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Short Communication

Enhanced Inhibition of Corrosion of Mild Steel by Triazole Derivative in Presence of Copper Ions

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The inhibition of the corrosion of mild steel in 0.5 M H_2SO_4 solution by 5-(4-Pyridyl)-1H-1,2,4-triazole-3-thiol (PTT) compound both in the presence and absence of copper ions has been studied using potentiodynamic measurements. It has been found that copper ions significantly enhance the inhibiting action of PPT. For instance, while the inhibition efficiency in the presence of 0.15 mM PTT is 23 %, it is tripled when a 0.05 mM of copper ions is added, pointing to the significant synergism between the adsorption of PTT and copper ions. The synergistic parameter was found to equal 2.39 in the presence of 0.15 mM PTT + 0.05 mM Cu^{2+}. The PTT acts as a mixed type inhibitor both in the presence and absence of copper ions, and it follows Langmuir adsorption isotherm.

Keywords: Corrosion inhibitor, Langmuir isotherm, Mild steel, Synergism, Adsorption, copper ions

1. INTRODUCTION

Organic inhibitors are often added to pickling solutions to avoid the dissolution of steel. In acid media steel should be protected from the further attack of the harsh environment. Organic inhibitors contain either heteroatoms with high affinity to adsorption and/or double bonds, triple bonds and aromatic rings. All these enhance the adsorption process and result in the formation of an effective coating on the surface of the metal. This coating forms a barrier between the metal and the corrosive environment and protects the metal from undergoing corrosion [1-7].

In the present work the inhibitive action of 5-(4-Pyridyl)-1H-1,2,4-triazole-3-thiol (PTT) compound (Fig. 1) on the corrosion of mild steel in 0.5 M H_2SO_4 is studied. Triazole derivatives have been reported as efficient inhibitors for steel [2, 8-13]. The possible synergistic action of copper ions on the inhibitive action of PTT is also investigated. The inhibition efficiency of a poor corrosion inhibitor can be enhanced by the so-called synergistic inhibition. It is a an alternative protocol to minimize the required concentration of certain costly inhibitor [14-17]. Potentiodynamic measurements are used for this purpose. Subsequently, the mode of adsorption is explored.

2. EXPERIMENTAL

2.1. Mild Steel Sample

Working electrode was mild steel of composition (wt. %): 0.07% C, 0.29% Mn, 0.07% Si, 0.012% S, 0.021% P and the remainder iron. Samples of 0.5 cm^2 were used.

2.2. Inhibitor

5-(4-Pyridyl)-1H-1,2,4-triazole-3-thiol (PTT) (Fig. 1) compound used here as a corrosion inhibitor, copper salt were obtained from Sigma-Aldrich and used without further purification.

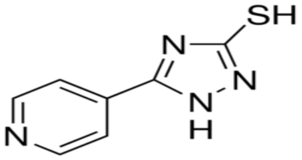

Figure 1. Structure of 5-(4-Pyridyl)-1H-1,2,4-triazole-3-thiol Solutions

The solution of 0.5 M H_2SO_4 was prepared by dilution of AR grade 98% H_2SO_4. Stock solutions of PTT and copper salt were prepared in 0.5 M H_2SO_4 and the required concentrations were obtained by dilution.

2.3. Electrochemical Measurements

Electrochemical measurements were conducted in a conventional three-electrode cell; platinum was used as the counter electrode (CE) and a $Hg/Hg_2SO_4/SO_4^{2-}$ coupled to a fine Luggin capillary was used as the reference electrode (RE). The ohmic contribution was minimized using the Luggin capillary close enough to the working electrode (WE). The WE surface area of 0.5 cm^2 was polished with emery paper down to 2000, rinsed with distilled water, degreased with acetone, and dried with a cold air stream. The electrode was immersed in the test solution at open circuit potential (OCP) for 15 min at 25 ^oC or until the steady state is obtained, then the Tafel plots were recorded. All electrochemical measurements were carried out using PGSTAT30 potentiostat/galvanostat. The potential was scanned from a potential of -150 mV vs. OCP, to 150 mV vs. OCP at a scan rate of 2 mV/s. The measurements were repeated at least three times to test the reproducibility of the results.

The open circuit potentials (OCP) of samples in 0.05 M H_2SO_4 solution were measured against standard Ag/AgCl electrode as a reference electrode for 60 min.

Electrochemical measurements were performed using a PGSTAT30 potentiostat/galvanostat. The working electrode and the counter electrode (a platinum spiral wire) were separated by a porous glass. An Ag/AgCl (KCl sat.) electrode was used as the reference electrode. A conventional three-electrode cell of around 20 ml was used for the cyclic voltammetric measurements. The polycrystalline gold (poly-Au) electrode (1.6 mm in diameter), used as working electrode, was polished with aqueous slurries of successively finer alumina powder (down to 0.06 μm), rinsed with water and then was sonicated for 10 min in bidistilled water. Poly-Au electrode was then electrochemically pretreated in N_2-saturated 0.05 M H_2SO_4 solution by repeating the potential scan in the potential ranges of – 0.2 to 1.5 V vs. Ag/AgCl (KCl sat.) at 100 mV s^{-1} for 10 min or until the CV characteristic of a clean Au electrode was obtained.

3. RESULTS AND DISCUSSION

The polarization curves of mild steel obtained in 0.5 M H_2SO_4 in the absence and presence of various concentrations of PTT at 25 ^{o}C are shown in Fig.2. Electrochemical parameters extracted from this figure such as the corrosion potential, E_{corr}, the current density at potential -510 mV (vs. Ag/AgCl), *I* Tafel slopes, b_c and b_a and the percentage inhibition, %*P* are given in Table 1. Several features can be extracted from this figure and this Table. The effect of PTT on the cathodic branch is smaller than the anodic one. The corrosion potential shifted to anodic direction and the shift increases slightly with increasing PTT concentration. The effect of the inhibitor concentration on the Tafel slopes is negligible indicating that the inhibitor exerts its action via simple blocking, and that the adsorption of the inhibitor does not change the mechanism [18].

The protection efficiency is given by:

$$\% P = \left[1 - \frac{I_i}{I_2}\right] 100 \qquad (1)$$

Where, I_1 and I_2 are current densities, obtained at potential -510 mV (vs. Ag/AgCl), in the absence and presence of inhibitor, respectively. The dependence of the protection efficiency on the concentration is of sigmoid shape (data are not shown); i.e. % *P* increases with the concentration until it reaches a plateau at protection efficiency ca. 62 % indicating the quiet poor inhibition efficiency of the present inhibitor under the present conditions.

Table 1. Polarization data for mild steel in 0.5 M H_2SO_4 both in the absence and presence of PTT.

[PTT], mM	E_{corr} (mV)	β_c (mV/dec)	β_a (mV/dec)	I^a (mA/cm^2)	θ	% *P*
0.0	-443	108	83	1.10	--	--
1.5	-438	110	81	0.86	0.23	23
2.5	-438	105	79	0.84	0.34	34
5.0	-432	107	76	0.85	0.48	48
7.5	-429	106	75	0.86	0.57	57
1.2	-427	107	76	0.85	0.61	61

[a] as calculated at -0.510 V

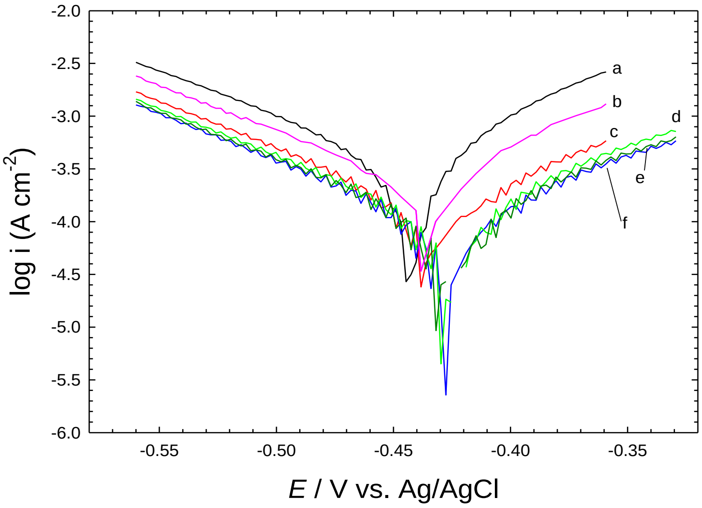

Figure 2. Potentiodynamic polarization curves for mild steel in 0.5 M H_2SO_4 containing different concentrations of PTT at 25 ^{o}C. [PTT]: (a) 0.0, (b) 0.15, (c) 0.25, (d) 0.5, (e) 0.75 and (f) 1.2 mM.

3.1. Synergism

The inhibition efficiency of an inhibitor is based on several factors including, for instance, the nature of the corrosive medium as well as the additives (anions and/or cations) that can be added to enhance the inhibitive action. The inhibition efficiency of PTT could be increased by the pre-adsorption of an anion and/or the complexation with cations, resulting in what is the so-called synergism which is expressed by synergism parameter (I_θ) [14] defined as,

$$I_\theta = \left[\frac{1 - I_{1+2}}{1 - I'_{1+2}}\right] 100 \qquad (2)$$

Where: $I_{1+2} = (I_1 + I_2) - (I_1 I_2)$; I_1 and I_2 are the degrees of surface coverage in the individual presence of the copper ions and the PTT, respectively, and I'_{1+2} is the one in their coexistence. I_θ approaches unity when no interaction takes place between the inhibitor molecules and the copper ions, $I_\theta > 1$ and $I_\theta < 1$ denotes synergistic and antagonistic effects, respectively [15]. Fig. 3 shows the Tafel plots of mild steel in (a) 0.5 M H_2SO_4 containing (a) 0.0 mM PTT + 0. mM Cu^{2+}, (b) 0.05 mM Cu^{2+}, (c) 0.15 mM PTT + 0.0 mM Cu^{2+} and (d) 0.15 mM PTT + 0.05 mM Cu^{2+}. The different electrochemical parameters are given in Table 2. As can be seen the inhibition efficiency in the presence of either copper ions or inhibitor is low. However, when both species are present, Tafel plots are bodily shifted to lower currents, i.e., a significant increase in the inhibition efficiency, in the presence of very low concentration of both species, is obtained (as shown in Table 2). The protection efficiencies in the presence of the individual species, i.e., 0.15 mM PTT and 0.05 mM Cu^{2+} equals 23 and 7 %, respectively. In the presence of the two species, i.e., 0.15 mM PTT and 0.05 mM Cu^{2+}, the protection efficiency equals 70 %. The extent of the enhancement is represented as synergistic parameters. In the presence of copper ions the I_θ value is larger than unity, indicating a real synergistic action of copper ions with the inhibitor. This reveals that PTT of lower concentrations can act effectively as a corrosion inhibitor in the presence of copper [16, 17].

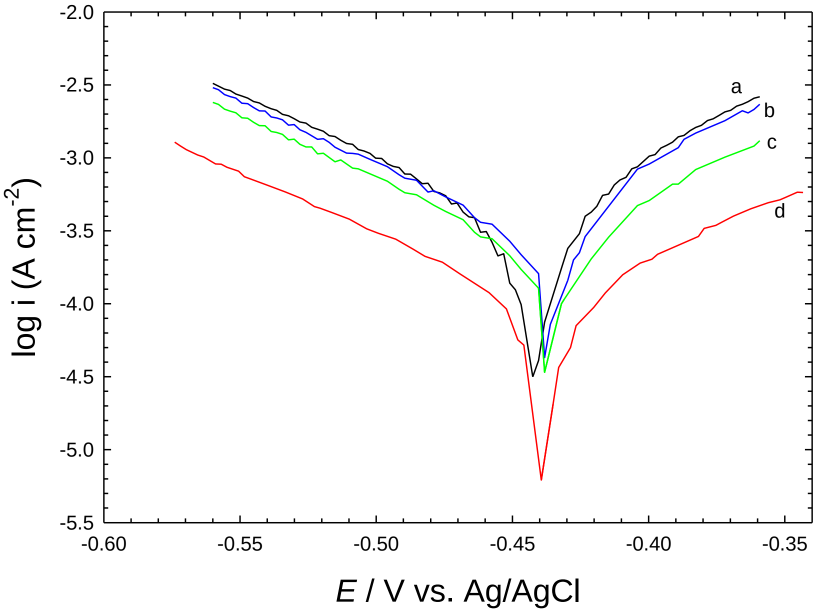

Figure 3. Tafel plots obtained at mild steel in 0.5 M H_2SO_4 containing (a) 0.0 mM PTT + 0. mM Cu^{2+}, (b) 0.05 mM Cu^{2+}, (c) 0.15 mM PTT + 0.0 mM Cu^{2+} and (d) 0.15 mM PTT + 0.05 mM Cu^{2+}.

Table 2. Polarization data and synergism parameter (S_θ) for PTT and copper ions on mild steel in 0.5 M H_2SO_4 at 25 °C.

System,	% *P*	θ	S_θ
Blank	--	--	
0.15 mM PTT	23	0.47	
0.05 mM Cu^{2+}	7	0.15	
0.15 mM PTT + 0.05 mM Cu^{2+}	70	0.66	2.39

3.2. Adsorption Isotherm

The adsorption of an inhibitor involves the substitution of the adsorbed water molecules (($H_2O_{(ads)}$) by the inhibitor molecules according to the following equation;

$$Org_{(sol)} + nH_2O_{(ads)} \rightarrow Org_{(ads)} + nH_2O_{(sol)} \quad (3)$$

where, $org_{(sol)}$ and $Org_{(ads)}$ are the organic molecules in the aqueous solution and the adsorbed one, respectively. n is the number of water molecules replaced by one inhibitor molecule. The basic information on the interaction between the inhibitor and the mild steel surface could be extracted from the so-called adsorption isotherms. Fitting of the experimental data to various isotherms has been examined, and it has been found that the experimental results in this study for PTT fit with Langmuir isotherm, given by Eq.4 [19, 20], and the plots are presented in Fig. 4.

$$\frac{C}{\theta} = \frac{1}{K} + C \qquad (4)$$

Where, *K* is the equilibrium constant for an adsorption process which reflects the extent of interaction between the inhibitor and the metal surface and *C* is the concentration of the inhibitor. The straight line obtained in Fig. 5 points to that PTT exerts its action via the formation of monolayer, and there is no interaction between the inhibitor molecules [21]. The equilibrium constant for adsorption process, *K*, was found to equal 2.1 x 10^4 mol^{-1}, and change in free energy of adsorption ΔG^o_{ads} (ΔG^o_{ads}= - RT ln(55.5K_{ads})) equals 34.61 KJ mol^{-1}. The large value of *K* reflects the stronger ability of adsorption of the inhibitor on the metal surface, where, *R* is the molar gas constant (8.314 J K^{-1}), *T* is temperature in Kelvin and value 55.5 is the concentration of water in mol dm^3 in solution [22, 23].

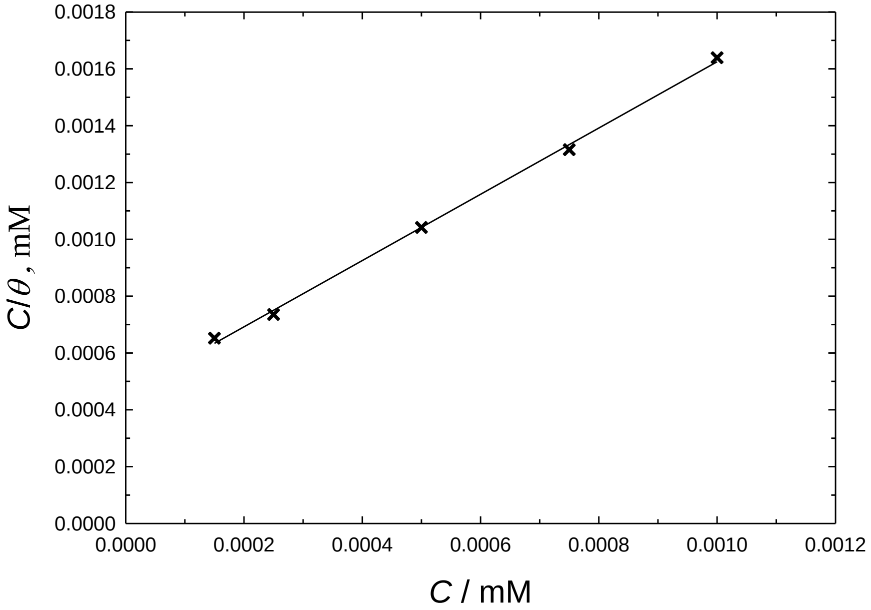

Figure 4. Langmuir isotherm for PTT adsorption on mild steel in 0.5 M H_2SO_4 at 25 ^oC.

The large negative value of ΔG^o_{ads} indicates the strong adsorption of the inhibitor. The mode of adsorption can be recognized from the ΔG^o_{ads}. In the present case chemisorption is the most probable mode with a small contribution of the physical mode, i.e., charge sharing between the inhibitor and the metal surface forming co-ordinate covalent bond [24].

Fig. 5 shows the cyclic voltammograms obtained at polycrystalline gold electrode in 0.5 M H_2SO_4, both in (a) the absence and presence of (b) copper ions and (c) PTT + copper ions. This figure reveals the characteristic behavior of bare gold electrode (curve a) in which the gold oxidation is revealed in the potential range 1-1-1.5 V is coupled with the reduction peak centered at ca. 0.9 V. In curve b, a new peak is obtained at around 0.3 V, probably belongs to the oxidation of copper which is deposited in the cathodic going scan, in agreement with literatures [25-27].

Interestingly in curve c, the peak corresponding to the gold oxidation-reduction is significantly reduced. In addition, the peak corresponding to copper oxidation is completely disappeared. This points to the strong adsorption of PTT on copper and gold explaining the high inhibition efficiency of PTT in the presence of copper ions.

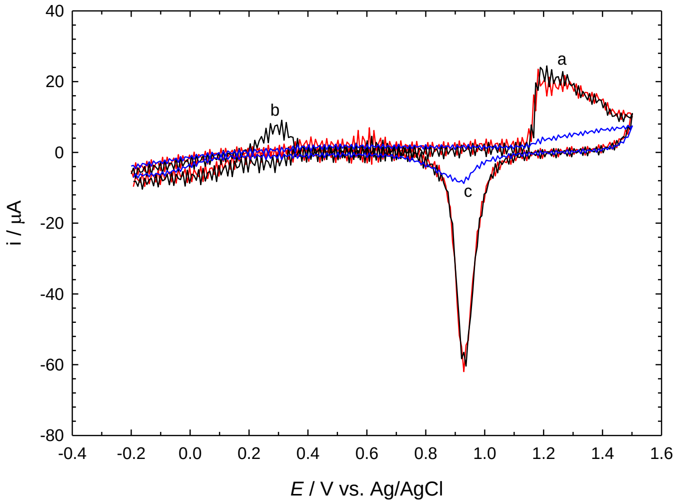

Figure 5. Cyclic voltammograms obtained at polycrystalline gold electrode in (a) 0.5 M H_2SO_4 containing (b) 0.25 mM copper ions and (c) 0.25 mM PTT + 0.25 mM copper ions.

4. CONSLUSION

The inhibitive action of 5-(4-Pyridyl)-1H-1,2,4-triazole-3-thiol (PTT) compound on the corrosion of mild steel in 0.5 M H_2SO_4 has been studied both in the absence and presence of copper ions. It has been found that copper ions significantly enhance the inhibitive action of PTT with a synergism parameter equals ca. 2.3 confirming the tremendous effect of copper ions on the inhibitive action of PTT. The adsorption of PTT accord with Langmuir isotherm with free energy of adsorption pointing to chemical type.

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