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Inhibition of Mild Steel Corrosion in Sulfuric Acid Solution by 2-Hydropyrimidine-2-Thione Derivative

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Abstract

The corrosion inhibition potential and efficacy of 2-hydropyrimidine-2-thione derivative on mild steel in 0.5 M sulfuric acid solution was investigated using electrochemical polarization and FTIR spectroscopic techniques. In addition, docking studies were carried out as theoretical investigation of adsorption inhibitor on iron surface. The results of polarization studies indicate the exceptionally strong efficiency of this compound as an inhibitor in H_2SO_4 solution. The electrochemical studies to elucidate the mechanism indicated adsorption obeying the Langmuir isotherm to be the main mode of action. The FTIR results indicated the presence of inhibitor molecules to formation protective layer on the surface of mild steel. Theoretical findings show that the most stable states of compound/iron system are via the molecular sites containing S atoms, ester groups and aromatic rings.

Keywords: *Corrosion Inhibitor, Sulfuric Acid, 2-Hydropyrimidine-2-Thione Derivative, Potentiostatic polarization, Docking Technique.*

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Introduction

Protecting ferrous metals, against acid media used for flushing industrial equipment, acid pickling and acid descaling as well as acidification of oil wells, is a real concern [1-2].

Sulfuric acid is generally the choice medium in the steel surface treatment because of its low cost, minimal fuming [3,4]. In order to moderate acid attack and its consumption, corrosion inhibitors are routinely added to acid solutions. From the outset, organic molecules were found to be most effective [5-7], specifically, those compounds containing nitrogen, sulphur and/or oxygen atoms in multiple bond, present in–C=O, –HC=N–, –N=N–, R–OH functional groups and aromatic rings even in small quantities are considered to be more effective corrosion inhibitions [8-10]. An appropriate inhibitor is mainly decide based upon acid type and concentration, its temperature and velocity of flow, presence of dissolved substances, and, of course, on the material exposed coming to contact with the medium [11]. The S and N containing compounds are useful as inhibitors for sulfuric and hydrochloric acid respectively [12] therefore, compounds containing both should perform satisfactorily in acidic media [13]. Inhibition performance of thiourea derivative compounds [14-23], pyrimidine derivatives [24-31], Pyrimidine thione derivatives [32 and 33] and hexahydropyrimidine thione derivatives [34] have been studied for iron and mild steel in acidic solutions. However, despite pyrimidine compounds relative ease of synthesis, as well as their noteworthy electronic structures, plus the low cost; these compounds have scarcely been studied [4 and 32] although they find diverse applications in pharmaceutical applications [35-39].

Generally, organic inhibitor molecules adsorb onto a corroding metal physically or chemically. Theoretical chemical calculations that can reveal the adsorption of the molecules onto the corroding metal surface at molecular level have been used to elucidate the interaction between inhibitor and metal surface [40-42]. These calculations demonstrate the conformation of adsorbed organic molecule on metal surface in addition to the interaction energy due to the bond formed [43-46]. In this work, the corrosion inhibition of mild steel in 0.5 M sulfuric acid solution byethyl 1,2,3,4-tetrahydro-4-(3,4-dimethoxyphenyl)-6-methyl-2-thioxopyrimidine-5-carboxylate($C_{16}H_{20}N_2O_4S$, Mw = 336.41)(Figure 1) was investigated.

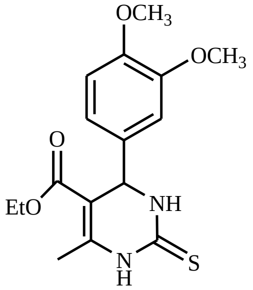

Figure 1. The structures of used compound.

The adsorption position of inhibitor on the iron surface also has been investigated by docking studies.

Experimental

Materials and Methods

Synthesis of Ethyl 4-(3,4-dimethoxyphenyl)-6-methyl-2-thioxo- 1,2,3,4-tetrahydropyrimidine-5-carboxylateand

This compound was prepared according to reported procedure in the literature [47]. The basic compounds for such synthesis i.e. Ethyl acetoacetate, 3, 4-dimethoxybenzaldehyde and thiourea were procured from Merck Chemical Co. and were used without further purification. A mixture of 3, 4-dimethoxybenzaldehyde (3 mmol, 0.5 g) ethyl acetoacetate (3 mmol, 0.39 g), thiourea (4.5 mmol, 0.34 g), and the catalyst (7% mmol) was mixed in a test tube and kept at 90◦ C for one hour and then left to cool. After cooling, it was poured on crushed ice (50 g) and stirred for 10 min so a precipitate was formed which was then filtered under suction and washed with cold water (20 mL) to remove excess urea. The residual solid was dissolved in ethanol and filtered to remove the catalyst and purified further by recrystallization in hot ethanol so that yellow crystals appearing. The process has a 92 % yield.

Electrochemical experiment

Specimens were cut from a 5mm diameter rod of mild steel (C = 0.15 %, Mn = 0.36 %, S = 0.28 %, P = 0.09%, Si = 0.017 %) and wet ground with successive emery papers up to 2000, then masked by Teflon to expose 0.785 $cm^2$of cross section area to the electrolyte. Consequently, it was washed in distilled water and acetone to remove dust and grease. Each experiment was repeated at least twice and some three times to ensure reproducibility. A conventional three electrode cell, a saturated calomel reference electrode (SCE) and a potentiostat (BHP-206X) were used. The potentiodynamic polarization curves were recorded from-700mV to -300 mV scan rate of 1.0 $mV.S^{-1}$. Tests were carried out under unstirred conditions, and at room temperature.

FTIR microscopy

FTIR spectra were recorded in a BRUKER spectrophotometer, which extended from 700 to 4000 cm^{-1}, using KBr disk technique. The pure compound was mixed with KBr and disk made. Then the steel specimen was prepared as described in electrochemical technique. After 24 h of immersion steel specimen in 0.5 M H_2SO_4 in presence of inhibitor; the specimens were cleaned with distilled water and dried at room temperature. Then formed thin adsorbed film on the steel surface was rubbed with a small amount of KBr powder. Then KBr disk was prepared using this powder.

Molecular docking studies

The inhibitor was docked onto the binding sites of the iron cluster using Argus Lab 4.0.1 (Mark Thompson and Planaria Software LLC) a free molecular modeling package that offers satisfactorily on-screen molecule building facilities and a library of molecule structures [48].

The structure of cluster with 338 atoms is $Fe_{338(117:104:117)}$ representing defect free iron surface which is built with 117 iron atoms in the first, 104 iron atoms in the second and 117 iron atoms in the third layer (Figure 2) separated by 1.4332 Å [49] and the distance of the closest adjacent atoms at 2.8664 Å.

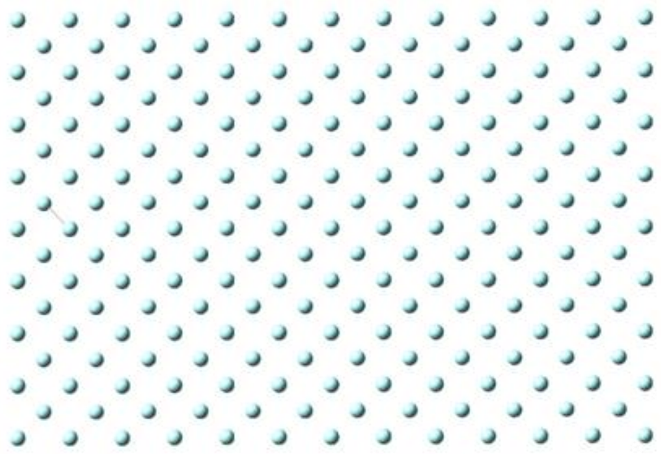

Figure 2. The structure of cluster with 338 atoms.

Results and Discussion

Polarization measurements

The potentiodynamic polarization curves for mild steel in 0.5 M H_2SO_4 solution with different concentrations of inhibitor at 25°C are shown in Figure 3.It can be observed that the addition of the inhibitor causes positive shift in corrosion potential (E_{corr}). Values of corrosion current density (i_{corr}) decreased further by addition of compound in 0.5 M H_2SO_4.

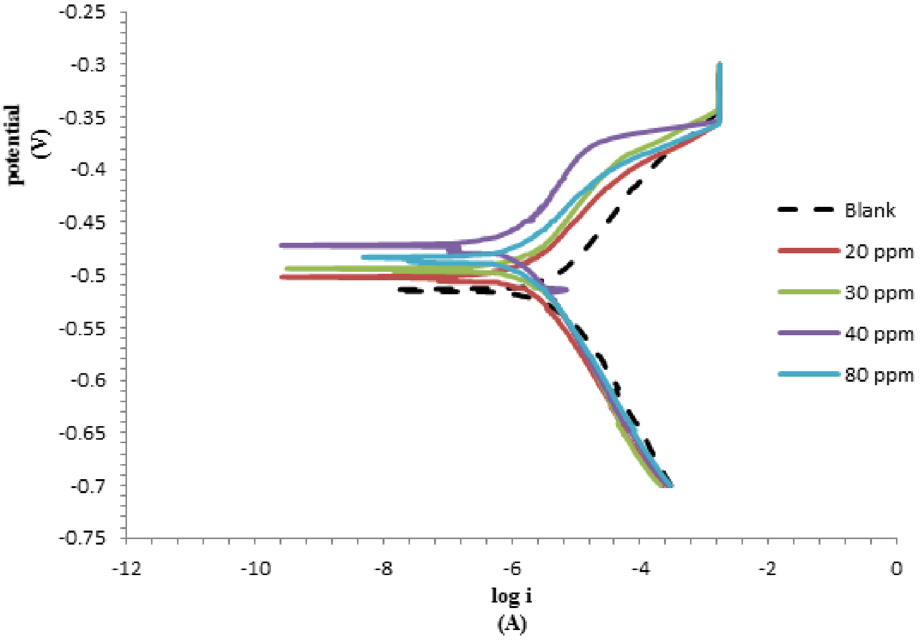

Figure 3. The potentiodynamic polarization curves for mild steel in 0.5 M H_2SO_4 solution with different concentrations of inhibitor.

The anodic and cathodic Tafel slopes changed slightly in the presence of inhibitors suggesting a simple reaction site blocking inhibition mechanism [50 and 51] and exhibiting mixed-type inhibitor characteristics. The electrochemical corrosion kinetics parameters, such as E_{corr}, cathodic and anodic Tafel slopes (β_a, β_c), corrosion current density (i_{corr}) derived from the Tafel extrapolation of the polarization curves, and the inhibition efficiency (IE%), are given in Table 1. The IE is calculated using the following equation:

$$IE = \left(\frac{i_0 - i_1}{i_0}\right) \times 100 \qquad (1)$$

Where i_0 and i_1 are the corrosion current densities in absence and presence of the inhibitor, respectively. Table 1 values indicate that studied organic compound shows 86 % efficiency at 40 ppm concentration which is compares well with the 80 % efficiency results reported for thiourea [15 and 16], pyrimidine [4] and Pyrimidine thione [33] but at much lower inhibitor concentration.

Table 1. The electro-chemical corrosion kinetics parameters of inhibitive compound.

Concentration (ppm)	E_{corr} (V)	i_{corr} (μA)	β_c\decade (mv)	β_a\decade (mv)	IE%
20	-490	2.40	-120	65	78.61
30	-485	2.14	-125	73	80.93
40	-468	1.47	-105	107	86.90
80	-474	1.70	-100	60	84.85
BLANK	-510	11.22	-90	-95	

Adsorption isotherm

Ascertaining the adsorption isotherms is essential in understanding the mechanism of inhibitors in acid media. To obtain the applicable isotherm, surface coverage (θ) of the inhibiting molecule must be plotted as a function of concentration. Degree of coverage can be calculated from the corrosion current density values using the following equation [52-56]:

$$\theta = \left(\frac{i_0 - i_1}{i_0}\right) \qquad (2)$$

Assuming the increase in inhibition is caused by adsorption of inhibitor on the mild steel surface the plot obeys the Langmuir adsorption isothermal equation, with the adjusted linear regression coefficient (R^2) = 0.997 [57-60]:

$$\frac{C}{\theta} = C + \frac{1}{K} \qquad (3)$$

Where C is the concentration of inhibitor in mol L^{-1}, K is the adsorptive equilibrium constant in L mol^{-1}, and θ is the surface coverage. A good linear relationship between C/θ and C in Figure 4, also ‹clearly proves that the adsorption of aromatic compound on mild steel surface obeys the Langmuir adsorption isotherm [61 and 62].

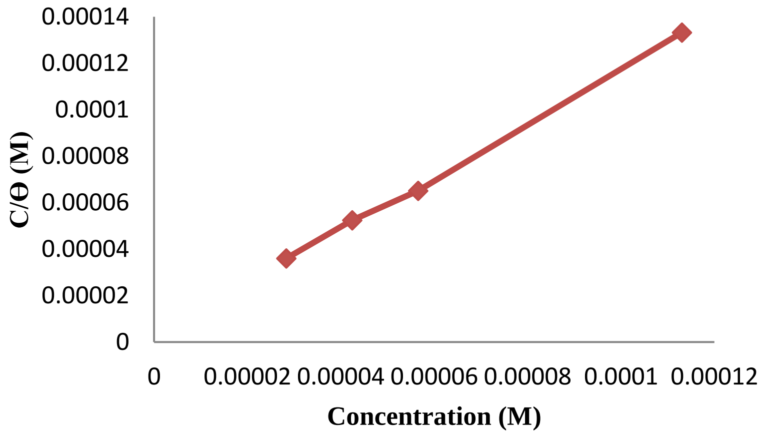

Figure 4. The Langmuir adsorption isotherm.

The equilibrium constant of the adsorption process, K in L mol^{-1}, is related to the standard free energy of adsorption, ΔG°_{ads}, by the following equation [59 and 60]:

$$\Delta G^{\circ}_{ads} = -RTln(55.55 \times K)(4)$$

The value of 55.55 is the molar concentration of water in expressed solution in mol L^{-1}[63].

The standard free energy value of adsorption (ΔG°_{ads}) is - 4.143 kJ mol^{-1} for this compound indicating a spontaneous process, commonly interpreted as physical adsorption by the formation of an electrostatically adsorbed film [64 and 65].

FTIR microscopy results

FTIR study was performed in order to evaluate the inhibitor protective layer on steel surface as well as the bonding formation on the steel surface. The FTIR spectrum of pure compound and spectra of formed adsorbed protective layer on the surface after immersion in 0.5 M sulfuric acid containing of inhibitors for mild steel are shown in Figure 5. Figure 5a shows FTIR spectra of pure compound. The infrared spectrum of the inhibitor show absorption bands at wavelengths 3188-3200 (N-H), 3055, 2978 and 2835 (C-H), 1757 and 1690 (C=O) and 1587 (C=C) cm^{-1} to stretching modes. Some of inhibitor absorption bands in Figure 5a also appearedin Figure 5b. These observations can be attributed to the presence of inhibitor molecules to formation protective layer on the surface of mild steel. In addition, a broad peak is observed at 3000-3700 cm^{-1} corresponding to O-H stretched mode for the spectra of compound in Figure 5b because of the adsorbed water [60].

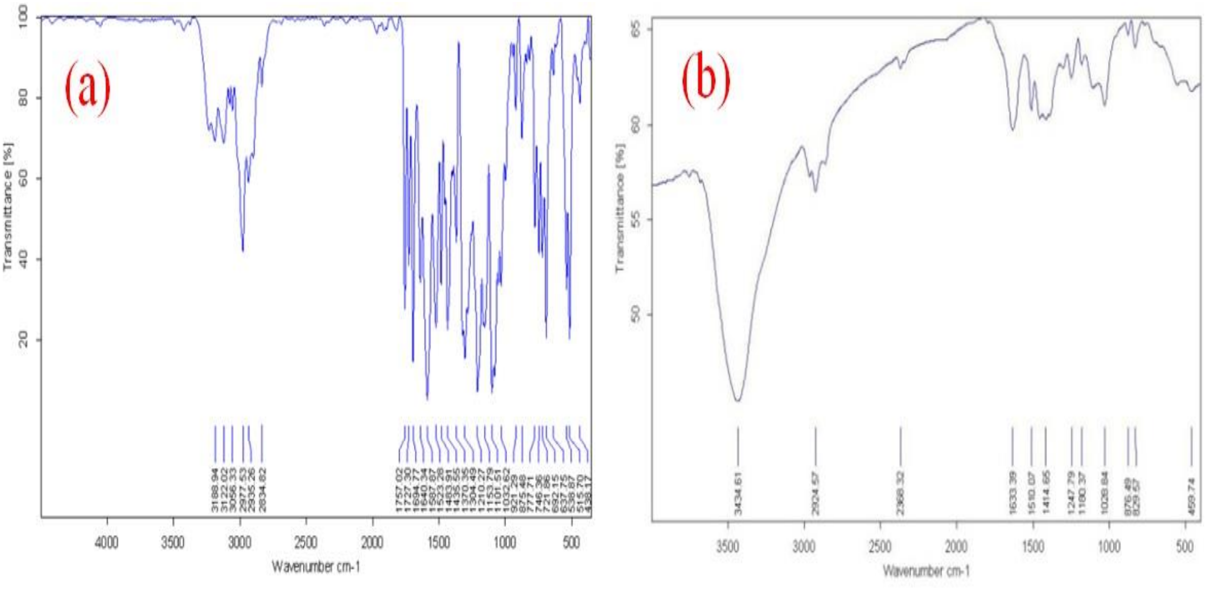

Figure 5. FT-IR of compound before (a) and after adsorption (b).

Docking studies

The results of docking studies for the compound/iron system show that the area containing S atom, ester groups and aromatic rings are possible sites for bonding with the iron surface as depicted in Figure 6. The results exhibit good agreement with the quantum chemical calculations of Pyrimidine-2-thione derivatives as mild steel corrosion inhibitor in acid environments, with S atom sites the most possible for bonding with the mild steel surface [32].

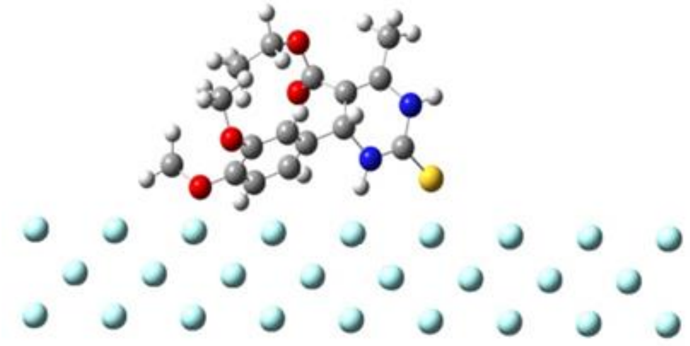

Figure. 6. The adsorption position of inhibitor in interaction with iron cluster $Fe_{338(117:104:117)}$.

Conclusion

The results show that the investigated organic compound isa good inhibitor and acts as mixed type inhibitor for mild steel in sulfuric acid solution through adsorption of the inhibitor on the mild steel surface. Inhibition efficiency increases by concentration optimization. The adsorption of this inhibitor obeys the Langmuir adsorption isotherm. Theoretical findings show that the most stable states of compound/iron system are via the molecular sites containing S atoms, ester groups and aromatic rings.

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