Int. J. Electrochem. Sci., 7 **(2012)** 3289 - 3298

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Corrosion Inhibition of Copper in Non-polluted and Polluted Sea Water Using 5-phenyl-1-H-tetrazole

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Received: 2 February 2012 / *Accepted:* 7 March 2012 / *Published:* 1 April 2012

Corrosion inhibition of copper in salt water using 5-phenyl-1-H tetrazole (PTAH) was investigated. Experiments were also performed in salt water polluted with thiosulfate or sulfide ions. Potentiodynamic and potentiostatic polarization tests were performed. Polarization tests indicate that the presence of PTAH results in a marked decrease of the anodic current density. The extent of reduction of the current density is increased with the increase of the inhibitor concentration. Standard free energy of adsorption (ΔG^o) of -49.15 kJ mol^{-1} was calculated at 20^{o}C. These values point to chemisorption occurring in the interaction of PTAH and the surface of copper. Activation energies of 71.8 KJ/mol and 17.7 KJ/mol were calculated for the dissolution of copper in the salt solution in the presence and in the absence of PTAH, respectively. The big differences in activation energies indicate the high inhibition efficiency of the PTAH inhibitor. The pollution of the salt solution with thiosulfate or sulfide ions diminishes the passivity of PTAH.

Keywords: Copper, inhibitors, tetrazoles, NaCl, sulfide, thiosulfate

1. INTRODUCTION

Copper and many of its alloys possess favorable combinations of thermal, electrical and mechanical properties [1-2] in addition to a moderate cost. They are attractive construction materials for tubes, pumps, valves, fittings, interconnects, circuit boards,…etc. Copper and its alloys are extensively used in various applications in Kuwait and the Gulf region. These materials face various forms of corrosion which limit their performance [3-6].

Tetrazoles are a class of synthetic organic heterocyclic compounds, consisting of a 5-member ring containing four nitrogen and one carbon atoms (plus hydrogen atoms) [7]. The simplest is tetrazole itself. A large variety of tetrazoles can be obtained through the substitution of H atom attached to the carbon or the nitrogen atoms of the tetrazole ring with other function groups like SH, NH_2, CH_3, phenyl, …ect. Tetrazoles are expected to have high tendency to adsorb on copper as they have four lone pairs of electrons on the nitrogen atoms of the tetrazole ring. These lone pairs of electrons are known to coordinate strongly with the Cu(I) ions, resulting from the readily oxidation of copper, to give a protective complex.

The use of tetrazoles as corrosion inhibitors were investigated by many authors [8-17]. The inhibiting action of tetrazole derivatives in 0.1M NaCl solution was investigated [8]. The following compounds were tested: tetrazole (T), 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-amino tetrazole ($5NH_2$-T) in the range of pH from 4 to 8 and at temperatures of 40 to 80^oC. Inhibitors show inhibition efficiencies (IE) between 50 and 99%. The best protective characteristics are shown by 5Mc-1Ph-T and 5Ph-T. The structure of the protective film formed using the above mentioned compounds is further investigated [9]. The film contains a layer of inert, insoluble and long-lasting polymeric Cu(I) complex.

The effect of 2-mercaptobenzothiazole (MBT) on the corrosion inhibition of copper in the ethanol solution was investigated [10]. The concentration of MBT of 0.001 M lead to reduction of current density 4 times.

The characteristics of adsorption and the influence of 2-mercaptobenzothiazole (MBT) and tetrazole (TTA) on the growth of oxide film on copper in 0.1M NaOH are also investigated [11]. The inhibition efficiency is strongly dependent on the structure and chemical properties of the species formed under the specific experimental conditions.

The inhibiting action of 5-mercapto-1-phenyl-tetrazole (5-MPhTT) in 0.001 M H_2SO_4 solution was investigated [12]. The results reveal that the anodic current density and mass loss are two times twice less lower in the presence of 5-MPhTT.

The influence of 1-phenyl-5-mercapto-1,2,3,4-tetrazole (PMT) on the corrosion inhibition of Cu in 0.1M HNO_3 was also studied [13]. The action effect of PMT is compared with the influence action of other organic compounds of this type of the same family. They behave as mixed type inhibitors. The mechanism of action is chemisorption on the copper surface that follows Langmuir isotherm.

The inhibition action and adsorption behavior of Guanidino tetrazole (GT) and 1-p-methylphenyl-5-mercapto-1,2,3,4-tetrazole (MMT) on copper in aqueous solution of 5% $NaHCO_3$ were investigated by using weight loss test and electrochemical test [14]. Results indicate that the two types of tetrazole derivative inhibitors have good corrosion inhibition ability for copper in $NaHCO_3$ solution, and they are both anode-type inhibitors.

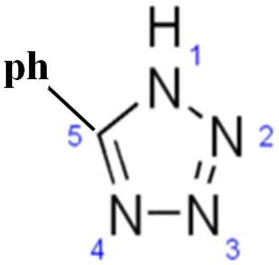
It is obvious that there is a lack of studies regarding the use of tetrazoles as corrosion inhibitors of copper or its alloys in non polluted and polluted sea water environments. The present work aims to investigate the corrosion inhibition of copper using 5-phenyl-1-H tetrazole in sea water. The effect of pollutants (sulfide and thiosulfate) on the corrosion inhibition efficiency of the tetrazoles is also investigated.

2. EXPERIMENTAL

Electrodes were prepared from electrolytic copper (99.9 %) in the form of rods having 0.96 cm diameter. The working electrode was the cross sectional area of the rod while the immersed length of the rod was coated with a protective adhesive so that the cross sectional area is only exposed to the solution. Electrical contact to the external circuit was made through the rod. The working electrodes were polished using SiC papers successively up to 2400 grits, followed by 0.3 micron alumina to acquire a mirror-like finish.

Potentiodynamic and potentiostatic polarization curves were measured on the Cu electrodes using a conventional three-electrode cell with a Ag/AgCl reference electrode and a Pt sheet counter electrode. The potential was controlled using a Gamry potentiostat. Experiments were carried out in 0.6 mol L^{-1} NaCl solution which simulates sea water environment. Tests were performed in the absence and in the presence of thiosulfate and sulfide pollutant ions.

Solutions were prepared using deionized water, Analar $Na_2S_2O_3$, Na_2S and NaCl from Fluka, 99% 5-phenyl-1H-tetrazole (PTAH) whose structure is presented below from Aldrich. The PTAH solution was prepared in 10% dimethylformamide (DMF) solution containing the desired salt content. Measurements were performed at 20 ± 1°C while the testing solution was open to air and stirred using a magnetic stirrer.



5-phenyl-1H-tetrazole

3. RESULTS AND DISCUSSION

3.1. Potentiodynamic polarization tests

During the anodic polarization of copper in the salt solution containing PTAH, anodic current density is considerably reduced compared to the current density obtained in the solution without the inhibitor (see Figure1). The extent of reduction of the current density is increased with the increase of the inhibitor concentration. A well defined passivation region (> 0.5 V) was obtained at concentrations 0.005 and 0.01 mol L^{-1} inhibitor. The passivation diminishes at higher potentials where the protective film on the surface of copper gets destroyed.

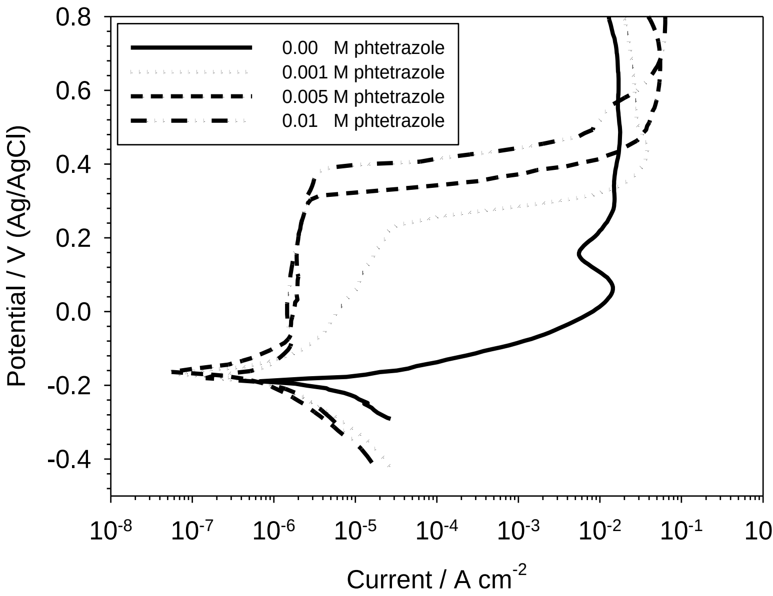


Figure 1. Effect of concentration of PTAH on the potentiodynamic polarization curves of copper in the 0.6 mol L^{-1} NaCl solution at voltage scan rate of 5 mV s^{-1} and 20^oC.

The reduction in the current density indicates the formation of a protective layer on copper surface. The strongest protective effect is exhibited at concentrations 0.005 and 0.01 mol L^{-1}. In weakly acidic, neutral, and weakly alkaline media the inhibitor has the form PTAH. The inhibition efficiency of PTAH can be attributed to the formation of a protective film of Cu(I)PTA complex on the copper surface, i.e. [18-21]:

$$\text{Cu} + \text{PTAH} \rightleftharpoons \text{Cu(1)PTA} + H^+ + e^- \qquad [1]$$

The degree of surface coverage at different concentrations of PTAH can be obtained from the following expression:

$$\theta = \frac{I_{corr(b)} - I_{corr(inh)}}{I_{corr(b)}} \qquad [2]$$

where $I_{corr(b)}$, $I_{corr(inh)}$ represent corrosion current densities in the absence and in the presence of the inhibitor, respectively. Table1 contains the surface coverage values for different inhibitor concentrations which were determined from polarization curves in Figure1. The interaction of PTAH with the copper surface was best described using the Langmuir isotherm. This isotherm is [22-23]:

$$\frac{\theta}{1-\theta} = AC\exp\left(\frac{-E^{\#}}{RT}\right) = KC \qquad [3]$$

where θ is the surface coverage, $E^{\#}$ is the activation energy, C is the concentration in mol L^{-1} and K is the constant of the adsorption process. The above equation can be simplified as:

$$\frac{C}{\theta} = \frac{1}{K} + C \qquad [4]$$

Table 1. The degree of surface coverage versus concentration of the inhibitor

Inhibitor Concentration, mol L^{-1}	**0.0**	**0.001**	**0.005**	**0.01**
E_{corr} , V (Ag/AgCl)	-0.236	-0.173	-0.161	-0.166
I_{corr} , A cm^{-2}	3.68E-5	5.13E-7	2.99E-7	2.17E-7
Surface coverage, Θ	0.0	98.6	99.19	99.41

A plot of C/θ versus C yields a straight line with intercept 1/*K*. Figure 2 shows the relationship between C/θ and C. The relationship between the adsorption constant and the standard free energy of adsorption (ΔG^o) is given by [24-25]:

$$K = \left(\frac{1}{55.55}\right)\exp\left(\frac{-\Delta G^0}{RT}\right) \qquad [5]$$

where R is the universal gas constant and T is the absolute temperature. Standard free energy of adsorption (ΔG^o) of -49.15 kJ mol^{-1} was obtained at 20°C. The value of ΔG^o indicates the spontaneity of the adsorption reaction of PTAH on the copper surface. It also points to chemisorption occurring in the interaction of PTAH and the surface of copper where charge sharing or transfer from the inhibitor molecules to the copper surface forms a co-ordinate type of bond [26-27].

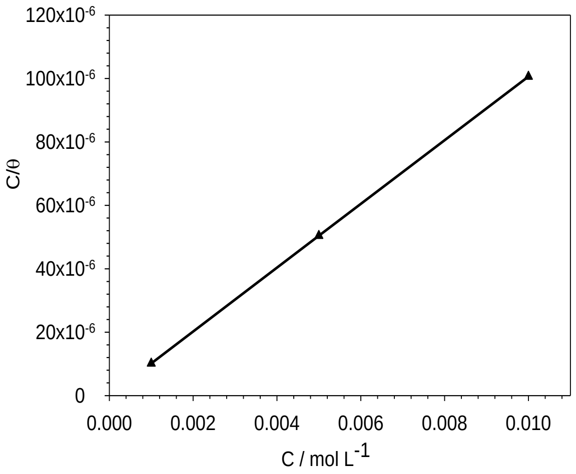


Figure 2. Langmuir adsorption isotherms of copper in 0.6 mol L^{-1} NaCl in the presence of PTAH at 20°C.

Figure 3 shows the effect of temperature on the polarization curves of copper in 0.6 mol L^{-1} NaCl in the absence and in the presence of 0.01 mol L^{-1} PTAH. The current density increases with the increase in temperature. Note the big differences in current densities obtained in the presence of PTAH and in its absence. The dependence of the limiting current, i_L, on temperature can be analyzed using the Arrhenius equation. i.e.

$$\ln i_L = \ln A - E^{\#} / RT \qquad [6]$$

where A is the preexponential factor, $E^{\#}$ is the activation energy, R is the universal gas constant and T is the absolute temperature. Arrhenius plot of ln i_L versus 1/T gives a straight line whose slope is used to calculate the activation energy of the dissolution reaction. Figure 4 illustrates Arrhenius plot of the passivation currents of copper dissolution in the PTAH inhibited salt solution. Passivation currents were determined from potentiodynamic polarization curves (see Fig.3). The plot gives activation energies of 71.8 KJ/mol. Arrhenius plot of the limiting currents of copper dissolution in the salt solution in the absence of PTAH is also shown in Figure 4. The activation energy calculated from this plot is 17.7 KJ/mol which is quite small compared to the one obtained in the presence of PTAH indicating the high inhibition efficiency of the PTAH inhibitor.

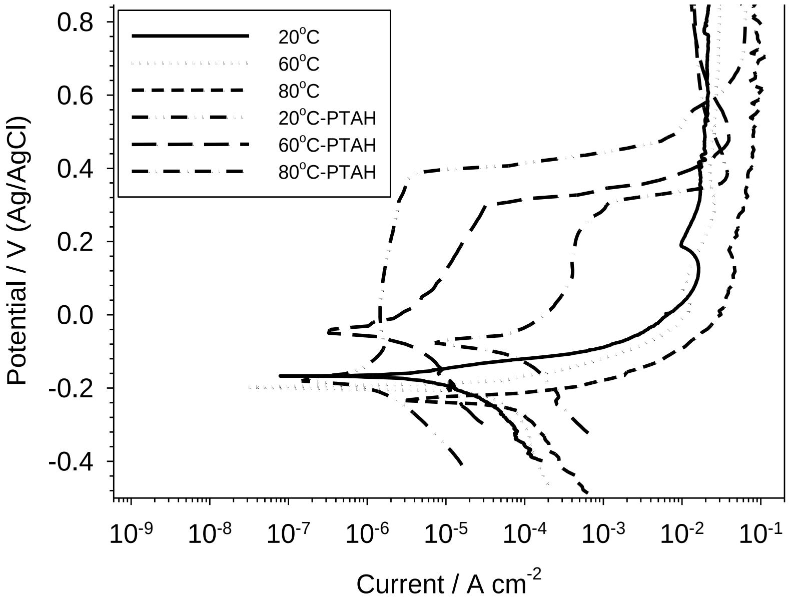


Figure 3. Effect of temperature on the potentiodynamic polarization curves of copper in the 0.6 mol L^{-1} NaCl solution in the absence and in the presence of 0.01 mol L^{-1} PTAH at voltage scan rate of 5 mV s^{-1}.

Fig.5 shows the effect of thiosulfate and sulfide ions (pollutants of salt water) on the potentiodyanmic polarization curves of copper in the PTAH inhibited salt solution. The addition of 0.001 mol L^{-1} $S_2O_3^{-2}$ to the testing solution leads to a shift in E_{corr} from -170 mV towards less noble value of -300 mV. The anodic currents obtained were increased by about one order of magnitude in the presence of $S_2O_3^{-2}$. A more pronounced shift in E_{corr} (~ 500 mV) was obtained in the presence of 0.001 M HS^-. The anodic current obtained was higher than the one obtained in the presence of $S_2O_3^{-2}$.

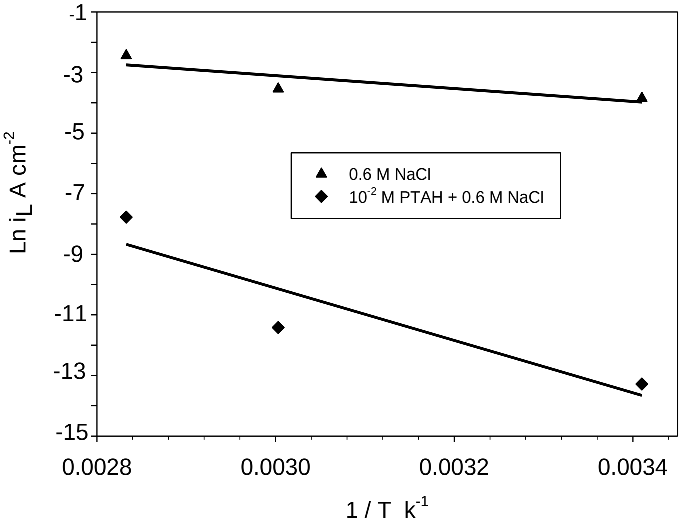


Figure 4. Arrehenius plots of the limiting currents of copper dissolution in 0.6 mol L^{-1} NaCl in the presence and in the absence of 0.01 mol L^{-1} PTAH.

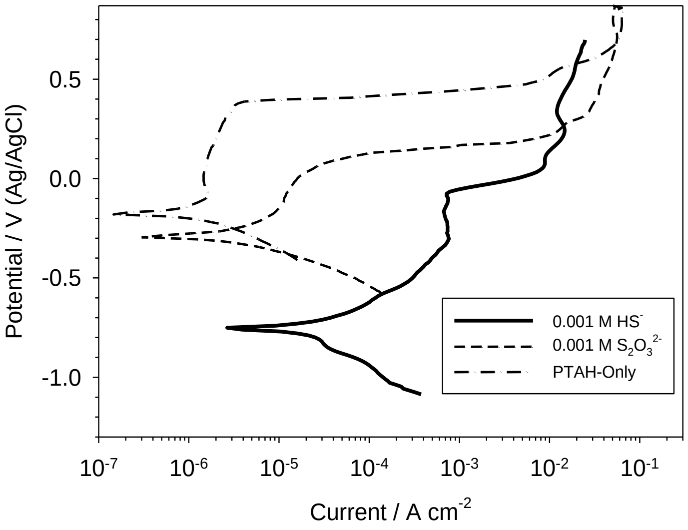


Figure 5. Potentiodynamic polarization curves of copper in the 0.6 mol L^{-1} NaCl solution containing 0.01 mol L^{-1} PTAH in the absence and in the presence of either sulfide or thiosulfate ions. Experiments were performed at voltage scan rate of 5 mV s^{-1} and 20°C.

3.2. Potentiostatic polarization tests

Figure 6 represents the effect of thiosulfate and sulfide ions on the potentiostatic curves of copper treated in the PTAH inhibited electrolyte at a potential of 0.0 V (Ag/AgCl), before the injection of these ions. The remarkable inhibiting efficiency of PTAH is reflected in a passive current of about

1 μA cm^{-2} in the presence of 0.01 mol L^{-1} PTAH after one hour. Upon injection of 0.001 mol L^{-1} of either $S_2O_3^{2-}$ or HS$^-$, a rapid increase in current to about 590 and 650 μA for the $S_2O_3^{2-}$ or HS$^-$, respectively. The magnitude of this sudden increase in current upon injection of thiosulfate or sulfide ions is taken as a measure of the intensity of thiosulfate or sulfide attack.

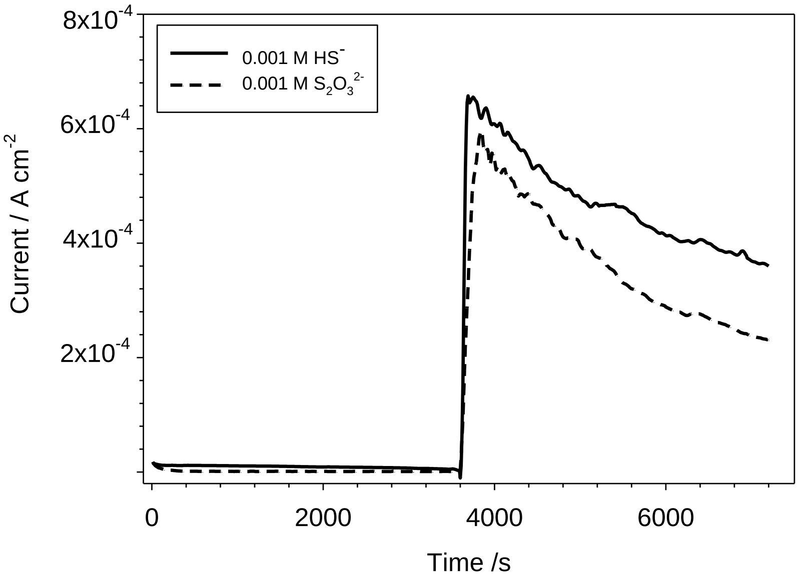


Figure 6. Effect of the injection of either sulfide or thiosulfate ions on the potentiostatic polarization curves of copper in the 0.6 mol L^{-1} NaCl solution containing 0.01 mol L^{-1} PTAH at 20^{o}C.

Figures 5 and 6 reveal a pronounced promoting effect of thiosulfate on the rate of anodic dissolution of copper. Thiosulfates are known to adsorb on copper surfaces [28-29]. The process can be represented by the following equation:

$$Cu_{(s)} + S_2O_3^{2-}{}_{(aq)} = Cu{:}S_2O_3^{2-}{}_{(ads)} \qquad [7]$$

The two sulfur atoms in the thiosulfate ion ($S_2O_3^{2-}$) are not equivalent. While the central sulfur atom is well bonded to the three oxygen atoms, the peripheral sulfur atom is weakly attached to the central sulfur atom via a weak, and hence fairly long, bond. Consequently both sulfur atoms behave differently towards the copper surface. For this reason, the adsorption of thiosulfate is described in terms of dissociative adsorption, i.e.

$$S_2O_3^{2-}{}_{(aq)} + 2Cu_{\square} = CuS + Cu{:}\ SO_3^{2-}{}_{(ads)} \qquad [8]$$

where $Cu_{\square}$ refers to the active adsorption sites on the copper surface, while $Cu{:}SO_3^{2-}{}_{(ads)}$ refers to adsorbed sulfite ions. The sulfite covered areas of the copper electrode undergo a rapid anodic dissolution reaction producing $CuSO_3$ and a fresh active site $Cu_{\square}$, i.e.

$$Cu{:}SO_3^{2-}{}_{(ads)} = CuSO_{3\,(aq)} + Cu_{\square} + 2e^- \qquad [13]$$

The overall process is the sum of the above two equations, i.e.

$$S_2O_3{}^{2-}{}_{(aq)} + 2Cu_{(s)} = CuS + CuSO_{3\,(aq)} + Cu_{\square} + 2e^- \qquad [14]$$

The above arguments suggest that the corrosion of copper in the presence of thiosulfates produces CuS, sulfite ions ($SO_3{}^{2-}$), and copper ions.

A strong promoting effect of sulfide ions (much more than thiosulfate) on the anodic dissolution of copper in the PTAH inhibited salt solution is also evidenced (see Figures 5&6). This can be understood knowing the relative stability of copper sulfide which is 10^{47} which is expected to be much higher than that of Cu(1)PTA complex [30]. The stability constant of Cu(I)PTA complex would be comparable to that of copper benzotriazole complex (Cu(1)BTA) complex which is about 10^2 [31]. This indicates that sulfide ions compete for Cu(I) ions under a much stronger driving force than PTAH [32-33]. Consequently, sulfide ions can extract the Cu(I) ions from the Cu(I)PTA complex,i.e.

$$Cu(1)PTA + HS^- = CuS + PTAH + e^-$$

This reaction leads to the disappearance of some of the protective Cu(I)PTA film and the appearance of copper sulfide. Once the protective film breaks down, corrosion occurs on the bare surface.

4. CONCLUSIONS

PTAH concentrations ≥ 0.005 mol L^{-1} show excellent corrosion inhibition (>97%) of copper in the 0.6 mol L^{-1} NaCl solution. This can be related to the formation of a passive layer of Cu(I)PTA on the copper surface. This layer was formed by chemisorption of the inhibitor on the copper surface.

Thiosulfate and sulfide ions have pronounced detrimental effects on the passivity caused by PTAH. The presence of these ions shifts the free corrosion potential in the active direction and increases the current density and hence the rate of anodic dissolution of copper. These effects were more obvious in the presence of sulfide ions.

ACKNOWLEDGEMENTS
The authors acknowledge the support of this work by the Research Administration of Kuwait University, Grant Numbers SC04/11.

References

1. Robert B. Ross, Metallic materials specifications handbook, Chapman and Hall, London (1992).
2. L. La Que, Marine corrosion, John Wiley & Sons, Inc., New York (1975).
3. ASM Handbook, 9th ed., Metals Handbook, Vol. 13 Corrosion, New York (1978).

4. H. Leidheiser, The Corrosion of copper, tin, and their alloys, The Electrochemical Society, New York (1979).
5. D. Tromans and J. C. Silvia, *Corrosion*, 53 (1997) 16.
6. G, Kear, B. D, Barker and F. C. Walsh, *Corros. Sci*., 46 (2004) 109.
7. F. J. Satchell and J. B. Smith, *Phys. Chem. Chem. Phys*., 4 (18) (2002) 4314.
8. F. Zucchi, G. Trabanelli and M. Fonsati, *Corros. Sci*., 38 (1996) 2019.
9. X.R.Ye, X.Q.Xin, J.J.Zhu and Z.L.Xue, *Appl. Surf. Sci*., 135 (1996) 307.
10. J. C. Marconato, L. O. Bulhões and M. L.Temperini, *Electrochim. Acta*, 43 (1998) 771.
11. Z. Xue-mei and L. Rui-quan, *Materials Protection*. 12 (2009) 15.
12. R.Subramanian and V. Lakshminarayanan, *Corros. Sci*,. 44 (2002) 535.
13. E.Szocs, G.Vastag, A.Shaban and E.Kalman, *Corros. Sci*., 47 (2005) 893.
14. M. Mihit, R. Salghi, S. El Issami, L. Bazzi, B. Hammouti, E. Ait Addi and S. Kertit, *Pigment and Resin Technology*, 35 (2006) 151.
15. Z. Xue-mei and L. Rui-quan, *Materials Protection*, 12 (2009) 15.
16. V. Violet Dhayabaran, I. Sharmila Lydia, J. Princy Merlin and P. Srirenganayaki, *Chemistry and Materials Science*, 10 (2004) 123.
17. K.F. Khaled and M.M. Al-Qahtani, *Mat. Chem. Phys*., 113 (2009) 150.
18. D. Tromans and R. Sun, *J. Electrochem. Soc*., 138 (1991) 3235.
19. D.M. Bastidas, *Surf. Interface. Anal*., 38 (2006) 1146.
20. E. Cano, J.L. Polo, A. La Iglesia and J.M. Bastidas, *Adsorption*, 10 (2004) 219.
21. N. K. Allam, A. Abdel Nazeer and E. A. Ashour, *J Appl Electrochem*., 39 (2009) 961.
22. S.S. El-Egamy, *Corros. Sci*., 50 (2008) 928.
23. S.M. Milic and M.M. Antonijevic, *Corros. Sci*., 51 (2009) 28.
24. M. Ehteshamzade, T. Shahrabi and M.G. Hosseini, *Appl. Surf. Sci*., 252 (2006) 2949.
25. M. Scendo, Corros. Sci., 49 (2007) 3953.
26. M. Donahue and K. Nobe, *J Electrochem. Soc*., 112 (1965) 886.
27. E. Kamis, F. Bellucci, R.M. Latanision and E.S.H. El-Ashry, *Corrosion*, 47 (1991) 677.
28. J. Degenhardt and A. J. McQuillan, *Langmuir*, 15 (1999) 4595.
29. T. Laiho, I. Lukkari, M. Meretoja, K. Laajalehto, J. Kankare and J.A. Leiro, *Surf Sci*., 584 (2005) 83.
30. J.A. Dean, Lange's Handbook of Chemistry, 14th ed., McGraw Hill, Inc., New York (1992).
31. D. Tromans and G. Li, *Electrochem. Solid St*., 5 (2002) B5.
32. E.A. Ashour, H.S. Hegazy and B.G. Ateya, *J. Electrochem. Soc*., 147 (2000) 1767.
33. F.M. Al Kharafi, A.M. Abdullah, I.M. Ghayad and B.G. Ateya, *Appl. Surf. Sci*., 253 (2007) 8986.