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Thiadiazole as a Potential Corrosion Inhibitor for Mild Steel in 1 M HCl

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ABSTRACT

Thiadiazole, as a corrosion inhibitor for mild steel in 1 M hydrochloric acid has been investigated using weight loss method and Scanning Electron Microscopy (SEM). The results showed that this inhibitor revealed a good corrosion inhibition at low and high concentrations. The optimum concentration of the investigated inhibitor showing the highest inhibition efficiency was also evaluated at four different temperatures in the range between 303 and 333 K. The inhibition efficiency was found to increase with increase in concentration of the inhibitors but decrease with rise in temperature. The adsorption the corrosion inhibitor on the mild steel surface in acidic media follows a Langmuir isotherm. Thiadiazole as corrosion inhibitor was prepared and it chemical structure was elucidate using Fourier transformer infra-red (FT-IR) and Nuclear Magnetic Resonance (NMR) spectroscopy.

1. Introduction

A corrosion inhibitor is a substance which, when added to a corrosive environment, significantly decreases the rate of corrosion attack caused by the environment. Corrosion inhibitors are commonly added in small amounts to pickling acids, acid stimulation fluids, cooling waters, oil and gas production streams, either continuously or intermittently to control corrosion [1]. In acidic media the corrosion inhibitors adsorb on the metal surface, resulting in a structural change of the double layer and reduced rate of the electrochemical partial reaction. The adsorption of inhibitor is influenced by the electronic structure of the inhibiting molecules and also by the steric factors, aromaticity and electron density at the donor atoms and also by the presence of functional groups [2]. Generally, the organic compounds containing hetero atoms like nitrogen, oxygen and sulphur etc. have been found to be very effective corrosion inhibitors [3]. The efficiency of these compounds depends upon the electron density of hetero atoms. The inhibition efficiency also depends upon the number of adsorption active centers in the molecule, their charge density, molecular size and mode of adsorption and formation of metallic complexes. Atoms such as nitrogen, oxygen and sulfur are capable of forming coordinate covalent bond with metal owing to their free electron pairs. Compounds with π bonds like aldehydes, ketones, imines also generally exhibit good inhibitive properties due to interaction of π orbital with metal surface [4]. The inhibition of corrosion of mild steel by acids was previously studied by some sulphur and/or nitrogen containing compounds [5]. An inhibitor may be effective in one system, while in another it is not, therefore, it is convenient to consider the following factors: (i) chemical structure of the inhibitor component; (ii) chemical composition of the corrosive medium; (iii) Nature of the metal surface; (iv) operating conditions (temperature, pressure, pH, etc.); (v) thermal stability of the inhibitor and (vi) corrosion inhibitors have temperature limits above which lose their effectiveness because they suffer degradation of the containing components and (vii) solubility of the inhibitor in the system [6-8]. The action mechanisms of corrosion inhibitors are: (i) adsorption, forming a film that is adsorbed onto the metal surface; (ii) Inducing the formation of corrosion products such as iron sulfide, which is a passivizing species and (iii) Changing media characteristics, producing precipitates that can be protective and eliminating or inactivating an aggressive constituent. It is well known that organic molecules inhibit corrosion by adsorption, forming a barrier between the metal and the environment. Thus, the polar group of the molecule is directly attached to metal and the nonpolar end is oriented in a vertical direction to the metal surface, which repels corrosive species, thus establishing a barrier against chemical and electrochemical attack by fluids on the metallic surface [9]. Ions pairs and pi-electron in chemical compounds expedite shifting of the electron from the inhibitor to the metal for complexation and this produce coordination bonds with different geometries depend on the active center. Chemical bonds force relies on the density of electrons for donor atoms that have found in the functional groups with the polarizability [10]. Inhibitors reactivity consist on adsorption rate and on metal surface. Electrostatically interaction between inhibitor and a metal are prominent during this inhibition action [11]. In continuation of previous studies [12-19], here in we had focused on synthesis of thiadiazole derivative named 4-(((5-mercapto-1,3,4-thiadiazol-2-yl)imino)methyl)-2-methoxyphenol as corrosion inhibitor. The chemical structure was confirmed using micro-elemental-analysis and some spectroscopically techniques. The inhibitory effect on the corrosion of mild steel in 1.0 M HCl are investigated using weight loss method and surface analyses are performed on the corroded surface using scanning electronic microscopy (SEM).

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2. Experimental Methods

2.1 Inhibitors Synthesis

The inhibitor was synthesized according to the Scheme 1. All the chemicals required for the synthesis were purchased from Sigma Aldrich. The IR spectra were recorded on a shimadzu FT-IR-8300 spectrometer. nuclear magnetic resonance (NMR) spectra were recorded on Bruker specrospin ultra shield magnets 300 MHz instrument utilizing TMS and DMSO-d6.

2.2 Synthesis of 2-Amino-5-Mercapto-1, 3, 4-Thiadiazole

A suspended mixture that consist of thiosemicarbazide (4.55 g, 0.05 mol), anhydrous sodium carbonate (5.3 g, 0.05 mol) and carbon disulphide (3.8 g, 0.05 mol) in absolute ethanol was stirred under reflux for for 5 h. Solvent was removed and the residue was dissolved in water, acidified with HCl. Yield 76% mp. 231-233 °C. FT-IR in cm^{-1}: 3293.3 and 3355.1 for NH_2, 2577.8 for thiol, 1609.2 (C=N), 1377.5 for thion and 680.5 (C-S). ^{1}H-NMR 12.44 (s, 1H, SH) and 8.11 (s, 2H, NH_2).

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2.3 Syntheses of Corrosion Inhibitor

A mixture of 2-Amino-5-mercapto-1, 3, 4-thiadiazole (4.0 g, 0.03 mol) and vanillin (4.56 g, 0.02 mol) was refluxed for 8 h. The solvent was evaporated in vacuum and the residue was recrystallized from methanol. FT-IR in cm^{-1}: 3192.1-3411.0 for OH, 3083.7 for C-H aromatic, 2547.4 for C-H aliphatic and 2583.1 for S-H. ^{1}H-NMR 12.09 (s, 1H, SH), 8.32 (s 1H for H-imine), 6.91-7.21 (m, 1H for C-H aromatic). 5.44 for O-H and 3.48 (s, 3H, CH3).

2.4 Weight Loss Method

MS specimens were supplied from Metal-Samples-Company and utilized as electrodes in our work. The weight percentage compositions of the MS specimens were: iron, 99.21; carbon, 0.21; silicon, 0.38; phosphorous, 0.09; s, 0.05; manganese, 0.05; aluminum, 0.01; active area of MS surface was 4.5 cm and cleaned as the standard procedure G1-03 mentioned in ASTM [20-26]. The specimens were suspended in duplicate in two hundreds milliliter of the solutions in presence and absence of various concentrations (0.0, 0.05, 0.1, 0.15, 0.2, 0.25 and 0.5 mM) of the synthesized inhibitor. After immersion times 1 h, 2 h, 3 h, 4 h, 5 h, 10 h, 24 h, 48 h and 72 h. The specimen was washed, dried and weighed accurately. Inhibition efficiency IE (%) was determined according to Eq. (1);

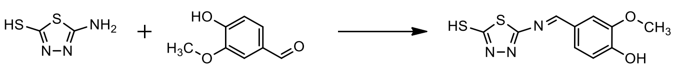
$$IE(\%) = \left(1 - \frac{W_2}{W_1}\right) \times 100 \qquad (1)$$

Where, W_1 & W_2 were weight loss of the MS in absence and in presence of the inhibitors.

3. Results and Discussion

3.1 Synthesis

To synthesize Schiff base namely 4-(((5-mercapto-1,3,4-thiadiazol-2-yl)imino)methyl)-2-methoxyphenol as corrosion inhibitor, the sequences of the reactions were outlined in Scheme 1, starting from commercially available thiosemicarbazie.



Scheme 1 Synthetic scheme of corrosion inhibitor

The synthesis of starting material 2-amino-5-mercapto-1,3,4-thiaiaole, was carried out by refluxing thiosemicarbazide, anhydrous sodium carbonate and carbon disulphide. Inhibitor 4-(((5-mercapto-1,3,4-thiadiazol-2-yl)imino)methyl)-2-methoxyphenol was easily synthesized in excellent yield by refluxing of 2-amino-5-mercapto-1,34-thiaiaole with the vanillin. The molecular weight of the synthesized corrosion inhibitor was 267 which was calculated based on the molecular formulas ($C_{10}H_9N_3O_2S_2$) and supported NMR and FT-IR spectrometry. The FT-IR spectrum of this inhibitor (3 and 4) show disappearance of the absorption bands at 3293.3 and 3355.1 cm^{-1} for hydrazide NH_2.

3.2 Weight Loss Results

Utilization of inhibitors constitutes one of the main economical method to mitigate the corrosion efficiencies and protects MS surface from corrosion in addition to preserve facilities of industry [27]. Organic molecules that act as inhibitors had been the main broad used in oil industries because of the ability to produce a barrier on the MS in high hydrocarbonic content media. Organic inhibitors belonging to various chemical families like amide, pyridine, imidazoline and azoles derivatives [28-30] in addition to polymers [31] and most of these families shown excellent efficiencies.

3.3 Concentration Effect

The inhibition efficiency for the inhibitor evaluated by weight loss technique for MS in hydrochloric acid solution with different concentrations of inhibitor for (1, 2, 3, 4, 5, 10, 24, 48 and 72 h), at 303 K are demonstrated in Fig. 1. Corrosion inhibitor diminish the corrosion of MS in hydrochloric acid. Inhibition efficiency was increased with a rise in concentration of the synthesized inhibitor and reached a maximum IE (%) at 0.5 mM concentration and this suggestive of the increase in the extent of protection efficiency.

3.4 Effect of Temperature

Comparison of inhibition efficiency of organic inhibitor on MS in acidic media in the absence or presence of deferent concentrations of inhibitor at various temperatures (303, 313, 323 and 333 K) indicated that inhibition performance enhance with increasing of inhibitor concentration and decreased with increasing temperatures. Fig. 2 show the effect of temperatures on inhibition efficiency for inhibitor with deferent concentrations. In the adsorption process of organic compound, the heat of adsorption is generally negative, and this indicated an exothermic process. This is the reason that the inhibition efficiency decrease at a higher temperature.

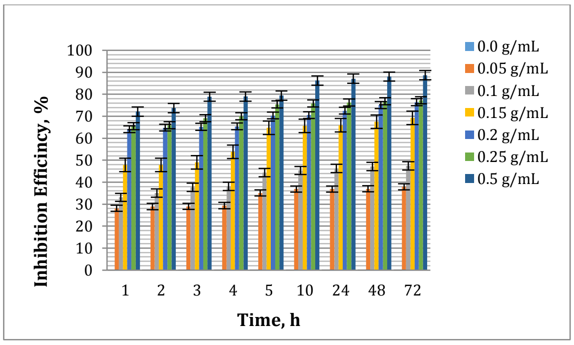


Fig. 1 Influence of concentration of inhibitor and time on inhibition efficiency of mild steel of mild steel at 303 K

3.4 Effect of Temperature

Comparison of inhibition efficiency of organic inhibitor on MS in acidic media in the absence or presence of deferent concentrations of inhibitor at various temperatures (303, 313, 323 and 333 K) indicated that inhibition performance enhance with increasing of inhibitor concentration and decreased with increasing temperatures. Fig. 2 show the effect of temperatures on inhibition efficiency for inhibitor with deferent concentrations. In the adsorption process of organic compound, the heat of adsorption is generally negative, and this indicated an exothermic process. This is the reason that the inhibition efficiency decrease at a higher temperature.

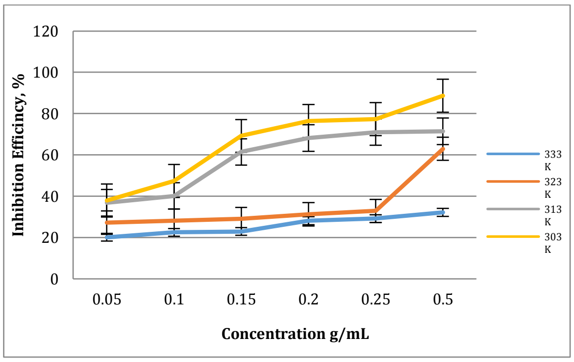


Fig. 2 Effect of temperature on inhibition efficiency of inhibitor with various concentrations

3.5 Postulated Mechanism of Inhibition

Inhibitor that was derived from thiadiazole was adsorbed on the MS surface and protect MS by block the cathodic or anodic reaction. Inhibitor with organic structure has the ability to form insoluble complex, by the reaction of inhibitor with metal and become as barrier on the surface of MS [32, 33]. Inhibition efficiency of studied inhibitor for the corrosion of MS in 1.0 M acidic media could be explained on the basis of the adsorption-sites, charges, size of molecules of inhibitors, nature of bonding with the MS surface and the ability for producing complexes. Unpaired electrons on nitrogen and oxygen atoms could bonds with the MS, as in Fig. 3.

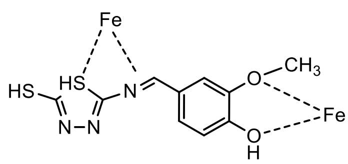


Fig. 3 Mechanisms of inhibition

The inhibition efficiencies for the synthesized inhibitor also could be explained based on Valence Bond Theory (VBT) or Crystal Field Theory

(CFT) or Molecular Orbital Theory (MOT) of complexation. Complexation between metal and ligand (inhibitor) should done through coordination bonds that formed by transfer the ion pair from the nitrogen, sulfur and/or oxygen atoms of inhibitor to d-orbital of metal

3.6 Scanning Electron Microscopy

SEM analysis was done to study the surface morphology of MS after immersion in 1.0 M HCl with and without of 0.5 mM inhibitor for 3 h at 30 °C as shown in Fig. 4. Damaged surface was observed in the absence of the inhibitor due to the high dissolution rate of iron at corrosive media, but a barrier for the MS surface was observed in presence of inhibitor. Result was evidence that inhibitor can be adsorbed on the MS surface and insulate the surface from hydrochloric acid solution.

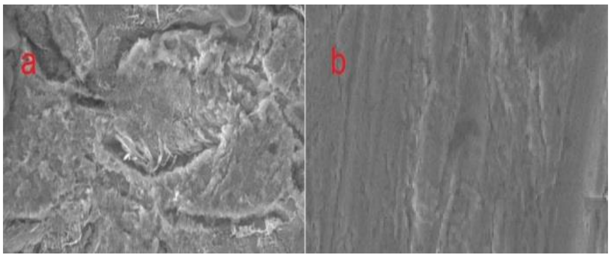


Fig. 4 SEM micrographs of mild steel in 1.0 M HCl solution at 303 K for studied inhibitor

4. Conclusion

In this study, corrosion inhibitor 4-(((5-mercapto-1,3,4-thiadiazol-2-yl)imino)methyl)-2-methoxyphenol was prepared and the structure was elucidate utilizing different spectroscopical techniques. Weight loss measurement was used to study the corrosion inhibition of mild steel in 1.0 M HCl solutions at 303, 313, 323 and 333 K using studied inhibitor. Corrosion inhibitor exhibited excellent inhibition performance. Generally, the MS corrosion in acidic medium was reduced by addition inhibitor. Inhibition efficiency increased with increasing of inhibitor concentration and reduced with increased of temperature. SEM micrograph shows that the inhibitor molecules form a protective film on the steel surface 1.0 M hydrochloric acid and exhibits a maximum inhibition efficiencies of 88% at 5×10^{-3} M.

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