



Pyrazole Methyl Substituted Compound used as a Corrosive Inhibitor for Mild Steel in Acidic Environment

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Abstract

The inhibitive effect of compound on mild steel in 1M H₂SO₄ and 1M HCl was investigated by weight loss, Potentiodynamic polarization and electro chemical impedance studies. The synthesized compound of 1-acetyl-4,5-dihydro-5-phenyl-3-(thiophen-2yl) pyrazoles was characterized by FTIR, ¹H NMR, ¹³C NMR. The structure are also elucidated and purity confirmed by TLC. The corrosion inhibition rate was increased in increasing the concentration of our synthesized inhibitor (1-acetyl-4, 5-dihydro-5-methyl phenyl-3-(thiophen-2yl) pyrazoles). The synergetic effect also studied and observed good correlation between halides and our inhibitor. The adsorption isotherm was also confirmed by langumuir adsorption isotherm.

Keywords: Pyrazole, mild steel, inhibition efficiency, synergetic effect, adsorption isotherm, kinetics.

Introduction

Pyrazoles are important class of five membered heterocyclic compounds with two adjacent nitrogens in a five-membered ring system. Among the two nitrogen atoms; one is basic and the other is neutral in nature. These are aromatic molecules due to their planar conjugated ring structures with six delocalized π -electrons. The aromatic nature arises from the four π electrons and the unshared pair of electrons on the -NH nitrogen¹. Heterocyclic compounds represent a potential class of corrosion inhibitors. Corrosion inhibition by N containing heterocyclic compounds has been widely reported. Heterocyclic compounds containing both N and S atoms are of particular importance as they often provide excellent inhibition compared to those containing only N or S. The planar π electrons and lone pair of electrons present on the heteroatoms are the important structural features that determine the adsorption of these molecules on the metal surface.

Although a vast number of heterocyclic compounds have been reported as corrosion inhibitors, no work has so far been reported on the use of pyrazoles as corrosion inhibitors for the metals especially mild steel. pyrazole is a 5 membered ring system which contains two N atom in it. pyrazoles are very useful units in the field of medicinal chemistry and have been reported to exhibit a variety of biological activities. Stainless steel is widely used in many applications such as desalination plants, construction materials, pharmaceutical industry, thermal power plant, chemical cleaning and pickling process, due to their stability, good corrosion resistance, high strength, workability and weldability. Corrosion is the deterioration of essential properties of a material due to reactions with its surroundings. Millions of dollars are lost each year because of corrosion. Much of this loss is due to the corrosion of iron and

steel although many other metals may corrode as well. Corrosion damage can cause leakage of fluids or gases. Even more dangerous is a loss of strength of the structure induced by corrosion and subsequent failure. The application of acid corrosion inhibitors in the industry is widely used to prevent or minimize material loss during contact with acid. It has been observed that the adsorption depends mainly on certain physico-chemical properties of the inhibitor molecule such as functional groups, steric factors, aromaticity, electron density at the donor atoms and P orbital character of donating electrons and also on the electronic structure of the inhibitor. It has been reported that many inorganic, organic and heterocyclic compounds containing hetero atoms like N, O, S and P have been proved to be an effective inhibitors for the corrosion of stainless steel in acid media²⁻⁵⁴. Pyrazole compounds have a good inhibition effect on mild steel in acidic environment⁶⁷.

The aim of this work is to synthesize (1-acetyl-4, 5-dihydro-5-phenyl-3-(thiophen-2yl) pyrazoles) characterized by FT-IR, ¹³C NMR, ¹H NMR, Elemental analysis and their inhibitive effect on mild steel in HCl and H₂SO₄ environments determined by weight loss, potentiodynamic polarization and electro chemical impedance studies.

Material and Methods

The composition of the mild strip: C-3.15, Mn-0.61, P-0.07, S-0.049, Cu-0.5, Cr- 0.155,Sn-0.035 and reminder iron were used for weight loss method.

Materials: Analytical grade chemical and triple-distilled water were used to prepare solution. The corrosion medium was an aqueous aerated solution 1 M H₂SO₄. The concentration of the inhibitors employed was 10,20,30 and 40 ml. The experiments

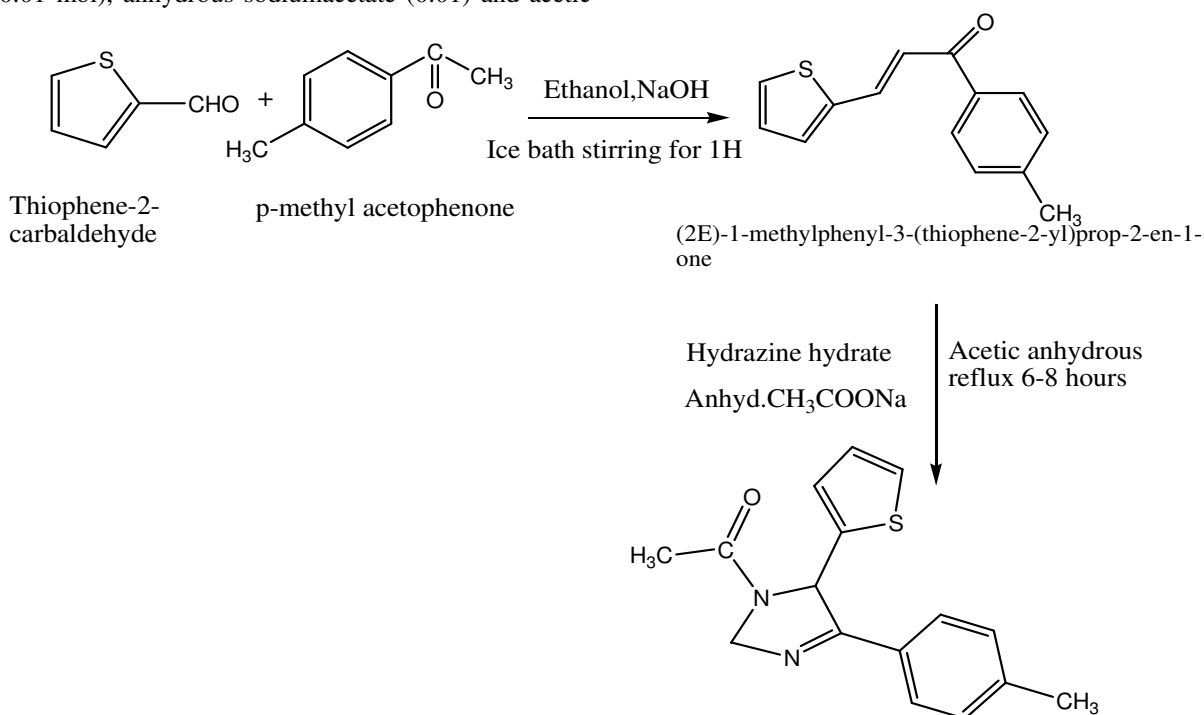
were performed by triplicate and the average value of the weight loss and electrochemical tests were reported. For each test, freshly prepared solutions and a cleaned set of electrodes were used. In weight and electrochemical tests one size of specimens were used. The metallic coupons for the weight loss tests have dimension of 1cm x 5 cm x 0.33 cm, and the working electrodes for the electrochemical tests a surface area of 0.339 cm². Before each experiment the electrode was first mechanically abraded with various grades of grinding paper (up to 1200 grit) and then polished successively using emery sheets of 400 and 600 grades to remove adhering impurities. At the end they were cleaned with double distilled water and ethanol.

Measurements and Equipments: The compounds were synthesised and characterized by ¹H and ¹³C NMR and IR spectroscopy. Melting points (uncorrected) were determined using a Guna melting point apparatus. FT-IR spectra were carried out on a Perkin-Elmer 1650 spectrophotometer and noteworthy absorption values (cm⁻¹) alone are listed. ¹H and ¹³C NMR spectra are recorded at 400MHz and 100 MHz respectively on Bruker AMX 400 NMR spectrometer using CDCl₃ as solvent. Chemical shifts (δ) were reported in ppm. The microwave- assisted reaction was performed using a controllable single- mode microwave reactor, CEM Discovery, designed for synthetic use. The reactor is equipped with a magnetic stirrer and device to control pressure, temperature (on-line IR detector) and power.

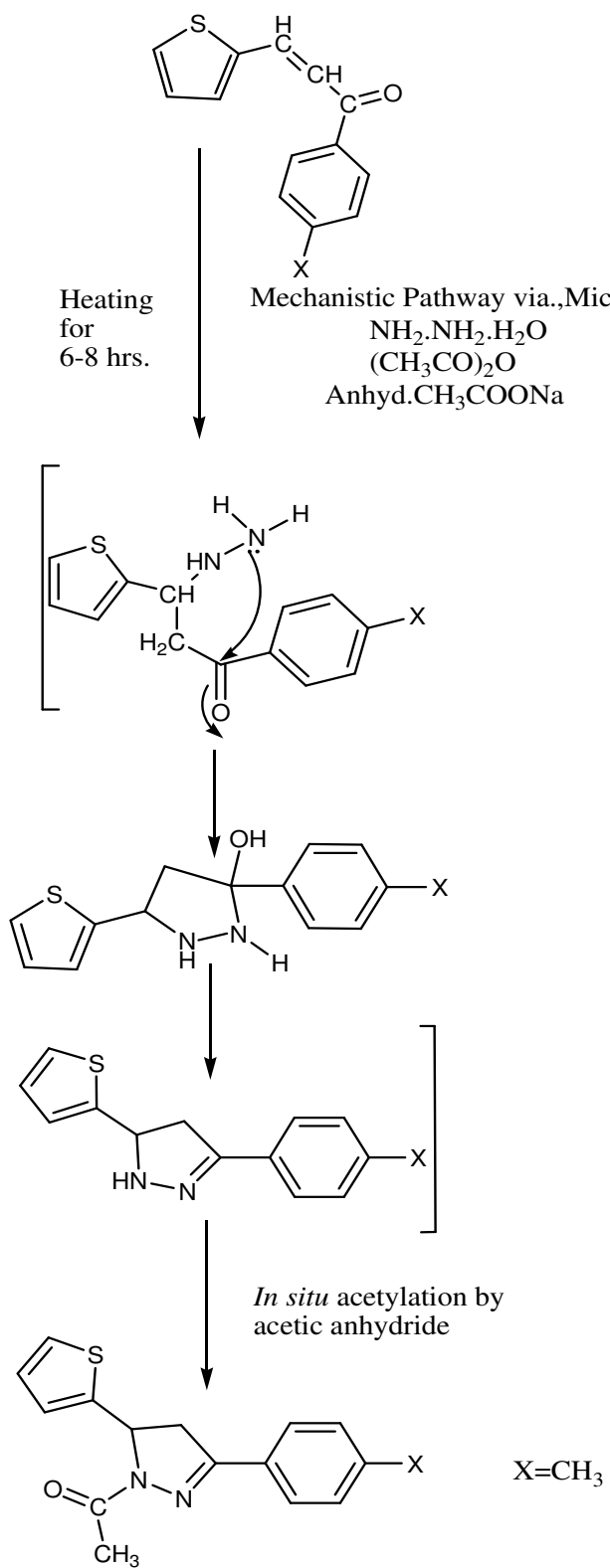
Synthesis of Compound: Chalcone, (0.01mol), hydrazine hydrate (0.01 mol), anhydrous sodium acetate (0.01) and acetic

anhydride taken in a round bottom flask and the reaction mixture flask was refluxed until the products are formed. The reaction is monitored by TLC. The reaction mixture is poured in to crushed ice and left overnight. The precipitate is separated by filtration. Washed well with water, dried and obtained solids are purified by column chromatography using toluene and ethylacetate (1:1) mixture as eluent which afford the title compound in excellent yields⁵⁵. From a chemical point of view, an important feature of chalcones is the ability to act as activated unsaturated system in conjugated addition reactions of carbanions in the presence of basic catalysts⁵⁶.

The effect of the structure of organic compounds on their inhibiting properties: Most organic inhibitors⁵⁷ contain at least one polar group with an atom of nitrogen, sulphur, or in some cases selenium and phosphorus. According to Hackerman⁵⁸, the inhibiting properties of many compounds are determined by the electron density at the reaction center. With an increase in the electron density at the reaction center, the chemisorption bonds between the inhibitor and the metal are strengthened. Hackerman established the protective properties of pyridine and its derivatives. He found that, the ability of these compounds to reduce corrosion, are actually enhanced at higher electron densities around the nitrogen atom, according to the sequence: pyridine < 3-picoline < 2-picoline < 4- picoline. It is assumed that for organic compounds during the first ionization one of the electrons of the unshared pair is detached, then the ionization potential can serves as a measure of the electron density at the nitrogen atom.



Scheme-1
1-acetyl-4,5-dihydro-5-methylphenyl-3-(thiophen-2-yl) pyrazole



Scheme 2 Synthetic Reaction Pathway towards the synthesis of title compound via., Michal Addition Pathway

Scheme-2
Synthetic Reaction Pathway towards the synthesis of title compound via, Michal Addition Pathway

Hackerman et al^{59,60} have been studied the adsorption of organic substances with a long hydrocarbon chain from organic solvents. These studies showed that the better the substance is adsorbed, the more effectively it protects the surface.

Corrosion monitoring methods: Weight loss tests: Weight loss measurements were performed at 35°C and 45°C for 1 h by placing the carbon steel coupons into the acid solution (20 ml) with and without 10ml of inhibitor. At the end of the testing period, the specimens were cleaned according to ASTM G0141 and finally its weight loss were recorded. The corrosion rate (V_{corr} mm/year), inhibition efficiency ($IE_w, \%$) and surface coverage (θ) were determined by the following equations.

$$V_{corr} = \frac{8.76 \times 10^{-4} W}{ATD} \quad (1)$$

$$\theta = \frac{V_{corr,0} - V_{corr,i}}{V_{corr,0}} \quad (2)$$

$$(IE_w, \%) = \frac{V_{corr,0} - V_{corr,i}}{V_{corr,0}} \times 100 \quad (3)$$

Where W is the weight loss(g), D is the steel density ($g\ cm^{-3}$), A is the surface area (cm^2), T is the exposure time (h), and $V_{corr,0}$ and $V_{corr,i}$ are the weight loss values in the absence and presence of inhibitors, respectively.

Electrochemical tests: Electrochemical measurements were performed in a conventional three-electrode glass cell. Electrode potentials were measured against a saturated calomel electrode (SCE), the counter electrode was a mesh of Pt (purity 99.9%) and the working electrode was made of mild steel ($0.339\ cm^2$).

The SCE was connected to a Luggin capillary, the tip of which was placed very close to the surface of the working electrode to minimize IR drop. Tests were performed at $25 \pm 1^\circ C$ and thermostatically controlled. Electrochemical testing was performed in a potentiostat Instrument Model: CHI604D controlled by a PC through the general purpose electrochemical system (GPES); the software provided by AUTOLAB. The specimen was immersed in the test solution for 40 minutes at the open circuit potential (E_{ocp}) to reach a steady-state condition. The polarization resistance measurements (R_p) were then performed in the potential range of $\pm 20\ mV$ versus E_{corr} at a scan rate of $1.0\ mVs^{-1}$.

$$(IE_{Rp}, \%) = \frac{R_p^i - R_p^0}{R_p^i} \times 100 \quad (4)$$

Where R_{op} and R_{ip} are the polarization resistances in the absence and presence of inhibitor, respectively.

Corrosion current densities (i_{corr}) obtained by Tafel extrapolations were used to determine the inhibition efficiencies using the equation:

$$(IE_T, \%) = \frac{i_{corr}^0 - i_{corr}^i}{i_{corr}^0} \times 100 \quad (5)$$

Where: i_{icorr} and i_{ocorr} are the corrosion current densities values

with and without inhibitor, respectively.

Synergistic effect of halide ions: Effect of the addition of 0.1 N KI and KCl to different concentrations of inhibitors on the corrosion inhibition of iron in 1M HCl and H_2SO_4 using weight loss technique was studied. This is called synergistic effect process.

Results and Discussion

Structural elucidation of synthesized organic compound: 1-acetyl-4,5-dihydro-5-methyl phenyl-3-(thiophen-2yl)pyrazoles are synthesis in excellent yields by the reaction of chalcones with hydrazine hydrate catalyzed by anhydrous sodium acetate/acetic anhydride under conventional method. In our present study, acetic anhydride is the best solvent for the facile synthesis of acetyl pyrazoles, in excellent yields without any solubility problem. In addition, insitu acetylation occurs in the course of the reaction due to solvent, acetic unhydride under the reaction conditions. An array of compound namely 1-acetyl-4,5-dihydro-5-methylphenyl-3-(thiophen-2yl) pyrazoles was synthesized under classical thermal method. The structures of the synthesized 1-acetyl-4,5-dihydro-5-methylphenyl-3-(thiophen-2yl) pyrazoles was confirmed by FT-IR, MS, 1H NMR and ^{13}C NMR spectral studies and elemental analysis (scheme-1).

FT-IR spectrum of compound shows characteristic absorption frequencies at $3086.11, 3001.24\ cm^{-1}$ due to aromatic CH stretching vibration. The absorption bands at $2885.51\ cm^{-1}$ are attributed to the aliphatic CH stretching vibration. The absorption frequency at $1658.78\ cm^{-1}$ is assigned to amide carbonyl stretching vibration. The absorption band at $1417.68\ cm^{-1}$ is assigned to $C=N$ stretching vibration. The absence of carbonyl band clearly supported for the formation of the required compound, besides the disappearance of NH stretching vibration, which conforms the situ acetylation reaction due to acetic anhydride solvent.

Elemental analysis of (Ccal 67.19, Cobs 67.13; Hcal 6.34, Hobs 6.29; Ncal 9.79, Nobs 9.78; Scal 11.21, Sobs 11.18. $m/z(M)^+$: 286 are consistent with the proposed molecular formula ($C_{15}H_{16}N_2SO$) of the compound.

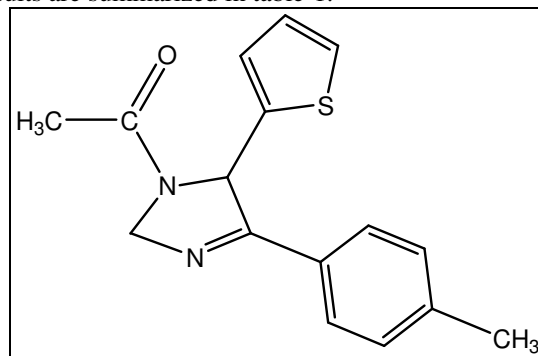
In the 1H NMR spectrum of 1-acetyl-4,5-dihydro-5-methylphenyl-3-(thiophen-2yl) pyrazoles, the methylene protons (H-4a and H-4e) of the pyrazoline moiety appeared as two doublets of doublets due to multiple coupling involving both geminal and vicinal protons. The signals for H-4a and H-4e are observed at 3.35 and 3.71 ppm. The doublet of doublet at 3.35ppm ($J_{4a,5a}=17.5\ Hz$ and $J_{4a,4e}=4.0\ Hz$) is assigned to H-4a proton of the pyrazoline moiety. Likewise, the doublet of doublet at 3.75 ppm ($J_{4e,4a}=17.5$ and $J_{4e,5a}=11.5\ Hz$) is assigned to H-4e proton of the pyrazoline moiety. Similarly, the methine proton (H-5) of the pyrazole moiety is expected to give signal as a doublet of doublet due to vicinal coupling with the

two magnetically nonequivalent protons of the methylene group (H-4a-H4e) of the pyrazoline moiety and the signals are observed at 5.91 ppm ($J_{5a,4a} = 11.5\text{ Hz}$ and $J_{5a,4e} = 4.0\text{ Hz}$). Also the acetyl methyl protons of pyrazoline moiety gives signal as a singlet at 2.43 ppm. The aromatic protons appear as a multiplet in the range of 6.93-7.68 ppm.

In the ^{13}C NMR spectrum of 1-acetyl-4,5-dihydro-5-methylphenyl-3-(thiophen-2-yl)pyrazoles, ^{13}C resonance at 55.16 ppm is assigned to C-5 of pyrazole moiety. The ^{13}C resonance observed at 42.07 ppm is due to C-4 of pyrazole moiety. The ^{13}C resonance observed at 153.98 ppm is assigned to C-3 of pyrazole moiety. The aromatic carbons are observed in the region of 124.54-128.48 ppm. The ^{13}C resonance observed at 21.98 ppm is due to acetyl methyl carbon. The remaining ^{13}C signal at 144.42, 140.78 is due to ipso carbon.

Weight Loss Method: The inhibition efficiency with different concentration of the inhibitor on the mild steel in 1M H_2SO_4 and 1M HCl has been evaluated by weight loss measurements and

the results are summarized in table-1.



The data reveals that inhibition efficiency increases with increase in concentration of the inhibitors. The behavior may be attributed to an increase in surface coverage (θ) by the adsorption of inhibitor on the mild steel surface, in the aggressive solution, which restricts the dissolution of the metal.

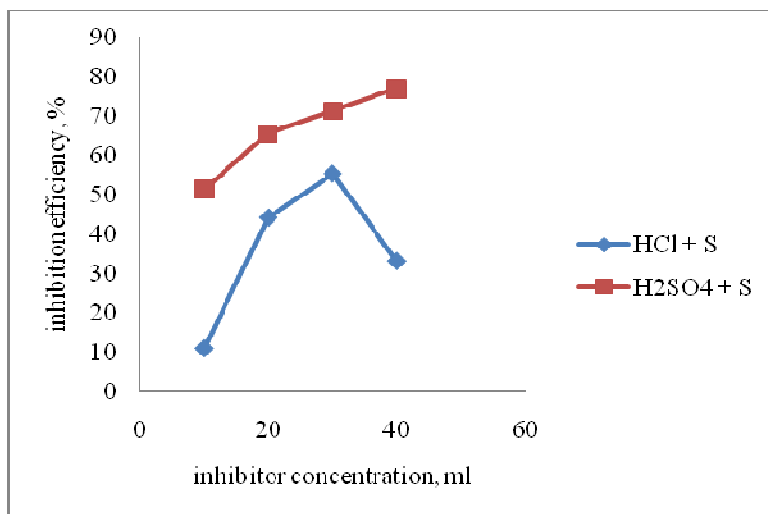


Figure-1

Plot of corrosion rate against inhibition efficiency of mild steel in 1M H_2SO_4 and 1M HCl in presence of the inhibitors

Table-1

Inhibition efficiency at various concentrations of pyrazole for the corrosion of mild steel in 1M H_2SO_4 and 1M HCl obtained by weight loss measurements at 28°C

Medium	Inhibitor concentration in %	Weight loss in mg	Inhibition efficiency in %	Degree of coverage in θ	C/ θ	Corrosion rate in $\text{mpy} \times 10^{-3}$
HCl	blank(10 ml) HCl	0.009				0.0115
	HCl + 0.1 S	0.008	11.11	0.11	90.9	0.01028
	HCl + 0.2 S	0.004	55.56	0.55	36.3636	0.00514
	HCl + 0.3 S	0.005	44.44	0.44	68.181	0.0064
	HCl + 0.4 S	0.006	33.33	0.33	121.2	0.0077
H_2SO_4	blank(10 ml) H_2SO_4	0.035				0.0449
	H_2SO_4 + 0.1 S	0.017	51.43	0.51	19.61	0.0218
	H_2SO_4 + 0.2 S	0.012	65.714	0.66	60.6061	0.01542
	H_2SO_4 + 0.3 S	0.008	77.1428	0.77	51.948	0.01028
	H_2SO_4 + 0.4 S	0.01	71.4	0.71	42.2535	0.0128

Effect of temperature: The effect of temperature on the inhibited acid-metal reaction is highly complex because many changes occur on the metal surface such as rapid etchings, desorption of the inhibitor and the inhibitor may undergo decomposition and rearrangement. To evaluate the effect of temperature on the adsorption behavior as well as to determine the activation parameters of the corrosion of mild steel in 1M H₂SO₄ solution and 1M HCl solution containing the inhibitors, the weight loss measurements were carried out in the temperature range of (301-318K) and the results are presented in table-2. The data reveal that as the temperature is increased the corrosion rate increased and the inhibition efficiency decreased. The decrease in the inhibition efficiency with increase in

temperature may be attributed to the increase in the solubility of the protective film or the reaction products precipitated on the surface of the metal that might otherwise inhibit the reaction^{61,62}. This is in accordance with Ergun et al⁶³.

The corrosion rate (CR) of the mild steel in acidic media is related to the temperature by the Arrhenius Equation,

$$\text{Log CR} = \text{log A} - \text{Ea}/ 2.303 \text{ RT} \quad (6)$$

Where: CR is the corrosion rate, Ea is the apparent activation energy, R is the molar gas constant, T is the absolute temperature and A is the frequency factor. The plot of log CR vs 1/T is shown in figure-2. Linear plots were obtained.

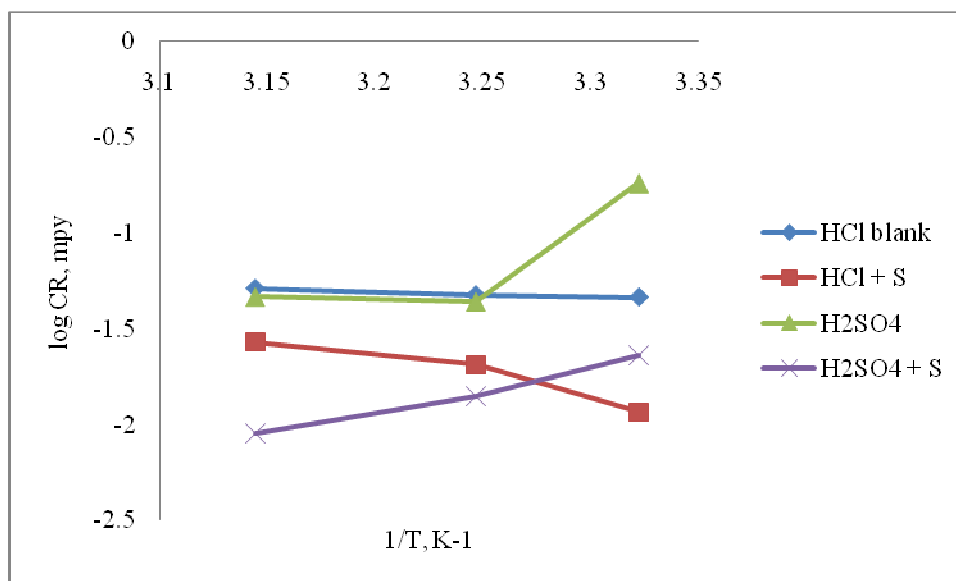


Figure-2

Arrhenius plot of corrosion rate of mild steel in 1M H₂SO₄ and 1M HCl in presence and absence of the inhibitors

Table-2

Effect of temperature on inhibition efficiency of pyrazole at 0.01 ml concentration in 1M H₂SO₄ and 1M HCl

Name of the medium	Temperature (K)	Weight loss (mg)	Inhibition Efficiency %	Corrosion Rate (mpy)
Blank HCl	301	0.036		0.0462
HCl + S	301	0.009	75	0.0116
Blank HCl	308	0.04		0.0475
HCl + S	308	0.016	60	0.02056
Blank HCl	318	0.037		0.0514
HCl + S	318	0.021	43.24	0.02698
Blank H ₂ SO ₄	301	0.142		0.1824
H ₂ SO ₄ + S	301	0.018	87.32	0.0231
Blank H ₂ SO ₄	308	0.034		0.0436
H ₂ SO ₄ + S	308	0.011	67.65	0.01413
Blank H ₂ SO ₄	318	0.036		0.0462
H ₂ SO ₄ + S	318	0.007	80.56	0.00899

Adsorption isotherm: Adsorption of the inhibitor molecules mainly depends on the charge and nature of the metal surface, electronic characteristics of the metal surface, temperature, adsorption of the solvent, ionic species and the electrochemical potential at the solution interface. The adsorption isotherm describes the adsorption behavior of organic compounds. The most frequently used adsorption isotherms are Langmuir, Tempkin, Frumkin and Freundlich. To obtain the adsorption isotherm, the degree of surface coverage (θ) was calculated for various concentrations of pyrazoles from the weight loss data and listed in table-1.

Adsorption behavior of thiazines is best explained by Langmuir adsorption isotherm. Langmuir isotherm is an ideal isotherm for physical or chemical adsorption where there is no interaction between the adsorbate and adsorbent^{64,65}. Assumption of Langmuir relates the concentration of the adsorbate in the bulk of the electrolyte (C) to the degree of surface coverage (θ) according to the equation,

$$C/\theta = 1/K + C \quad (7)$$

Where: 'K' is the equilibrium constant of adsorption.

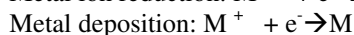
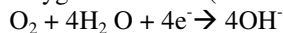
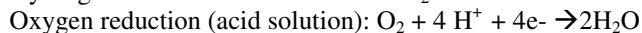
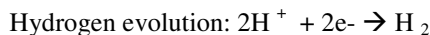
Applicability of Langmuir adsorption isotherm to the adsorption of pyrazole on mild steel confirms the formation of multimolecular layer of adsorption where there is no interaction between the adsorbate and the adsorbent.

Potentiodynamic polarization tests: In iron or steel corrosion, electrochemical reactions may take place as follows⁵⁷:

At the anodic areas



When iron corrodes, the rate is usually controlled by the cathodic reaction. There are several different cathodic reactions that are frequently encountered in metallic corrosion. The most common are:



Hydrogen evolution is a common cathodic reaction since acidic media are frequently encountered. Oxygen reduction is very common, since any aqueous solution in contact with air is capable of reducing this reaction. Metal ion reduction and metal deposition are less common. All the above reactions are consuming electrons.

Since the anodic and cathodic reactions occurring during corrosion are mutually dependent, it is possible to reduce corrosion by reducing the rates of either reaction. So, if the surface of the metal is coated with paint or other conducting film, the rates of both anodic and cathodic reactions will be greatly reduced and corrosion will be retarded. The corrosion behaviour of metals, and thus the corrosion-inhibiting processes as well, depend greatly on the anion composition of the electrolyte.

The values of electrochemical parameters, i.e., corrosion current density (i_{corr}), corrosion potential (E_{corr}), Tafel slopes (β_c) and inhibitor efficiency (IET,%) obtained as function of different are measured.

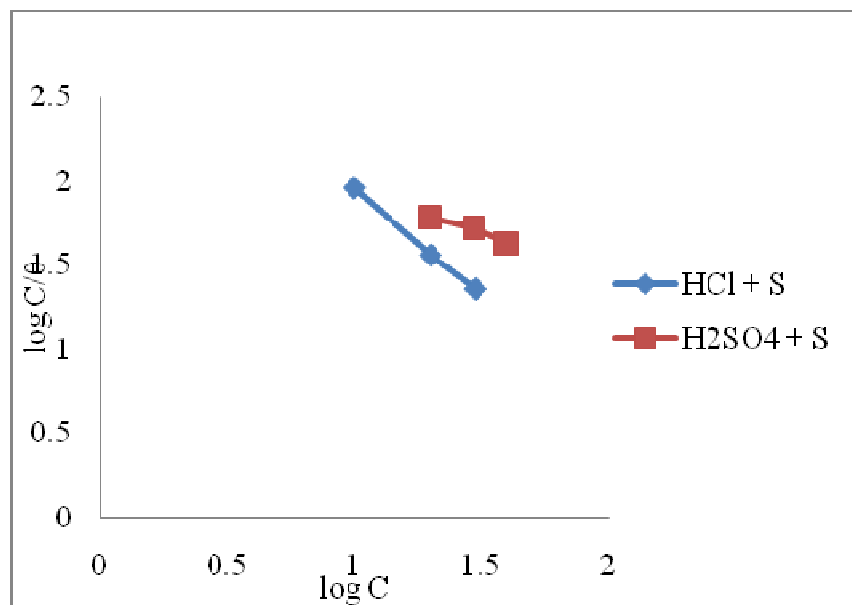


Figure-3

Langmuir adsorption isotherms after the addition of inhibitor used for carbon steel in 1 M HCl and 1M H₂SO₄

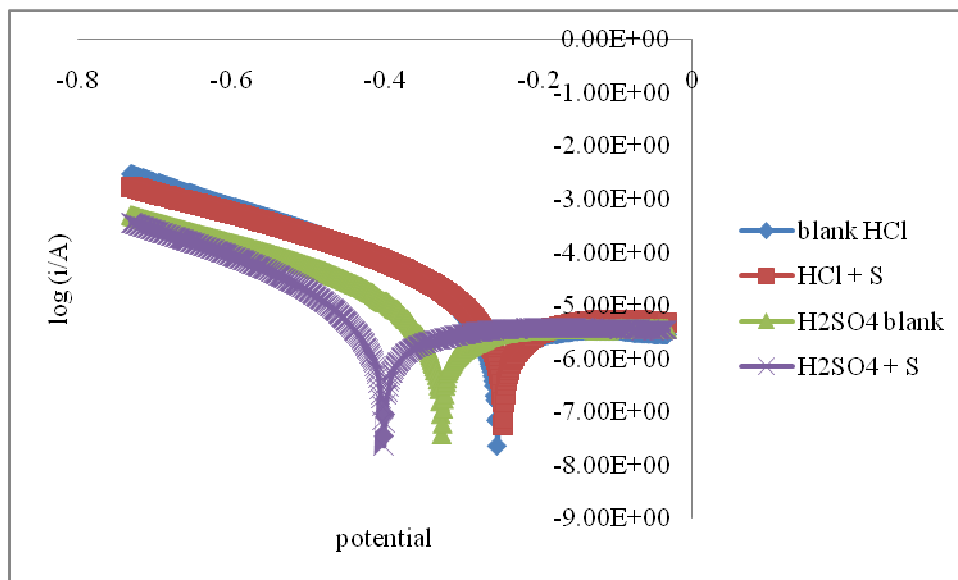


Figure 4

Potentiodynamic polarization curves for carbon steel in 1M H₂SO₄ and 1M HCl solution and after addition of inhibitor S

Kinetic-thermodynamic corrosion parameters: The effect of temperature (28°C, 35°C and 45°C) on the corrosion rate of iron in 1M HCl and H₂SO₄ at different concentrations of inhibitors was studied using weight loss measurements. Plots of log k (corrosion rate) against 1/T (figure-5), for iron dissolution in at different concentrations of inhibitor, give straight lines. The values of the slopes obtained at different temperatures permit the calculation of Arrhenius activation energy (Ea*). Activation parameters for corrosion of iron in 1M HCl and 1M H₂SO₄ were calculated from Arrhenius type plot⁶⁶:

$$k = A \exp(-E_a^*/RT) \tag{9}$$

and transition state type equation:

$$k = RT/Nh \exp(\Delta S^*/R) \exp(-\Delta H^*/RT) \tag{10}$$

The almost similar values of ΔE_a^* suggested that the inhibitors are similar in the mechanism action and the order of the efficiency may be related with the pre-exponential factor A in Equation 10(not shown).

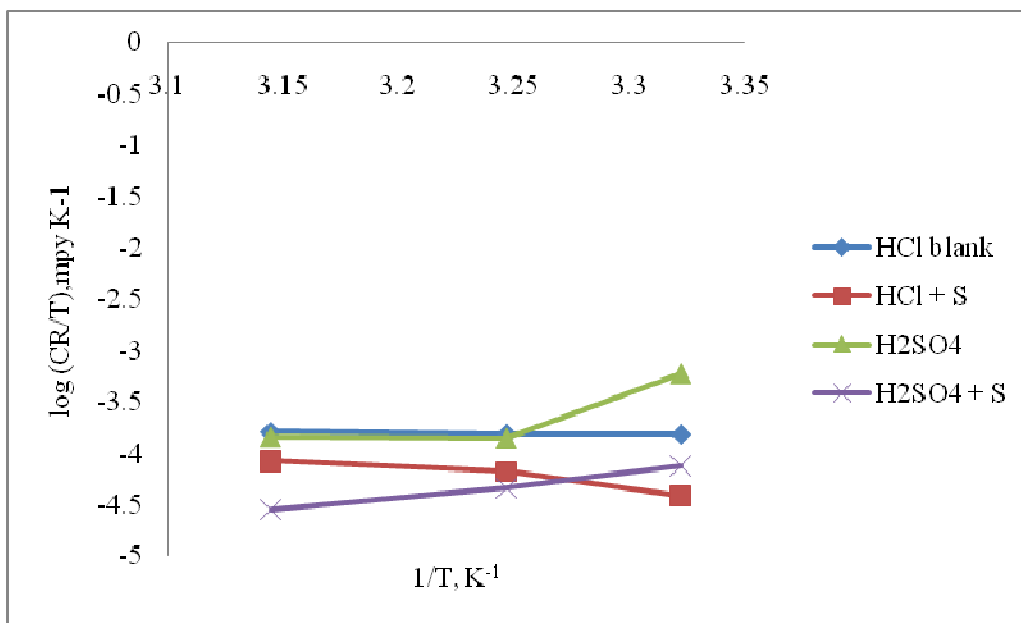


Figure-5

Log (corrosion rate/T) – (1/T) curves for dissolution in 1M HCl and 1M H₂SO₄ in absence and presence of inhibitor

The presence of investigated derivatives increases the activation energy of iron indicating strong adsorption of the inhibitor molecules on the metal surface. The presence of these additives induce energy barrier for the corrosion reaction and this barrier increases with increasing the additive concentration. The values of ΔH^* are reported are positive. The positive sign of the enthalpy reflects the endothermic nature of Fe dissolution process. Also, the values of entropy of activation are negative. The negative values of entropy imply that the activated complex in the rate determining step represents an association rather than dissociation step, meaning that a decrease in disordering takes place on going from reactants to activated complex. A decrease in inhibition efficiency with rise in temperature, suggests a possible desorption of some adsorbed inhibitor molecules from the metal surface at higher temperatures. Such behaviour indicates that inhibitor molecules were physically adsorbed on the metal surface.

Synergistic effect: The synergistic effect provided by the addition of halide ions such as I⁻, and Cl⁻ to the solution containing 1M H₂SO₄ and 1M HCl in the presence of inhibitors was studied by weight loss method and the data are presented in table. Analysis of the data reveals that the addition of halides to the inhibitors increases the inhibition at each concentration of the inhibitor tested. This increase in inhibition efficiency shows that the mechanism of the synergistic action is due to the co-adsorption of halides and the inhibitor. The strong chemisorptions of halide ions on mild steel surface make the iron surface to a negatively charged one. Organic compounds containing nitrogen in aqueous acidic solutions may exist either as neutral molecules or cations¹. The positively charged propagated cations may then be absorbed by columbic attraction on the metal surface where halide ions are already adsorbed. This leads to more surface coverage and hence greater inhibition.

The order of synergism of halide ions with the tested inhibitors has been found to be I⁻ > Cl⁻. The reason for better synergism with iodide ion is due to the large size and ease of polarisibility of I⁻ ion, which facilitates chemisorptions on the iron surface.

Conclusion

Corrosion inhibition study on using mild steel in acidic environment with various concentration of inhibitors and additives at room temperature has been reviewed. Electrochemical studies like Polarization, AC impedance and surface morphology such as Fourier Transform infrared Spectroscopy, ¹H NMR and ¹³C NMR have also been analyzed for the synthesized pyrazole compound.

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Table-3

Synergistic effect of 1M KCl and KI on the inhibition efficiency of inhibitors in 1M H₂SO₄ and 1M HCl by weight loss method at 28°C

Name of the medium	Inhibitor concentration in %	Weight loss in mg	Inhibition efficiency in %	Degree of coverage in θ	C/ θ	Corrosion rate in mpy $\times 10^{-3}$
HCl	blank HCl	0.009				0.0115
	HCl+ S+ 0.1KI	0.005	44.44	0.44	22.95	0.0064
	HCl+ S+ 0.2KI	0.0024	73.33	0.73	27.39	0.0031
	HCl+ S + 0.3KI	0.003	66.67	0.67	44.776	0.00385
	HCl+ S+ 0.4KI	0.0032	64.44	0.64	62.5	0.0041
H ₂ SO ₄	blank H ₂ SO ₄	0.035				0.0449
	H ₂ SO ₄ + S+ 0.1KI	0.003	91.4	0.91	11.098	0.0038
	H ₂ SO ₄ + S+ 0.2KI	0.009	74.28	0.74	27.027	0.0116
	H ₂ SO ₄ +S + 0.3KI	0.006	82.85	0.83	36.145	0.0077
	H ₂ SO ₄ +S+ 0.4KI	0.004	88	0.88	45.45	0.0054

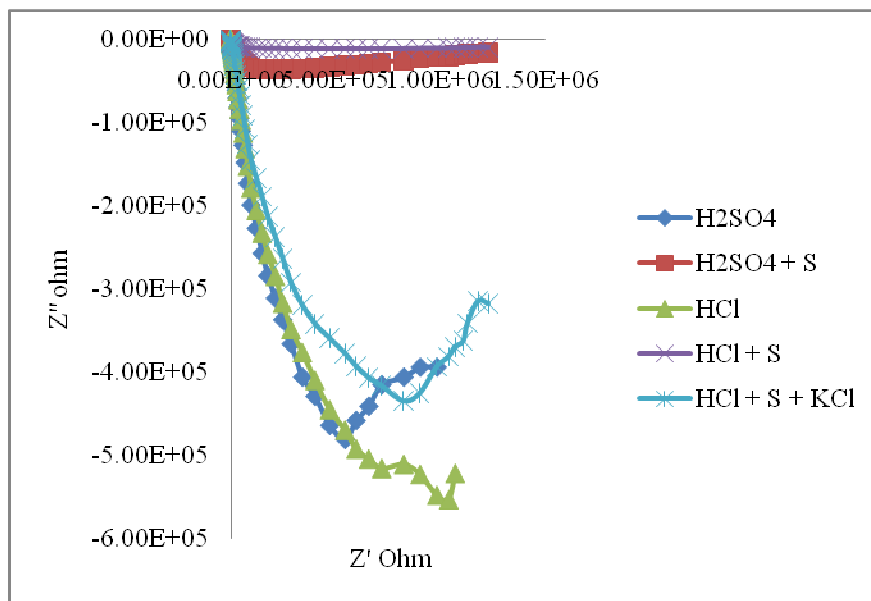


Figure-6

Nyquist diagram for mild steel in 1M H₂SO₄ and 1M HCl in presence and absence of the inhibitor.

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