

Corrosion Inhibition of Mild Steel by 4-Allyl-5-pyridin-4-yl-4*H*-1,2,4-triazole-3-thiol

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Abstract: 4-Allyl-5-pyridin-4-yl-4*H*-1,2,4-triazole-3-thiol has been synthesized and characterized by IR, ¹H NMR, ¹³C NMR analysis. The corrosion protection of mild steel in a 0.1 M H₂SO₄ solution by 4-allyl-5-pyridin-4-yl-4*H*-1,2,4-triazole-3-thiol was studied by electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM). Results showed that 4-allyl-5-pyridin-4-yl-4*H*-1,2,4-triazole-3-thiol inhibited mild steel corrosion in a 0.1 M H₂SO₄ solution and indicated that the inhibition efficiencies increased with the concentration of inhibitor. Changes in impedance parameters suggested the adsorption of 4-allyl-5-pyridin-4-yl-4*H*-1,2,4-triazole-3-thiol on the mild steel surface, leading to the formation of protective films.

Keywords: 1,2,4-Triazole, Corrosion, Mild steel, Inhibition

Introduction

Mild steel is a well-known material used extensively in various industries. However, its tendency to corrode makes it unsuitable for exposure to acids. The use of inhibitors is one of the practical methods for protection against corrosion in acidic media¹. Organic compounds have long been known to inhibit the corrosion of mild steel in acidic media. Compounds previously studied as inhibitors include triazole derivatives²⁻⁵, bipyrazolic derivatives⁶, surfactants^{7,8}, aromatic hydrazides⁹, organic dyes^{10,11}, poly (4-vinylpyridine)¹² and thiosemicarbazide-type organic compounds^{13,14}. These compounds can adsorb on to the mild steel surface and block active sites, thus decreasing the corrosion rate.

Triazoles are important class of heterocyclic compounds. These compounds, rich in heteroatoms, such as sulfur, nitrogen and oxygen, can be used as environmentally friendly inhibitors because of their strong chemical activity and low toxicity¹⁵⁻²⁰. Examples are triazole-type compounds containing several heterocyclic structures, which have excellent corrosion properties for the corrosion of many metals in various aggressive media²¹⁻²³.

The aim of this study is to investigate the inhibitive properties of title compound on the corrosion of the steel in 0.1 M H₂SO₄ solution. The chemical structure of the compounds studied is as follows (Figure 1).

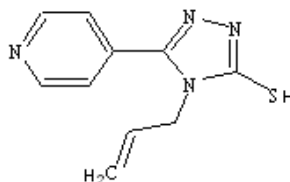


Figure 1. 4-Allyl-5-pyridin-4-yl-4H-1,2,4-triazole-3-thiol

Experimental

The synthesis of 4-allyl-5-pyridin-4-yl-4H-1,2,4-triazole-3-thiol was carried out according to a method are given in the literature²⁴. The structures of synthesized compounds were confirmed by analytical and spectroscopic methods (FT-IR, ¹H NMR, ¹³C NMR).

All reagents were of analytical grade. The stock solution of 4-allyl-5-pyridin-4-yl-4H-1,2,4-triazole-3-thiol (10⁻² M) was prepared in ethanol. Britton-Robinson buffer was used for varying pH. Due to the low solubility of this compound in aqueous media, 10% v/v ethanol solutions were used. The cyclic voltammograms were recorded by a Metrohm Model 757 VA computrace with conventional three-electrode cell, glassy carbon electrode (GCE) as the working electrode, an Ag/AgCl/KCl_(sat) as the reference and Pt wire as counter electrode. All the voltammetric measurements were conducted at the room temperature under the argon atmosphere. The pH values were measured with pH meter Metrohm Model 744.

Mild steel specimens obtained from were used as the working electrodes throughout the study. The composition of the mild steel was: %0.08 C, %1 Mn, %1 S, %16–18 Cr, %14 Ni, %0.04 P, %0.03 S. The cell contains three electrodes reference electrode, as working electrode comprised of mild steel, a glass electrode. The inhibiting action of this compound against the corrosion of carbon steel in 0.1 M H₂SO₄ solution was investigated by electrochemical techniques including electrochemical impedance spectroscopy. The potentiodynamic current–potential curves were swept from –0.25 to +0.25 VSCE at a scan rate of 0.5 mVs. Impedance measurements were carried out using AC signals of 5 mV peak to peak amplitude at the open circuit potential in the frequency range of 100 kHz–0.1 Hz. Electrochemical measurements were initiated about 30 min after the working electrode was immersed in solution to stabilize the steady state potential.

Results and Discussion

Electrochemical behavior of 4-allyl-5-pyridin-4-yl-4H-1,2,4-triazole-3-thiol

Koparir *et al.* reported that the crystal structure of thiol compounds corresponded to the thione form, but they showed thiol-thione tautomerism in solutions (Figure 2)²⁴. Due to the thiol-thione tautomerism of 4-allyl-5-pyridin-4-yl-4H-1,2,4-triazole-3-thiol it mostly appeared thiol form in solution. Thus it has oxidizable –SH group. Therefore, the electrochemical behavior of 4-allyl-5-pyridin-4-yl-4H-1,2,4-triazole-3-thiol was studied by using cyclic voltammetric technique (CV) at GCE. In order to see the effect of pH on electrochemical behavior of 4-allyl-5-pyridin-4-yl-4H-1,2,4-triazole-3-thiol, the cyclic voltammograms of this compound were recorded in Britton Robinson buffer solution with various pH. Figure 3 shows the cyclic voltammograms of 4-allyl-5-pyridin-4-yl-4H-1,2,4-

triazole-3-thiol at pH 2, 8 and 10 BRT buffer solution. As can be seen from this figure, the oxidation peak potential related with thiol oxidation was decreased by increasing pH value of buffer solution. This reflects that a proton transfer in the electrode process was participated.

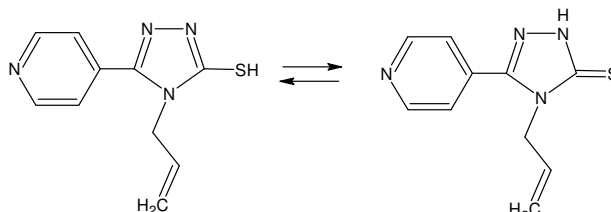


Figure 2. Thiole-thione tautomerism of 4-allyl-5-pyridin-4-yl-4H-1,2,4-triazole-3-thiol

In the cyclic voltammograms of 4-allyl-5-pyridin-4-yl-4H-1,2,4-triazole-3-thiol in all pHs, two oxidation peaks were observed. These peaks can be attributed to the oxidation of thiol groups. Electrochemical oxidation of this compound can be explained with electrochemical mechanism, because the electrooxidation leads initially to the generation of radical species with simultaneous H^+ release followed by a dimerization step. In the electro-oxidation process of 4-allyl-5-pyridin-4-yl-4H-1,2,4-triazole-3-thiol, firstly thiol groups (R-SH) are changed to radical species (R-S \cdot) and give one H^+ and e^- . Then disulphide (RS-SR) was formed by the chemical reaction of two mole radical species (Figure 4). The disappearance of the first anodic peak in the second scan of the cyclic voltammograms supported our discussion. As a result, it can be concluded that this thiol compound was oxidized irreversibly at GCE. Its oxidation process includes one oxidation electron transfer followed by a dimerization chemical step which shows that the oxidation behavior of this compound follows the EC mechanism in RSH compounds.

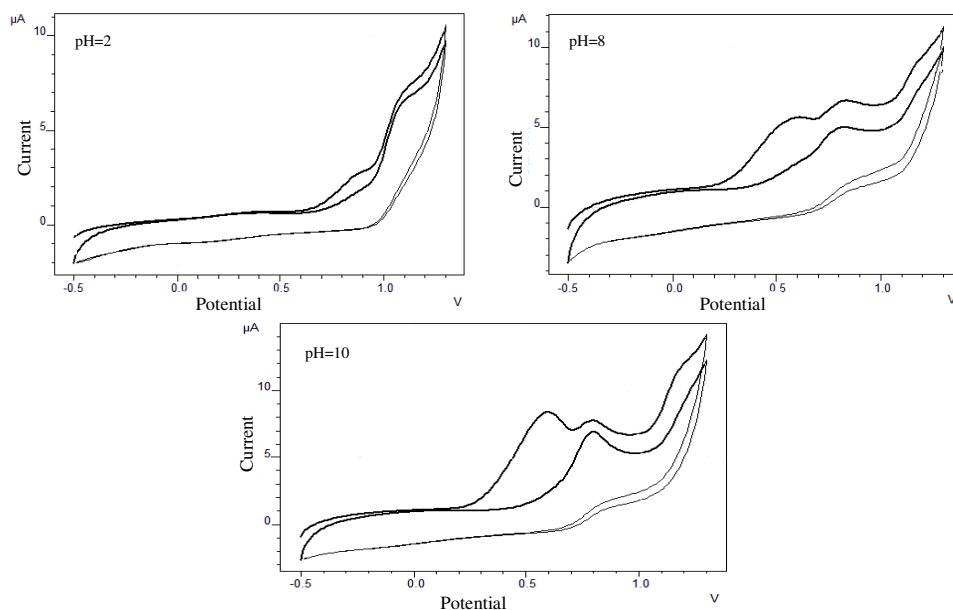


Figure 3. The pH dependence of the oxidation of 4-allyl-5-pyridin-4-yl-4H-1,2,4-triazole-3-thiol

When we evaluate the effect of pH on the oxidation peak current (I_p), I_p was increased and peak shape was apparent as sharply by increasing pH from 2 to 10. When we take into consideration of electrochemical mechanism (EC), thiyl radical form was formed in the first step (Figure 4). In this reaction, thiolic form is oxidized to radical form giving one H^+ and e^- . Thus, radical species were strongly formed in the basic media due to easily releasing of H^+ . In addition, the solubilities of thione or thiol compounds in basic medium are higher than that acidic medium²⁵. Due to the maximum peak current was obtained at the pH 10 BR buffer solution, this supporting electrolyte was used for the recording of cyclic voltammograms of this compound at various scan rates. Thus, the electrochemical behavior of the triazole was investigated by recording cyclic voltammograms in BR buffer solution (pH 10.0), at various scan rates. A typical cyclic voltammogram of triazole in the pH 10 BR buffer solution at various scan rates was shown in Figure 5. The linear increase in the oxidation peak current with the square root of scan rate showed that diffusion controlled process was took placed in the oxidation of triazole compound²⁵.

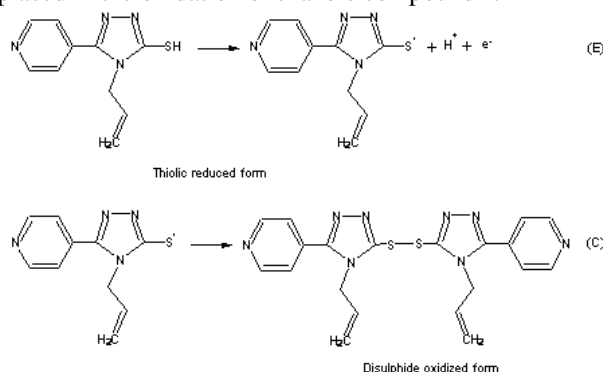


Figure 4. E: Electrochemical Reaction, C: Chemical Reaction

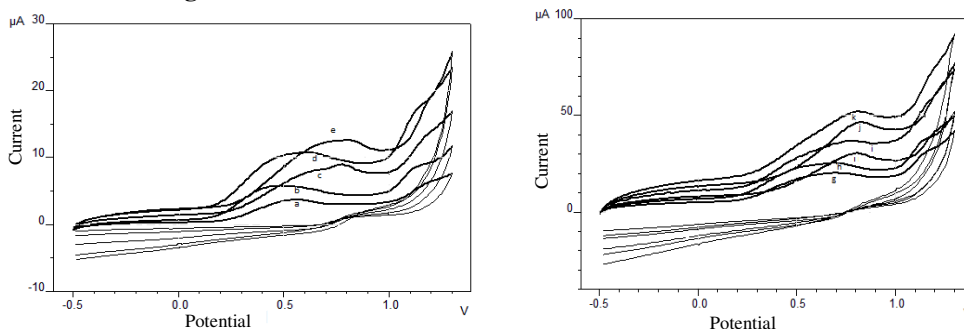


Figure 5. Cyclic voltammograms of 4-allyl-5-pyridin-4-yl-4H-1,2,4-triazole-3-thiol at GCE scan rates: a: 0.01 V/s, b: 0.02 V/s, c: 0.05 V/s, d: 0.08 V/s, e: 0.1 V/s, f: 0.2 V/s, g: 0.3 V/s, h: 0.4 V/s, i: 0.6 V/s, j: 1.0 V/s

Electrochemical impedance spectroscopy (EIS) measurements

The corrosion behavior of mild steel in 0.1 mol/L H_2SO_4 solution, in the presence of these 4-allyl-5-pyridin-4-yl-4H-1,2,4-triazole-3-thiol inhibitions, was investigated by the EIS method at 25 °C. Typical Nyquist diagrams in 0.1 mol/L H_2SO_4 containing compound 4-allyl-5-pyridin-4-yl-4H-1,2,4-triazole-3-thiol at different concentrations are shown in Figure 6.

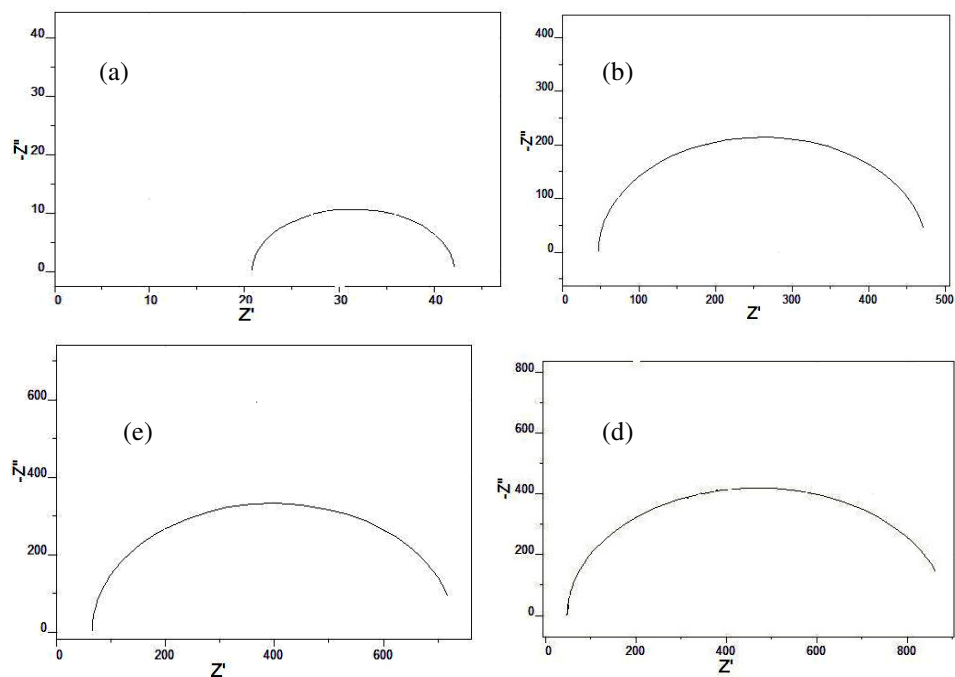
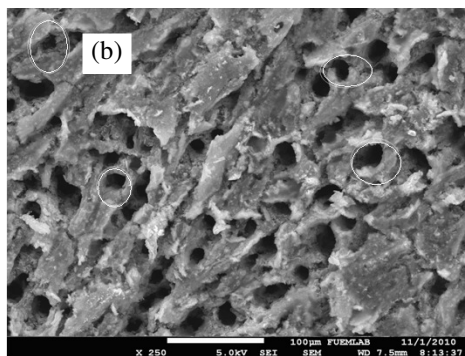
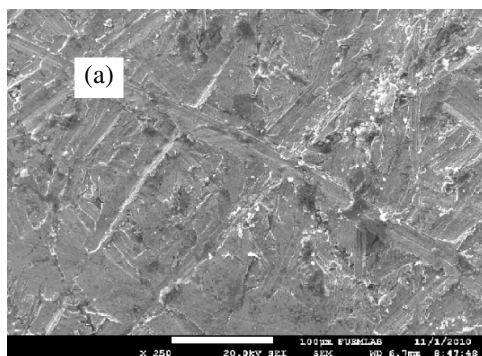


Figure 6. Nyquist plots for mild steel in 0.1 M H_2SO_4 at room temperature containing various concentrations of 4-allyl-5-pyridin-4-yl-4H-1,2,4-triazole-3-thiol: (a) 0.0, (b) 10^{-5} M, (c) 10^{-4} M, (d) 10^{-3} M

As can be seen from the impedance results shown in Figure 6, it is obvious from the results that the 4-allyl-5-pyridin-4-yl-4H-1,2,4-triazole-3-thiol inhibits the corrosion of mild steel in 0.1 M H_2SO_4 solution at all concentrations used in this study was seen to increase with increasing additive concentration at 25 °C.

So as to confirm the corrosion inhibition ability of the 4-allyl-5-pyridin-4-yl-4H-1,2,4-triazole-3-thiol derivative, scanning electron microscopy was applied. Figure 7a shows the micrograph only surface polishing, Figure 7b the morphology after exposure to the acid media for 3 h, Figure 7c the morphology after immersion in 0.1 M H_2SO_4 solution of 1.0×10^{-3} M 4-allyl-5-pyridin-4-yl-4H-1,2,4-triazole-3-thiol for 3 h.



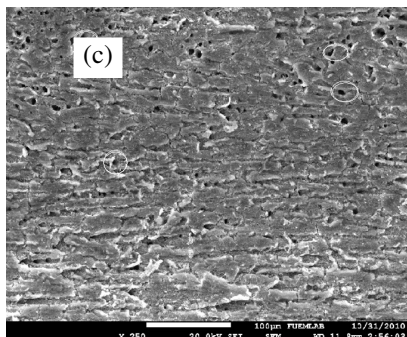


Figure 7. SEM micrographs of mild steel samples: (a) only surface polishing, (b) after immersion in 0.1 M H₂SO₄ solution without inhibitor (c) after immersion in 0.1 M H₂SO₄ solution of 1.0×10^{-3} M 4-allyl-5-pyridin-4-yl-4H-1,2,4-triazole-3-thiol.

Conclusion

Electrochemistry experiments were used to study the inhibitory effects of 4-allyl-5-pyridin-4-yl-4H-1,2,4-triazole-3-thiol on mild steel corrosion in a 0.1 M H₂SO₄ solution at room temperature. The 4-allyl-5-pyridin-4-yl-4H-1,2,4-triazole-3-thiol derivative can be regarded as a good inhibitor for mild steel corrosion in H₂SO₄ solution.

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