kharafi, Ahmed Abdel Nazeer, Ahmed Galal

Department of Chemistry, Faculty of Science, Kuwait University, P.O. Box 5969 Safat 13060, Kuwait

^{*}E-mail: binsabtm@gmail.com

Received: 22 October 2016 / Accepted: 29 November 2016 / Published: 30 December 2016

The inhibiting effect of 1-phenyl 1-H-tetrazole 5-thiol (PhTT) on corrosion of copper-nickel alloy, 90Cu-10Ni, in different electrolytes was studied. Polarization measurements were performed in sodium chloride solution in absence and presence of sulfide ions. The surface morphology and its structure were examined using SEM and EDX to evaluate the effect of using inhibitor. In absence of sulfide the inhibition in the studied media was attributed to the formation of protective film of Cu⁺-tetrazole on the alloy surface. The rate of inhibition decreases with increasing temperature and the activation energy for the corresponding processes were determined. The presence of sulfide decreases the inhibition due to the incorporation of sulfur in the protective film that enhances the corrosion. SEM images revealed the formation of protective layers on the alloy surface in presence of PhTT which is affected in presence of sulfide with the inhibitor. In absence of sulfide EDX showed the presence of carbon, sulfur and nitrogen on alloy surface that proved the presence of the inhibitor on the alloy surface which decreases in presence of sulfide. The composition of the protective layer in polluted and non-polluted media studied with EDX was compared to the results obtained from the inductively coupled plasma analyses of the ions in the electrolyte side.

Keywords: 90Cu-10Ni alloy; Corrosion Inhibition; Sulfide; PhTT; SEM; EDX; ICP.

1. INTRODUCTION

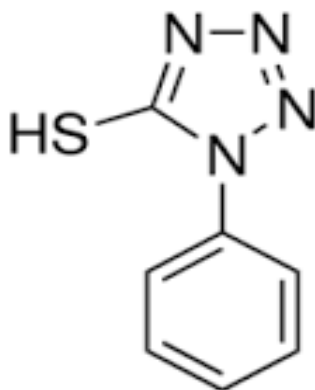
Copper and its alloys possess favorable combinations of excellent electrical, thermal and mechanical properties that justify its use in power generation, fresh water supply lines, desalination, and petrochemical industries [1-4]. Formation of protective and adherent film of corrosion products namely (Cu₂O), (Cu₂(OH)₃Cl), (CuO) and other oxides of the alloying elements resulted in its stability in these environments [5, 6]. Among the copper alloys, 90Cu10Ni alloy has been extensively studied

in different environments and still attracting increasing attention to understand its performance in different working conditions. In spite of the remarkable resistance of this alloy towards the influence of several chemicals and atmosphere, it is still susceptible to corrosion in aggressive media. In chloride containing solutions it forms unstable and non-protective film of CuCl [7]. Moreover, its corrosion is promoted by sulfide present in the seawater from industrial waste discharge, sulfide reducing bacteria and seaweed [8]. In presence of sulfide the most significant corrosion product was non-protective black layer of Cu₂S [9]. Many researchers studied the aggressive effects of common pollutants on the corrosion behavior of copper and its alloys, particularly of sulfide ions [10-16].

One of the effective procedures used to protect metals and alloys against corrosion in many industries is the administration of organic corrosion inhibitors. The protection was explained by the presence of heteroatoms (S, N, P, and Se) in the molecular structure of the inhibitors [17]. In absence of sulfide it is found that the azoles form protective barriers of polymeric Cu(I) complex covering the initially formed Cu₂O on copper surface [18].

Azoles are the most common corrosion inhibitors used for copper and its alloys in industry. The inhibition effect of these compounds is based on their chelating action and formation of an insoluble film on the electrode surface which suppress the metal oxidation [18]. Many researchers reported the inhibiting effect of azoles in different environments [19-22]. They concluded that the azoles show marked corrosion inhibition efficiency for copper base alloys. The inhibiting effect of different tetrazole derivatives namely, 5-mercapto-1-methyl-tetrazole (5Mc-1Me-T), 5-mercapto(Na salt)-1-methyl-tetrazole (5NaMc-1Me-T), 5-mercapto-1-acetic acid (Na salt)-tetrazole (5Mc-1Ac-T), 5-mercapto-1-phenyl-tetrazole (5Mc-1Ph-T), 5-phenyl-tetrazole (5Ph-T) and 5-aminotetrazole (5NH₂-T) were studied in 0.1M NaCl solution [23]. In this study [23], the effect of pH (from 4 to 8) and temperatures (from 40 to 80 °C) were also recorded. The data show good inhibition efficiency of these compounds except in case of 5Mc-1Ac-T which promotes the corrosion. The inhibition was explained on the basis of adsorption mechanism and formation of complex with the surface metal. Also, 5-mercapto-1-phenyltetrazole (PMT) was found to be good inhibitor for different metals against the corrosion in different acidic media due to the adsorption on metal surface through the sulfur atom or coordination with nitrogen from the tetrazole ring [24-26]. PMT has good inhibition efficiency for copper in nitric acid compared to 1,2,3,4-tetrazole (TTZ), 5-amino-1,2,3,4-tetrazole (AT) and 1-phenyl-1,2,3,4- tetrazole (PT) [27]. The inhibiting effect of 5-mercapto-1phenyl-tetrazole (5-MPhTT) in sulfuric acid solution was also investigated. The inhibition reaches more than 99% and the inhibition interpreted by the chemisorptions of 5-MPhTT on metal surface [28]. Ye et. al, studied the composition of the protective film formed in presence of 5-MPhTT and found that it was composed of insoluble polymeric Cu(I) complex formed over Cu₂O that naturally present on the metal surface [29].

The aim of the current work is to study the inhibiting action of 1-phenyl 1-H-tetrazole 5-thiol on 90Cu-10Ni alloy in sulfide polluted and non-polluted media of 0.58M NaCl. The inhibitor performance in presence and absence of sulfide ions will be compared. It will be important to investigate the composition of the protective films in the different electrolytes. The molecule used in this work is 1-phenyl 1-H-tetrazole 5-thiol (PhTT) whose formula is shown in Scheme 1.



Scheme 1. Molecular structure of 1-phenyl 1-H-tetrazole 5-thiol

2. EXPERIMENTAL AND METHODS

The working electrode was prepared from Cu-Ni alloy sheets with composition given in Table 1. The Cu-Ni alloy was purchased from Goodfellow Company (England). Samples for all electrodes used have a geometrical area of 1.0 cm^2 made of sheets 2 mm thick were embedded in a Teflon holder and were exposed to the solution. The electrodes were polished with fine emery paper of SiC 400 to 1000 grit and alumina powder ($0.05 \text{ }\mu\text{m}$) followed by ultrasonication in a distilled water bath. Electrochemical cell is a one compartment glass-cell that is provide with a Teflon cap equipped with gas purge. All chemicals are AnalaR-grade and were used as received without further purification. Sodium sulfate, sodium chloride, sodium sulfide and sulfuric acid were obtained from Sigma Aldrich (Milwaukee, WI, USA). Aqueous solutions were prepared using de-ionized water and diluted from stock solutions.

Table 1. Composition of the 90Cu-10Ni Alloy

Element	Cu	Ni	Fe	Mn	Pb	Al	Others
Composition %	88.510	9.88	1.09	0.411	0.0458	0.0380	0.0252

A potentiostat model Gamry PCI4/750 (Gamry, Inc.) was used for electrochemical measurements. The potentiostat was controlled by a PC and the data were analyzed using the Gamry Corrosion Software provided with the instrument. A Pt sheet counters electrode having surface area of 1 cm^2 and a saturated silver-silver chloride electrode (Ag/AgCl) as a reference electrode was used. Potentiodynamic polarization experiments were performed between an initial potential $E_i = -1.0 \text{ V}$ up to a final potential $E_f = +1.0 \text{ V}$ at a sweep rate of 1.0 mV s^{-1} ; the potential sweep started after a wait period of 20 minutes. Electrochemical impedance spectroscopy measurements were performed at $E_{\text{app}} = 0.0 \text{ V}$ (vs. the “open circuit potential”) with an ac voltage amplitude of 10 mV in the frequency range from $10^5 - 0.1 \text{ Hz}$. The data analysis software was provided with the instrument and applied nonlinear

least square fitting with Levenberg-Marquardt algorithm. Potentiostatic experiments were performed by applying a constant potential $E_{\text{app}} = +0.15$ V for different extended times of 30 seconds, 30 minutes, and 60 minutes in the given electrolyte following the same approach as cited earlier [30]. The corresponding electrolyte was analyzed for Cu and Ni ions using inductively coupled plasma (ICP) emission. The surface of the electrodes was examined using field-emission scanning electron microscope (FE-SEM) (LEO SUPRA 50VP) and energy dispersive X-ray diffraction (EDX) using (Quantax QX2). Samples were freshly prepared and kept in vacuum desiccator and immediately brought to surface analysis.

3. RESULTS AND DISCUSSION

3.1 Open circuit potential measurements

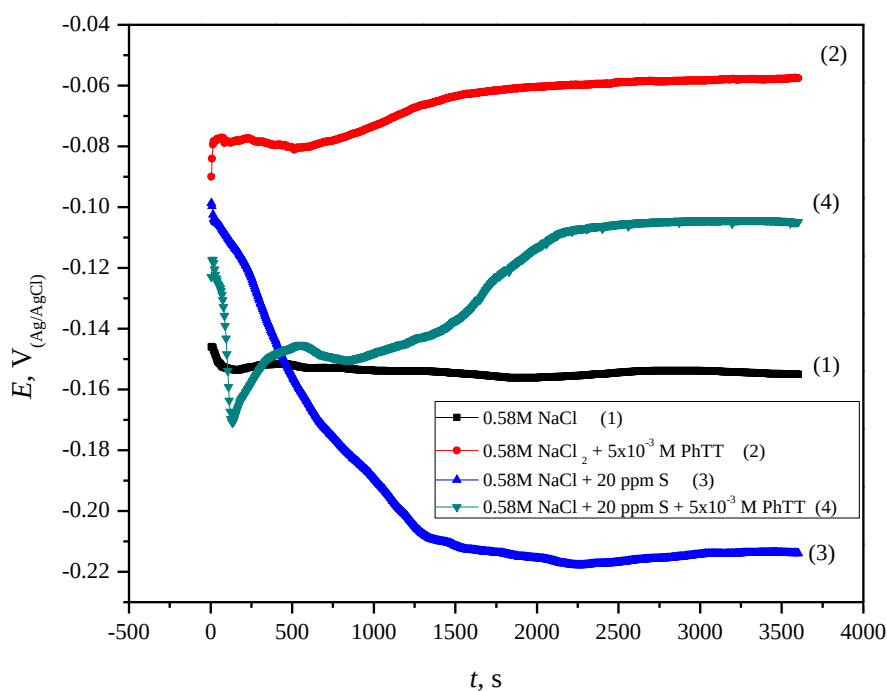


Figure 1. Open circuit potential of 90Cu10Ni alloy in (1) 0.58 M NaCl, (2) 0.58 M NaCl + 5×10^{-3} M PhTT, (3) 0.58 M NaCl + 20 ppm S, (4) 0.58 M NaCl + 5×10^{-3} M PhTT + 20 ppm S solutions recorded for 60 minutes.

It is important to determine the corrosion potential reached under steady state conditions. A preliminary understanding of the film formation will be correlated. In this study, the open circuit potential of 90Cu10Ni alloy was measured and referred relative to (Ag/AgCl) electrode as a function of the exposure time within a period of 60 minutes. The effect of the 5×10^{-3} M PhTT addition on open

circuit potential (OCP) values of the naturally aerated stagnant solution of 0.58 M NaCl in presence and absence of 20 ppm sulfide was recorded as noticed in figure 1.

In absence of the inhibitor, the open circuit potential dropped gradually and this gradual drop in the potential suggested a gradual removal of the naturally grown oxide film on the copper nickel surface until the steady state potential is achieved after about 30 minutes. The obtained potential values are -15 , -21 mV (Ag/AgCl) for 0.58 M NaCl and with the addition of 20 ppm sulfide, respectively.

More negative potential value was obtained in presence of sulfide and the potential shifted in the active direction compared to the unpolluted media. Decreasing the potential in presence of sulfide is due to the deterioration of the oxide film resulted from the incorporation of sulfide ions in the lattice of the film. This resulted in dissolution and/or the anodic oxidation of the sulfide ions [31].

In presence of 5×10^{-3} M PhTT it is observed that the potential sharply increases towards more noble direction suggesting the build-up of a protective layer containing the inhibitor on copper nickel surface as will be confirmed by SEM and EDX results. The thickness of the protective layer increases with time until it reaches the steady state through the first four minutes. The potential values recorded in 0.58 M NaCl + 20 ppm sulfide in presence of 5×10^{-3} M PhTT are 95 and 89 mV (Ag/AgCl), respectively. The effect of the inhibitor on OCP values is noticed in all studied media as presented in Table 2. More positive potentials are reached in presence of PhTT compared to its values in inhibitor-free electrolyte. This suggests the protection of the thin film formed over the alloy's surface mainly by adsorption of inhibitor. The efficiency of protection of copper-nickel alloy surface by the inhibitor decreases in the presence of sulfide ions due to the adsorption of sulfide species on the alloy surface which hinders the inhibition efficiency of PhTT and catalyzes further corrosion of the alloy [32].

3.2 Potentiodynamic polarization measurements

The effect of addition of PhTT on the polarization behavior of 90Cu10Ni alloy in solution of 0.58 M NaCl in presence and absence of sulfide ions was studied. The polarization curves in NaCl were recorded and presented in figure 2.

The polarization measurements were carried out in aerated solutions and after reaching a steady state potential (30 min after electrode immersion in the test solution) at a scan rate of 1.00 mV s^{-1} and the potentials were measured (vs. Ag/AgCl). The electrochemical corrosion data including the corrosion potential (E_{corr}) and corrosion current density (j_{corr}) obtained from extrapolation of the cathodic (β_c) and anodic (β_a) Tafel slopes are given in Table 2. From the data obtained it is clear that in absence of sulfide, the values of the corrosion rates changed according to the type of electrolyte used and its pH. The highest corrosion rates were observed in chloride and sulfide containing electrolytes (0.228 and 0.652 mm y^{-1} , respectively). The lowest corrosion rates were recorded in presence of inhibitor in unpolluted and polluted chloride solutions (0.0355 , 0.099 mm y^{-1}).

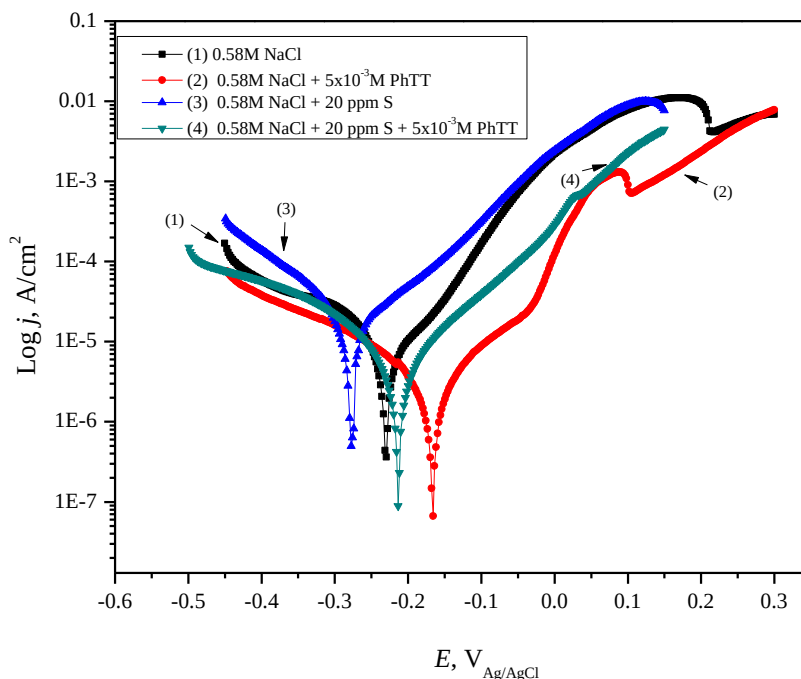


Figure 2. The potentiodynamic polarization curves of 90Cu10Ni alloy recorded after 20 minutes of immersion in (1) 0.58 M NaCl, (2) 0.58 M NaCl + 5×10^{-3} M PhTT, (3) 0.58 M NaCl + 20 ppm S, (4) 0.58 M NaCl + 5×10^{-3} M PhTT + 20 ppm S solutions. The sweep rate was 1 mV s^{-1} .

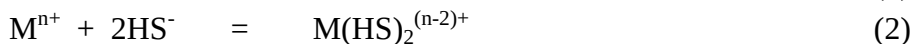
Table 2. Polarization parameters of the 90Cu-10Ni Alloy in 0.58 M NaCl, 0.58 M NaCl + 5×10^{-3} M PhTT, 0.58 M NaCl + 20 ppm S and 0.58 M NaCl + 20 ppm S + 5×10^{-3} M PhTT solutions at scan rate 1 mV s^{-1} . (Potential values are recorded vs. $4 \text{ mol L}^{-1} \text{ Ag/AgCl}$, $\pm 5 \text{ mV}$)

Electrolyte	j_{corr} ($\mu\text{A cm}^{-2}$)	E_{corr} (mV)	β_c (mV dec^{-1})	β_a (mV dec^{-1})	E_{OCP} (mV)	I %	Corrosion Rate (mm y^{-1})
0.58 M NaCl	14.5	-230	268	209	-155	-	0.228
0.58 M NaCl + 5×10^{-3} M PhTT	2.21	-168	407	261	-57	84.76	0.035
0.1 M NaCl + 20 ppm S	41.4	-277	195	169	-215	-	0.652
0.1 M NaCl + 20 ppm S + 5×10^{-3} M PhTT	6.28	-214	248	189	-105	84.83	0.099

The presence of 5×10^{-3} M PhTT decreases the corrosion rate in both sodium chloride and sodium chloride containing-sulfide. The protection can be attributed to complex formation of Cu(I)-tetrazole on the alloy surface. The inhibition efficiencies of PhTT are 84.76% and 84.83% in 0.58 M NaCl and 0.58 M NaCl + 20 ppm sulfide, respectively.

In presence of sulfide, the corrosion currents and the corrosion rates increased noticeably in chloride-containing electrolytes. This increase can be attributed to the deterioration of the protective film and/or the anodic oxidation of the sulfide ions [33].

The measured pH values of 0.58 M NaCl and 0.58 M NaCl + 20 ppm sulfide solutions are 6.6 and 8.9, respectively. The pK_a value of H_2S/HS^- (acidic/basic) is 6.95/7.00 and the stepwise conditional stability constants have been measured for the complex formation reactions for copper and nickel with hydrogen sulfide in sea water are according to:



The two stability constants of the corresponding complexes are ($10^{14.1}$; $10^{21.6}$) for copper and ($10^{3.8}$; $10^{11.4}$) for nickel in sea water, respectively [34]. On the other hand, the stability constants for complexes of copper with tetrazole derivatives are in the order of 10^9 and 10^{16} for bidentate and tridentate chelation, respectively [35]. Therefore, the possibility of sulfide formation for copper and nickel cannot be ruled out considering the stability constant values. The following electrochemical equilibria and their corresponding formal potentials are also considered [36]:



The formation of a barrier oxide layer containing copper oxide and/or hydroxide and nickel oxide and/or hydroxide and the corresponding sulfides are possible in the potential window studied. Therefore, the presence of sulfide ions in solution will lead to the deterioration of the oxide layer. The pH of the electrolyte is another factor that should also be considered as the equilibrium will be affected [37].

Therefore, a competitive adsorption between the sulfur-containing species and the inhibitor on the alloy surface results in the formation of (CuS , Cu_2S , NiS and Ni_2S) and $Cu:Inh$ and $Ni:Inh$ complexes. Comparing the stability constants of $Cu:Inh$ and $Ni:Inh$ complexes to those of CuS , Cu_2S , NiS and Ni_2S , it was concluded that the former represents the film composition. The interaction of both inhibitor and sulfide with the Cu and Ni oxide layer cannot be excluded.

The corrosion rates are: 0.228, 0.035, 0.652 and 0.099 mm y^{-1} for the Cu90Ni10 alloy in 0.58 M NaCl, 0.58 M NaCl + 5×10^{-3} M PhTT, 0.1 M NaCl + 20 ppm sulfide, and 0.1 M NaCl + 20 ppm sulfide + 5×10^{-3} M PhTT, respectively. The effect of sulfide ions is more pronounced on the corrosion of the alloy in the chloride containing solutions. Also the free corrosion potential is shifted towards more negative value which is attributed to the presence of sulfide ions. The addition of sulfide to the studied solutions in presence of the inhibitor increases the corrosion current and hence decreases the

inhibition efficiency showing strong detrimental effect on the passivity due to the protective oxide layer and that caused by PhTT (Table 2).

3.3 Adsorption isotherm of inhibitor

At this stage it is important to define the type and extent of adsorption of the inhibitor onto the surface of the alloy. Physical and chemical adsorption patterns are thought and different isotherms are suggested such as Langmuir, Frumkin and Temkin isotherms. The formation of chemical bonds between the copper or nickel atoms on the surface of the alloy and the inhibitor is possible through the lone-pairs interactions with the d-orbitals of metallic atoms. The extent of surface coverage is therefore studied for the inhibitor with different concentrations. The following equation determines the surface coverage, θ , [38]:

$$\theta = \frac{j_{\text{corr}}(\text{uninhibited}) - j_{\text{corr}}(\text{inhibited})}{j_{\text{corr}}(\text{uninhibited})} \quad (15)$$

The obtained θ values (Table 3) fitted well with the Langmuir isotherm adsorption model and accordingly the following equation will be applied:

$$\frac{\theta}{1 - \theta} = KC \quad (16)$$

$$K = \frac{1}{55.5} e^{(-\Delta G_{\text{ads}}/RT)} \quad (17)$$

A plot of C/θ versus C (where C is the inhibitor concentration) (figure 3) resulted in a straight line relationship and the slope is estimated as 0.9999 and 0.9994 for NaCl + PhTT and NaCl + S + PhTT electrolytes, respectively.

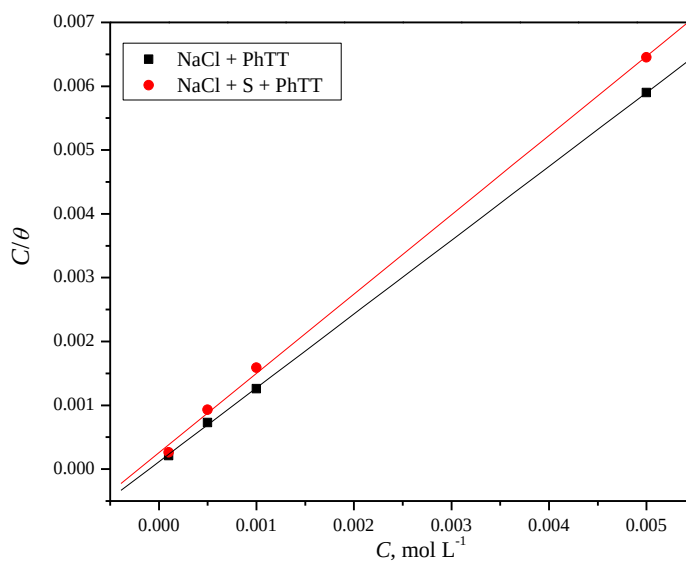


Figure 3. Langmuir adsorption isotherm plotted as C/θ vs. concentration of PhTT for corrosion of 90Cu10Ni alloy in 0.58 M NaCl and 0.58 M NaCl + 20 ppm S.

The linear relationship confirms that the adsorption of the inhibitor follows a Langmuir model as the slopes are nearly equal 1. The free energies of adsorption can therefore be estimated from equation (17) as ΔG_{ads} in 0.58 M NaCl + 5×10^{-3} M PhTT as $-32.403 \text{ kJ mol}^{-1}$ and $-30.434 \text{ kJ mol}^{-1}$ in 0.58 M NaCl + 20 ppm sulfide + 5×10^{-3} M PhTT. The values obtained for ΔG_{ads} indicate a physical adsorption process for the inhibitor as the values were less than -40 kJ mol^{-1} . Similar values were also reported when using 5-methyl 1-H benzotriazole when used as inhibitor in similar electrolytes [39].

Table 3 lists the surface coverage and the inhibition efficiencies upon the addition of different concentrations of PhTT in presence and absence of sulfide ions. A noticeable increase in surface coverage is observed, assuming the Langmuir model is applicable, as the concentrations increases from 1×10^{-4} M PhTT to 5×10^{-3} M PhTT. The concentrations of PhTT used throughout this study is 5×10^{-3} M PhTT. This realized a surface coverage of 0.847 and inhibition efficiency of 84.8%. Further increase in PhTT concentrations to 1×10^{-2} M PhTT did not result into appreciable change in θ or $I \%$.

Table 3. Surface coverage and inhibition efficiencies values obtained in 0.58 M NaCl and 0.58 M NaCl + 20 ppm S in presence of different concentrations of PhTT.

Electrolyte	Inhibitor concentration	θ	$I \%$
0.58 M NaCl	1×10^{-4} M PhTT	0.472	47.2
	5×10^{-4} M PhTT	0.687	68.7
	1×10^{-3} M PhTT	0.795	79.5
	5×10^{-3} M PhTT	0.848	84.8
0.1 M NaCl + 20 ppm S	1×10^{-4} M PhTT	0.481	48.1
	5×10^{-4} M PhTT	0.674	67.4
	1×10^{-3} M PhTT	0.789	78.9
	5×10^{-3} M PhTT	0.848	84.8

3.4 Effect of temperature

In this part of the study, we investigated the temperature effect on the corrosion of 90Cu10Ni alloy in presence of 5×10^{-3} M PhTT in sulfide polluted and non-polluted solution 0.58M NaCl using the potentiodynamic polarization technique in the temperature range 25-55°C. Generally, the corrosion rate increases with the rise of temperature in all studied media and hence the inhibition efficiency

decreases. The dependence of corrosion rate on temperature can be expressed by the Arrhenius equation from which the activation energy (E_a) of the corrosion process can be calculated [40]:

$$\log j_{\text{corr}} = -E_a / 2.303 RT + \log A \quad (18)$$

Where E_a is the apparent activation energy of the corrosion process, j_{corr} is the corrosion current, A is the pre-exponential factor, R is the universal gas constant and T is the absolute temperature.

The slope of the straight lines obtained when plotting $\log j_{\text{corr}}$ vs. $1/T$ were used to calculate the activation energy values in all studied media containing 5×10^{-3} M PhTT in absence and presence of sulfide ions as shown in figure 4 (for NaCl). The calculated E_a values in 0.58 M NaCl + 5×10^{-3} M PhTT in absence and presence of sulfide are $42.69 \text{ kJ mol}^{-1}$ and $34.22 \text{ kJ mol}^{-1}$, respectively.

From the above data, it is concluded that the addition of the inhibitor resulted in an increase in the activation energy in all studied media in comparison to its absence due to the physical adsorption of PhTT [41]. Also the presence of sulfide increases the dissolution of the copper nickel alloy and affects the inhibition efficiency of PhTT which is observed in decreasing the activation energy.

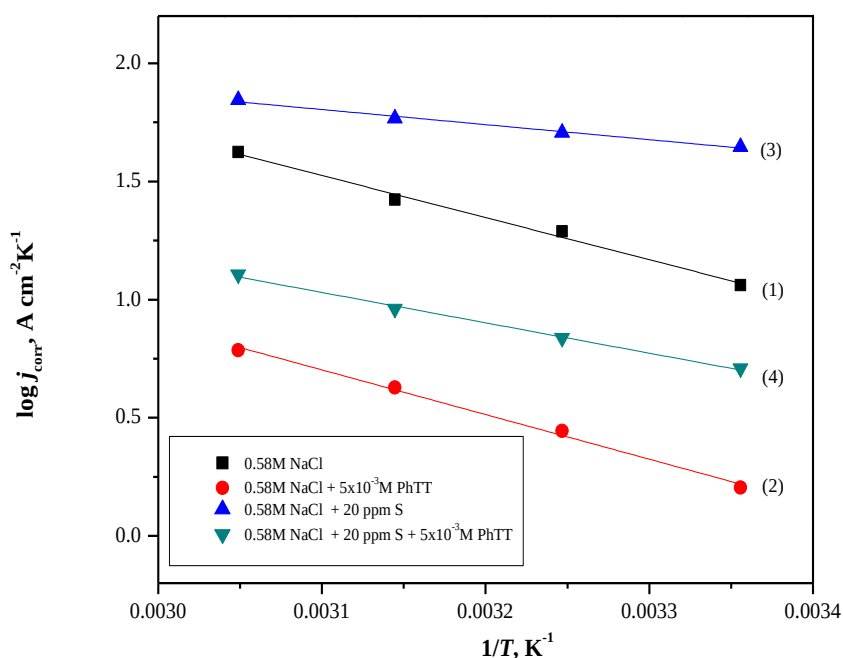


Figure 4. Variation of $\log j_{\text{corr}}$ against $1/T$ of 90Cu10Ni alloy in (1) 0.58 M NaCl, (2) 0.58 M NaCl + 5×10^{-3} M PhTT, (3) 0.58 M NaCl + 20 ppm S, (4) 0.58 M NaCl + 5×10^{-3} M PhTT + 20 ppm S solutions at different temperatures.

3.5 Electrochemical impedance spectroscopy

Further knowledge of the surface interactions of the inhibitor used and the surface of the alloy can be obtained from EIS measurements. Since adsorption is an important step in the corrosion inhibition process, information regarding double layer structure and barrier film resistance will be of paramount importance [42].

Figure 5 shows the Nyquist plots (A) and Bode plots (B) with an applied frequency range from 100 kHz to 0.1 Hz at an applied dc potential of 0.0 V versus the "open circuit" potential. As could be noticed that in presence of 5×10^{-3} M of 1-phenyl 1-H-tetrazole 5-thiol two time constants can be identified in the EIS Bode diagram. In the Nyquist plot the difference between the two time constants is not noticeable, therefore a depressed capacitance semi-circle is observed. An equivalent circuit as shown in figure 5C is constructed and in which R_s is the electrolytic resistance, R_{ct} is the charge transfer resistance, C_{dl} is the double layer capacitance, R_f is the film resistance and Y_{o1} is a constant phase element that describes the surface roughness of the oxide [43]. The first two parameters describe the solid/electrolyte interface where charge transfer and inhibitor adsorption take place. The second two components are related to the film characteristics and therefore to the barrier oxide film stability. The experimental data were fitted to the circuit model of figure 5C using Z view software and the resulting fitted parameters are given in Table 4. The data of the error analysis are: $\chi^2 = 2.12 \times 10^{-4}$, weighed sum of squares = 2.46×10^{-2} and goodness of fit = 1.05×10^{-3} .

The charge transfer resistance, R_{ct} , value increases noticeably in presence of inhibitor in sulfide-polluted and non-polluted solutions. This insures the coverage and protection of the surface and results in a decrease in the rate of corrosion. The double layer capacitance values, C_{dl} , on the other hand show a variation according to the electrolyte composition. For instance, the value of C_{dl} decreases two orders of magnitudes in 0.58 M NaCl compared to 0.58 M NaCl + 5×10^{-3} M PhTT. Specific adsorption is more pronounced as the sulfur-containing inhibitor covers the surface. In presence of sulfide ions the charge transfer resistance decreases as the oxide barrier layer deteriorates due to the formation of sulfide products. The double layer in the latter case should maintain a relative consistency as the sulfide ions/PhTT competitive adsorption lead to C_{dl} values being intermediate compared to the sulfur non-polluted electrolytes. Film resistance, R_f , values decrease dramatically in presence of sulfide ions. This is due to the chemical reaction that leads to the formation of sulfide products that decreases the oxide barrier film thickness [11].

These data are in good agreement with those obtained from the polarization measurements and in accordance with the findings correlated for the ICP-measurements. The indication of the formation of the sulfide products and the dissolution of the barrier layer is confirmed and is also verified from the surface characterization from the EDX data. The inhibition efficiency is calculated from the EIS according to the equation [44]:

$$\eta\% = \frac{R_{ct}(\text{inh}) - R_{ct}(\text{uninh})}{R_{ct}(\text{uninh})} \times 100 \quad (19)$$

The values for the inhibition efficiencies are 85.02% in NaCl + PhTT and 80.1% in NaCl + S + PhTT (comparison in this case is between corresponding solutions, i.e. sulfide-polluted versus non-polluted electrolytes). The values of inhibition efficiencies calculated from the EIS data are in excellent agreement with those calculated from the polarization curves (see Table 3).

The impedance was calculated from the following equations (42, 45):

$$Z_M(\omega) = R_s + \frac{R_{ct}}{1 + j\omega R_{ct} C_{dl}} \quad (20)$$

$$Z_M(\omega) = R_s + \frac{R_{ct}}{1 + (2\pi f R_{ct} C_{dl})^a} \quad (21)$$

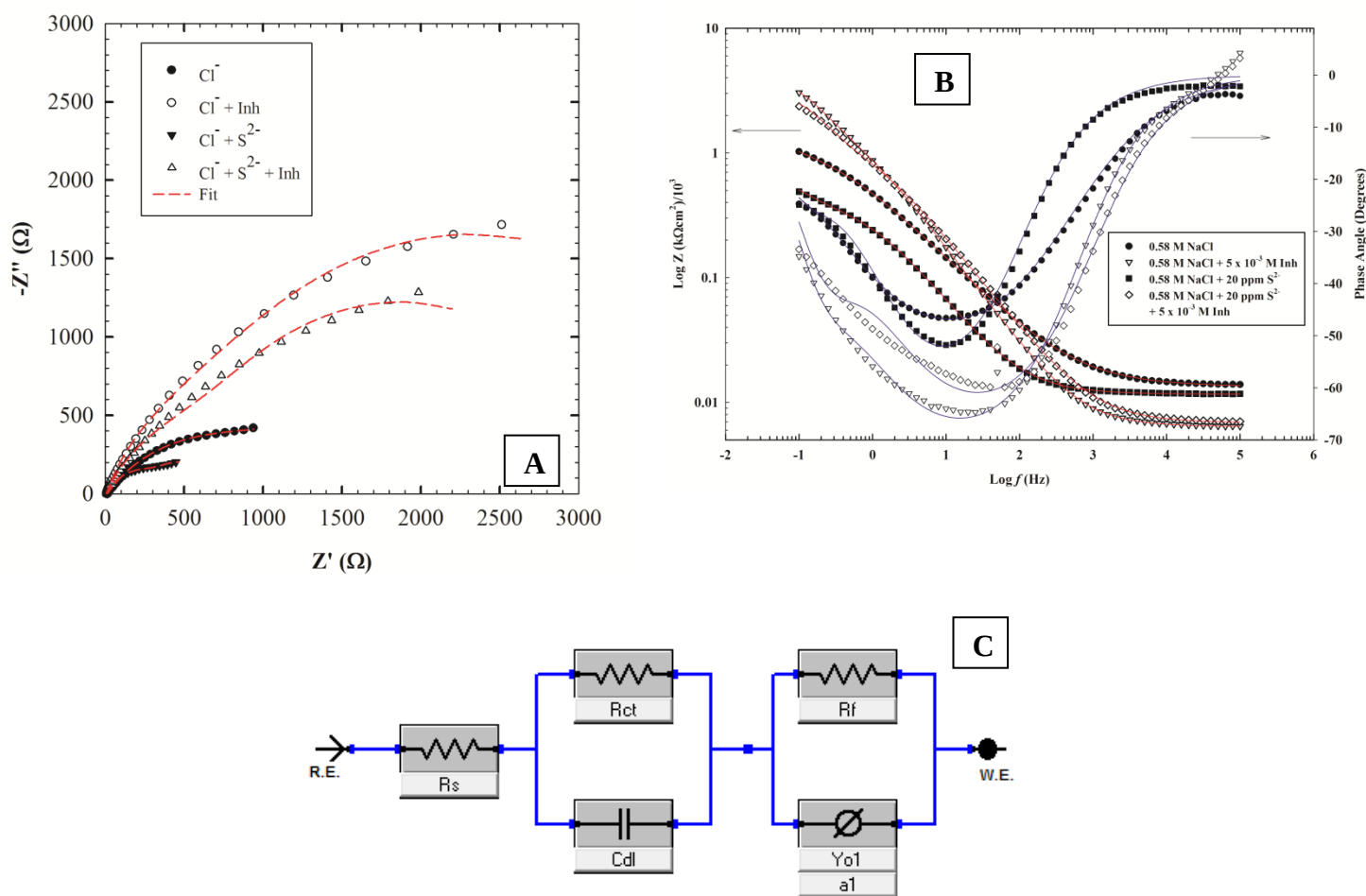


Figure 5. The impedance spectra of 90Cu10Ni alloy in (1) 0.58 M NaCl, (2) 0.58 M NaCl + 20 ppm S (3) 0.58 M NaCl + 20 ppm S + 5×10^{-3} M PhTT and (4) 0.58 M NaCl + 5×10^{-3} M PhTT solutions under open circuit potential (A) Nyquist and (B) Bode plots, (C) Equivalent circuit.

Table 4. Electrochemical kinetic parameters obtained by EIS technique for the corrosion of the 90Cu-10Ni Alloy in 0.58 M NaCl, 0.58 M NaCl + 5×10^{-3} M PhTT, 0.58 M NaCl + 20 ppm S and 0.58 M NaCl + 20 ppm S + 5×10^{-3} M PhTT solutions.

	NaCl	0.58 M NaCl + 5×10^{-3} PhTT	0.58 M NaCl + 20 ppm S	0.58 M NaCl + 20 ppm S + 5×10^{-3} PhTT
$R_s (\Omega \text{ cm}^2)$	13.4	6.4	11.7	6.87
$R_{ct} (\Omega \text{ cm}^2)$	428	2857	305	2150
$C_{dl} (\text{F cm}^{-2})$	1.2×10^{-2}	5×10^{-4}	6.7×10^{-3}	6×10^{-3}
$R_f (\Omega \text{ cm}^2)$	1261	1176	372	974
$Y_{01} (\text{F cm}^{-2} \text{ s}^3)$	5.35×10^{-4}	2.7×10^{-4}	7×10^{-4}	2.4×10^{-4}
A	0.62	0.77	0.75	0.74
I %	-	85.02	-	85.81

$$\chi^2 = 2.12 \times 10^{-4}$$

$$\text{Weighed sum of squares} = 2.46 \times 10^{-2}$$

The extent of surface coverage, θ , was also calculated from the EIS data and compared to those obtained from the polarization measurements. The values are found to be 0.850 in NaCl + PhTT and 0.801 in NaCl + S + PhTT. This again confirms that the inhibitor interaction with the surface of the alloy/barrier oxide layer in this study follows a Langmuir model as deduced from the linear polarization or the AC measurements under steady state conditions.

3.6 Scanning electron microscopy

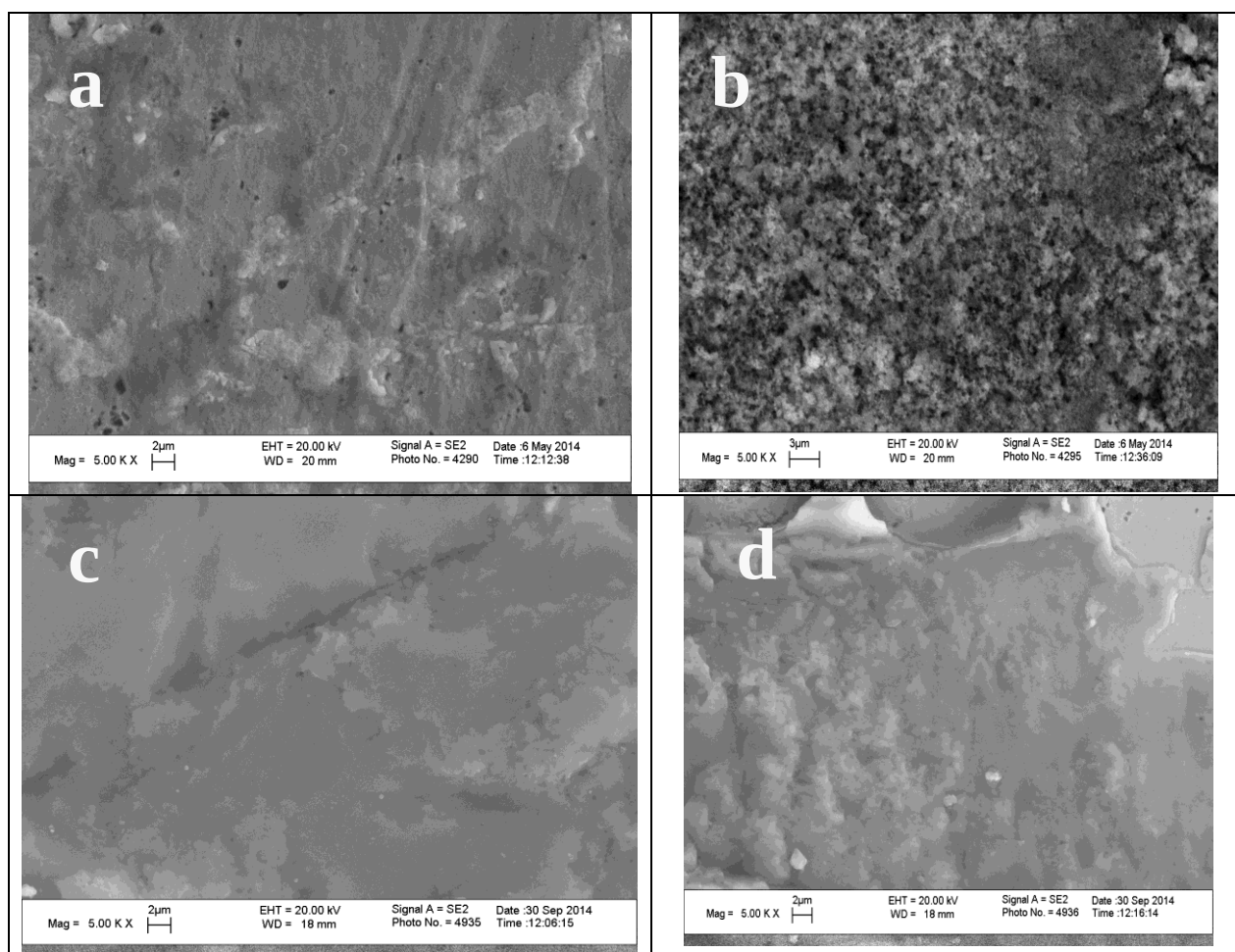


Figure 6. SEM pictures of 90Cu10Ni alloy in (a) 0.58 M NaCl, (b) 0.58 M NaCl + 20 ppm S (c) 0.58 M NaCl + 5×10^{-3} M PhTT and (d) 0.58 M NaCl + 20 ppm S + 5×10^{-3} M PhTT solutions after 60 minutes at magnification ($\times 5000$).

The surface morphology of 90Cu10Ni alloy was investigated in 0.58 M NaCl solutions in absence and presence of 20 ppm sulfide ions. The effect of addition of 5×10^{-3} M PhTT on the surface morphology was also studied after 60 minutes of immersion at OCP (figure 6). From this figure; it is clear that in presence of sulfide damaged areas of the surface were observed due to the sulfide attack that led to formation of thick and porous black layer composed of mixture of Cu_2S , NiS and Cu_2O [11]. A marked inhibiting effect is shown in presence of PhTT especially in solutions free from sulfide

however in presence of sulfide the protective film affected due to PhTT will competes with sulfide ions for adsorption on the same active sites on the surface and the attack of sulfide ions to alloy surface and incorporation in the protective film formed.

The energy dispersive X-ray spectroscopy (EDX) was used to characterize the corrosion products and it shows the existence of C and N in presence of PhTT which suggest the adsorption of PhTT on the electrode surface. The percentage of C and N decreased in presence of sulfide which confirms the aggressive effect of sulfide and replacement of sulfur ion instead of the inhibitor molecules. Table 5 summarizes the mass percentage composition of the elements analysis.

Table 5. Surface composition (wt %) of 90Cu10Ni alloy in 0.58 M NaCl, 0.58 M NaCl + 20 ppm S, 0.58 M NaCl + 5×10^{-3} M PhTT and 0.58 M NaCl + 20 ppm S + 5×10^{-3} M PhTT solutions after 60 minutes.

(Mass %)	Cu	Ni	O	C	N	Cl	S
0.58 M NaCl	49.65	3.11	18.55	-	-	24.88	-
0.58 M NaCl + 20 ppm S	43.45	2.94	26.17	-	-	16.24	12.2
0.58 M NaCl + 5×10^{-3} M PhTT	39.4	4.66	7.21	19.24	20.25	4.52	4.72
0.58 M NaCl + 20 ppm S + 5×10^{-3} M PhTT	42.58	5.68	9.40	13.80	16.13	3.81	7.13

3.7 Potentiostatic polarization measurements

Potentiostatic experiments were conducted on the alloy to give more insight about the concentrations of copper and nickel ions in the solution using ICP. Constant potential of +0.150 V (Ag/AgCl) was applied for one hour for all studied electrolytes. It was also important to study the current time transients in absence and presence of sulfide and the effect of 5×10^{-3} M PhTT addition to these electrolytes.

Figure 7 shows the current transients-time curves for 90Cu10Ni alloy in 0.58 M NaCl in presence of 20 ppm sulfide ions and the effect of addition of 5×10^{-3} M PhTT to these media. Similar curves were obtained in the others electrolytes in absence and presence of the studied inhibitor. From this figure, it is clear that in absence of inhibitor a rapid decrease in current occurs due to the presence of the naturally formed oxide film mainly Cu_2O . This is followed by an increase in current as a result of the aggressive effect of chloride and sulfide ions which destroy the passive film formed and enhance the dissolution of alloy. The current values reach a steady state at the end of polarization. In presence of inhibitor (5×10^{-3} M PhTT) gradual decrease in current was observed with time in absence and presence of sulfide ions until reaching the steady state. The effect of inhibitor is more pronounced in chloride solution where the current decreases from 0.0024 A cm^{-2} to 0.0002 A cm^{-2} in NaCl and in NaCl + 5×10^{-3} M PhTT, respectively. The presence of sulfide ions affects the protection efficiency of the inhibitor and the corrosion current decreases from 0.0055 A cm^{-2} in NaCl + 20 ppm sulfide to

0.0011 A cm⁻² in NaCl + 20 ppm sulfide-containing 5×10^{-3} M PhTT. The current transient results are in good agreement with the inhibition efficiency trend obtained from the potentiodynamic data.

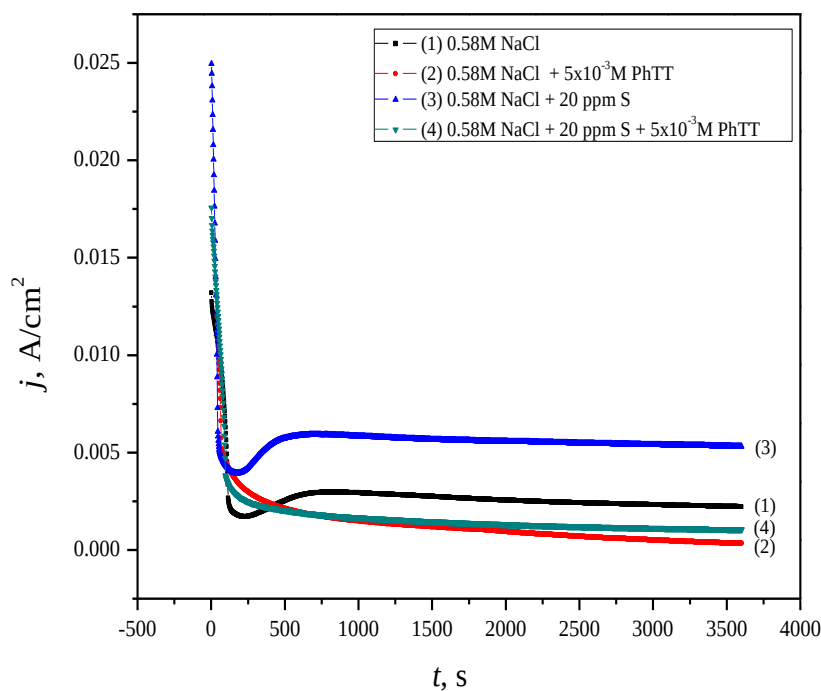


Figure 7. Current-time curves of 90Cu10Ni alloy in (1) 0.58 M NaCl + 20 ppm S, (2) 0.58 M NaCl + 20 ppm S + 5×10^{-3} M PhTT, (3) 0.58 M NaCl, (4) 0.58 M NaCl + 5×10^{-3} M PhTT solutions recorded for 60 minutes at $E_{app} = +0.15$ V.

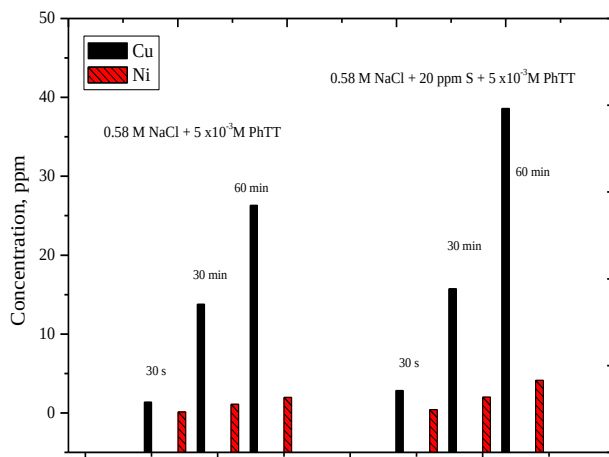


Figure 8. Cu and Ni concentrations (in ppm) in 0.58 M NaCl + 5×10^{-3} M PhTT and 0.58 M NaCl + 20 ppm S + 5×10^{-3} M PhTT solutions after different times (30 s, 30 min and 60 min) at $E_{app} = +0.150$ V.

Figure 8 shows the concentrations of copper and nickel recorded using ICP measurements to study the effect of addition of 5×10^{-3} M PhTT to all studied electrolytes in presence and absence of 20

ppm sulfide. Thus, chronoamperometric experiments were performed at constant potential of +0.15 V (vs. Ag/AgCl) for different time intervals (30 s, 30 min and 60 min). From this figure, it was observed that the presence of sulfide ions increases the dissolution of copper and nickel ion the studied electrolyte. The sharp decrease in the concentrations of copper and nickel in the studied electrolyte in presence of PhTT shows that this compound acts as effective inhibitor in chloride containing electrolytes [30].

4. CONCLUSION

The presence of sulfide ions in chloride-containing electrolytes affected the corrosion behavior of Cu90-Ni10 alloy. Sulfide ions mainly attacked the protective thin oxide barrier layers of copper oxide (or hydroxide) and nickel oxide (or hydroxide) due to the formation of copper and nickel sulfide products. The presence of sulfide resulted in a three-fold increase in corrosion rate. PhTT inhibitor proved efficient in protecting the surface of the alloy when subjected to sulfide-polluted and unpolluted 0.58 M chloride. The protection efficiency was 85% in the electrolytes studied, the results were confirmed from both polarization and impedance measurements. A Langmuir isotherm model is suggested for the interaction of the inhibitor with the surface. SEM images showed a relative protection of the surface and sulfur was identified in the surface structure in case of exposure to sulfide and/or the inhibitor. A competitive adsorption mechanism was suggested between the sulfide ions and the inhibitor. ICP data showed that the ionic concentration of copper and nickel in the electrolyte side relatively increased in presence of sulfide ions. The values of the activation energy for the corrosion process are $42.69 \text{ kJ mol}^{-1}$ and $34.22 \text{ kJ mol}^{-1}$ for the alloy exposed to 0.58 M NaCl + 5×10^{-3} M PhTT and 0.58 M NaCl + 20 ppm sulfide + 5×10^{-3} M PhTT, respectively.

ACKNOWLEDGEMENT

The financial support of the University of Kuwait through the fund provided through grant number SC05/10 and research facilities through grant number GS01/01 is appreciated.

References

1. B. Syrett and S. Wing, *Corrosion*, 36 (1980) 73.
2. N. Allam, A. Abdel Nazeer, G. Youssef and E. Ashour, *Corrosion*, 69 (2013) 77.
3. T. Hodgkiess and G. Vassiliou, *Desalination*, 183 (2005) 235.
4. N. Allam, A. Abdel Nazeer and E. Ashour, *Ind. Eng. Chem. Res.*, 49 (2010) 9529.
5. R. North and M. Pryor, *Corros. Sci.*, 10 (1970) 297.
6. A. Abdel Nazeer, N. Allam, A. Fouda and E. Ashour, *Mater. Chem. Phys.*, 136 (2012) 1.
7. F. Al-Kharafi, A. Abdel Nazeer, R. Abdullah and A. Galal, *ECS Trans.*, 58 (2013) 93.
8. J. Gudas and H. Hack, *Corrosion*, 35 (1979) 67.
9. A. Abdel Nazeer, N. Allam, G. Youssef and E. Ashour, *Ind. Eng. Chem. Res.*, 50 (2011) 8796.
10. D. Starosvetsky, O. Khaselev, M. Auinat and Y. Ein-Eli, *Electrochim. Acta*, 51 (2006) 5660.
11. S. Yuan and S. Phenkonen, *Corros. Sci.*, 49 (2007) 1276.
12. C. Kato, B. Ateya, J. Castle and H. Pickering, *J. Electrochem. Soc.*, 127 (1980) 1897.
13. Z. Mountassir and A. Srhiri, *Corros. Sci.*, 49 (2007) 1350.

14. X. Xie, L. Du, L. Pan, S. Cao, M. Yan and W. Yang, *Anti-Corros. Meth. Mater.*, 54 (2007) 34.
15. J. Alhajji and M. Reda, *J. Electrochem. Soc.*, 141 (1994) 1432.
16. M. Vazquez and S. De Sanchez, *J. Appl. Electrochem.*, 28 (1998) 1383.
17. N. Allam, *Appl. Surf. Sci.*, 253 (2007) 4570.
18. X. Ye, X. Xin, J. Zhu and Z. Xue, *Appl. Surf. Sci.*, 135 (1998) 307.
19. B. Trachli, M. Keddam, A. Srhiri and H. Takenouti, *Corros. Sci.*, 44 (2002) 997.
20. F. Al-kharafi and B. Ateya, *J. Electrochem. Soc.*, 149 (2002) 206.
21. H. Otmacic and E. Stupnisek-Lisac, *Electrochim. Acta*, 48 (2003) 985.
22. N. Allam, A. Abdel Nazeer and E. Ashour, *J. Appl. Electrochem.*, 39 (2009) 961.
23. F. Zucchi, G. Trabanelli and M. Fonsati, *Corros. Sci.*, 38 (1996) 2019.
24. M. Mihit, S. El Issami, M. Bouklah, L. Bazzi, B. Hammouti, E. AitAddi, R. Salghi and S. Kertit, *Appl. Surf. Sci.*, 252 (2006) 2389.
25. S. Kertit and B. Hammouti, *Appl. Surf. Sci.*, 93 (1996) 59.
26. G. Vastag, E. Szocs, A. Shaban and E. Kalman, *Pure Appl. Chem.*, 73 (2001) 1861.
27. M. Mihit, R. Salghi, S. El Issami, L. Bazzi, B. Hammouti, E. AitAddi and S. Kertit, *Pigm. Resin Technol.*, 35 (2006) 151.
28. E. Szocs, Gy. Vastag, A. Shaban and E. Kalman, *Corros. Sci.*, 47 (2005) 893.
29. X. Ye, X. Xin, J. Zhu and Z. Xue, *Appl. Surf. Sci.*, 135 (1998) 307.
30. F. Al-Kharafi, A. Galal, A. Abdel Nazeer and R. Abdullah, *Corrosion*, 71 (2015) 455.
31. B. Atya and F. El-Kharafi, *Electrochem. Solid-State Lett.*, 6 (2003) 137.
32. F. El-Kharafi and B. Atya, *J. Electrochem. Soc.*, 149 (2002) 206.
33. M. Vazquez and S. Desanchez, *J. Appl. Electrochem.*, 28 (1998) 1383.
34. J. Zhang and F. Miller, *Anal. Chim. Acta*, 284 (1994) 497.
35. E. Lodyga-Chruscinska, D. Sanna, G. Micera, L. Chruscinski, J. Olejnik, R.J. Nachman and J. Zabrocki, *Acta Biochem. Pol.*, 53 (2006) 65.
36. A. Bard and M. Stratmann, *Encyclopedia of electrochemistry*, Wiley-VCH, 7 (2006) 41.
37. M. Pourbaix. *Atlas of Electrochemical Equilibria in Aqueous Solutions*, 2nd edition, (1974). National Association of Corrosion (NACE), Texas, USA.
38. E. McCafferty, *Introduction to Corrosion Science*, Springer New York, (2006).
39. A. Abdel Nazeer, E. Ashour and N. Allam, *Mater. Chem. Phys.*, 144 (2014) 55.
40. I. Putilova, S. Balezin, V. Barannik, *Metallic Corrosion Inhibitors* (Pergamon, Oxford, 1960).
41. F. Al-Kharafi, A. Abdel Nazeer, R. Abdullah and A. Galal, *ECS Trans.*, 64 (2015) 121.
42. M. Orazem, B. Tribollet, *Electrochemical Impedance Spectroscopy*, John Wiley & Sons, New York, (2008), 173.
43. S. Muralidharan, S. Azim, L. Berchmans and S. Iyer, *Anti-Corros. Meth. Mater.*, 44 (1997) 30.
44. D. Jones, *Principles and Prevention of Corrosion* (2nd Edition), Prentice Hall, New York, 1995.
45. Y. Elkacimi, M. Achnin, Y. Aouine, M. EbnTouhami, A. Alami, R. Tourir, M. Sfaira, D. Chebabe, A. Elachqar and B. Hammouti, *Port. Electrochim. Acta*, 30 (2012) 53.