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Research Article

Mild Steel Corrosion Inhibition Effect on Pyrazole Compound in Acidic Media

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Abstract

The inhibitive of compound on mild steel in 1M H_2SO_4 and 1M HCl was investigated by weight loss, Potentio dynamic polarization and electro chemical impedance studies. The synthesized compound of 1-acetyl-4,5-dihydro-5-methoxyphenyl-3-(thiophen-2yl) pyrazoles was characterized by FTIR, ^{1}H NMR, ^{13}C NMR. The purity of the compound was confirmed by TLC. The corrosion inhibition rate was increased in increasing the concentration of our synthesized inhibitor (1-acetyl-4, 5-dihydro-5-methoxyphenyl-3(thiophen-2yl) pyrazoles). The synergetic effect also studied and observed good correlation between halides and our inhibitor. The Electro-chemical impedance studies are carried out for the inhibitor activity with as well as without presence of halides. The adsorption isotherm was also confirmed by Langmuir adsorption isotherm.

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

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Introduction

Organic compounds containing polar functions with nitrogen, oxygen, or sulphur atoms as well as heterocyclic's containing conjugated double bonds are usually used to mitigate the electrochemical corrosion attack on metallic materials and have been reported as effective inhibitors of mild steel corrosion in acidic media even in very small concentrations [1-4]. These organic compounds are adsorbed on metallic surface and decrease the corrosion rate. 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&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 hetero atoms are the important structural features that determine the adsorption of these molecules on the metal surface.

C-steel is the most widely used as constructional material in many industries due to its excellent mechanical and low cost. It is used in large tonnages in marine applications, chemical processing, petroleum production and refining, construction and metal processing equipment. Acid solutions are widely used in industry, which leads to corrosive attack. Therefore, the consumption of inhibitors to reduce corrosion has increased in recent years. The corrosion controls by inhibitors is one of the most common effective and economic methods to protect metals in acid media [5-20].

Metals are the pre-eminent important materials used in structural and decorative applications. The corrosion, deterioration or destruction of metals is an unavoidable but controlled process [21]. There are little reports on the corrosion characteristics of different metal in sulphamic acid media. The sulphamic acid has the advantage of bing a crystalline solid,and compatible for use with stainless stell and low alloy steels [22]. There are two types of correlations between the adsorbed inhibitor and metallic surface which are physisorption and chemisorptions [23].

The present work was established to study the corrosion inhibition of C-steel in 1 M HCl and 1M H_2SO_4 solution by new ionic liquids derivatives as corrosion inhibitors using weight loss method and theoretical studies. The effect of concentration on the inhibition efficiency has been examined. The thermodynamic parameters for dissolution processes were calculated and discussed. The chemical structure of the studied (1-acetyl-4, 5-dihydro-5-methoxyphenyl-3-(thiophen-2yl) pyrazole) ionic liquids are given in **Figure 1**.

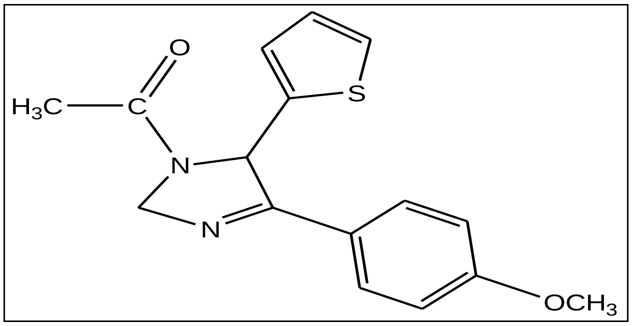


Figure 1 Structure of inhibitor.

Experimental Work

Metal composition of mild steel which was used for weight loss method is given in **Table 1**.

Table 1 Metal percentage in the mild steel strips.

S.No	Metal	Percentage in (%)
1.	C	3.15
2.	Mn	0.61
3.	P	0.07
4.	S	0.049
5.	Cu	0.5
6.	Cr	0.155
7.	Sn	0.035
8.	Fe	Remaining

Materials

Analytical grade chemical and triple-distilled water were used to prepare solution. The corrosion medium was an aqueous aerated solution 1 M H_2SO_4. The concentration of the inhibitors employed was 10,20,30,40 and 50 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 cm^2. 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, 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 ^{13}C NMR and IR spectroscopy. Melting points (uncorrected) were determined using a Guna melting point apparatus. FT-IR spectra were carried out onaPerkin-Elmer1650 spectrophotometer and noteworthy absorption values (cm^{-1}) alone are listed.^1H and^{13}C NMR spectra are recorded at 400MHz and 100 MHz respectively on Bruker AMX 400 NMR spectrometer using $CDCl_3$ 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. Mass spectra were obtained on Maspec MSW 9629 spectrophotometer, important fragments are given with the relative abundance in the bracket.

Inhibitor Molecule

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 yields. 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 catalysts [24].

Corrosion monitoring methods

Weight loss tests

Weight loss measurements were performed at various concentrations of acids(10,20,30 & 40 ml) with and without 10ml 0f inhibitor solution, different temperatures (28^0C, 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 and depending on time variations (1,2 and 3 hours) with concentration of 20 ml of acids & with 10ml of inhibitor as well as without 10ml inhibitor. At the end of the testing period, the specimens were cleaned and finally their weight losses were recorded. The corrosion rate (V_{corr} mm/year), inhibition efficiency (IE_w %) and surface coverage (θ) were determined by the following equations.

$$V_{corr} = \frac{8.76\times10^4 W}{ATD} \qquad (1)$$

$$\emptyset = \frac{V_{corr,o} - V_{corr,i}}{V_{corr,o}} \qquad (2)$$

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

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±1°C and thermostatically controlled. Electrochemical testing was performed in a potentio-static 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 ±20 mV versus E_{corr} at a scan rate of 1.0 mVs^{-1}.

$$(IE_{Rp}\,,\%) = \frac{R_p{}^i - R^o{}_p}{R^i{}_p} \times 100 \qquad (4)$$

Where, $R^o{}_p$ and $R^i{}_p$ are the polarization resistances in the absence and presence of inhibitor, respectively.

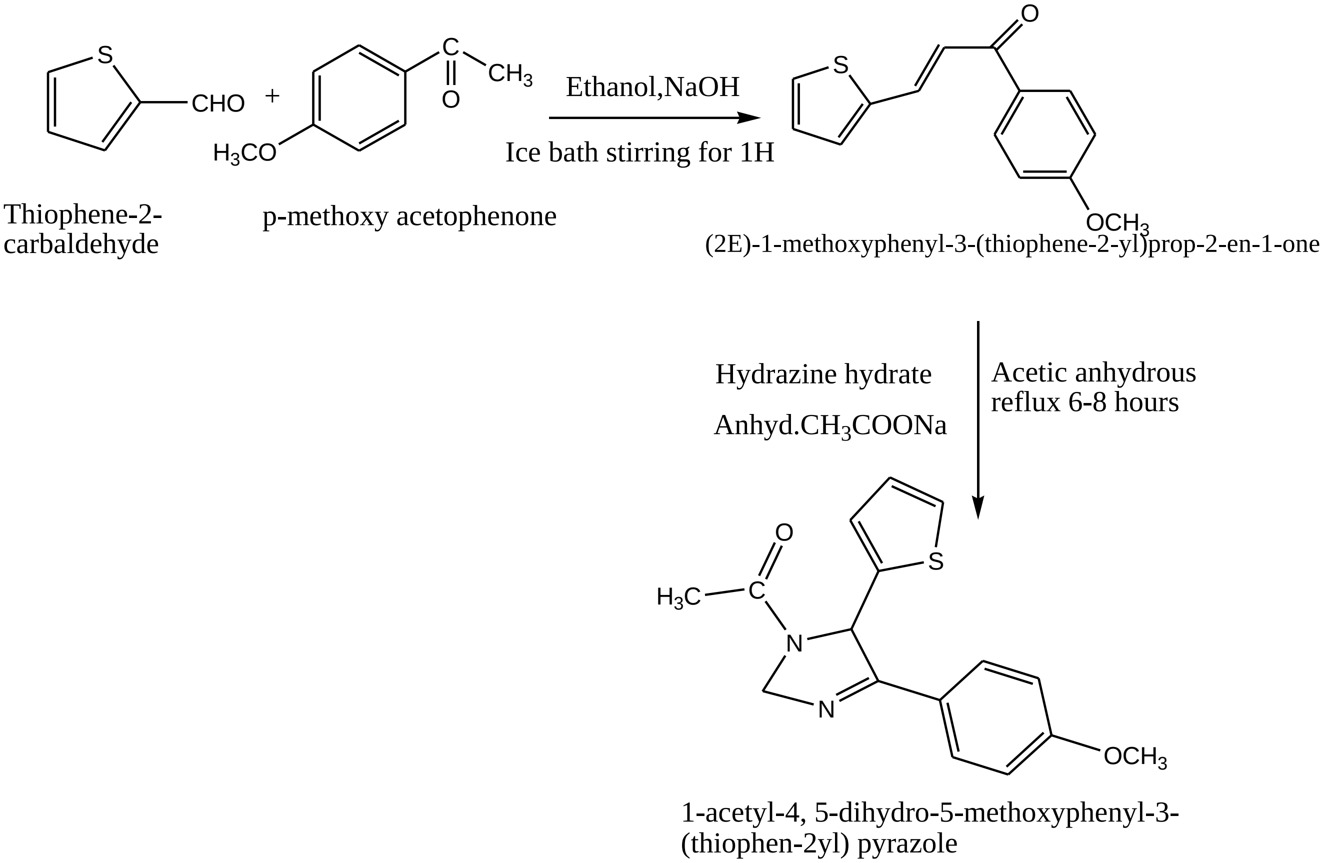
Synergistic effect of halide ions

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 1M H_2SO_4 using weight loss technique was studied. This is called synergistic effect process.

Results and Discussion

Structural elucidation of synthesized inhibitor compound

1-acetyl-4,5-dihydro-5-phenyl-3-(thiophen-2yl)pyrazole were synthesized 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 anhydride under the reaction conditions. An array of compound namely 1-acetyl-4, 5-dihydro-5-methoxy phenyl-3-(thiophen-2yl) pyrazole were synthesized under classical thermal method. The structures of the synthesized 1-acetyl-4, 5-dihydro-5-methoxyphenyl-3-(thiophen-2yl) pyrazole was confirmed by FT-IR,^{1}HNMR and ^{13}C NMR spectral studies and elemental analysis (**Scheme 1**).



Scheme 1

FT-IR spectrum of compound shows characteristic absorption frequencies at 3026.31 cm^{-1} due to aromatic CH stretching vibration. The absorption bands at 2899.01 cm^{-1} are attributed to the aliphatic CH stretching vibration. The absorption frequency at 1660.71 cm^{-1} is assigned to amide carbonyl stretching vibration. The absorption band at 1425.4 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.

Table 2 Elemental analysis of the synthesized compound

Molecular Formula	Molecular Weight (m/z)	Elements Present in % (Calculated value)				Elements Present in % (Observed value)			
		C	H	N	S	C	H	N	S
$C_{16}H_{18}N_2SO_2$	258	63.63	6.00	9.27	10.61	63.57	5.96	9.23	10.59

In the H^1 NMR spectrum of 1-acetyl-4,5-dihydro-5-methoxyphenyl-3-(thiophen-2yl) pyrazole, 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 3.33 and 3.70 ppm. The doublet of doublet at 3.33ppm (J_{4a5a}=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 3.87 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 non-equivalent protons of the methylene group (H-4a-H4e) of the pyrazoline moiety and the signals are observed at 5.90 ppm ($J_{5a,4a}$= 11.5Hz and $J_{5a,4e}$ =4.0 Hz).Also the acetyl methyl protons of pyrazoline moiety gives signal as a singlet at 2.41 ppm. The aromatic protons appear as a multiplet in the range of 7.03-7.72 ppm.

In the ^{13}C NMR spectrum of 1-acetyl-4,5-dihydro-5-methoxyphenyl-3-(thiophen-2yl) pyrazoles, ^{13}C resonance at 55.42 ppm is assigned to C-5 of pyrazole moiety. The ^{13}C resonance observed at 42.17 ppm is due to C-4 of pyrazole moiety. The ^{13}C resonance observed at 153.70 ppm is assigned to C-3 of pyrazole moiety. The aromatic carbons are observed in the region of 114.20-128.23 ppm. The ^{13}C resonance observed at 21.96 ppm is due to acetyl methyl carbon. The remaining ^{13}C signal at 144.48 is due to ipso carbon and the ^{13}C resonance observed at 55.13 ppm is due to the presence of methoxy phenyl substituted 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 3**.

The **Table 1** shows that the inhibition efficiency increases with increase in concentration of the inhibitors. The behaviour 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.

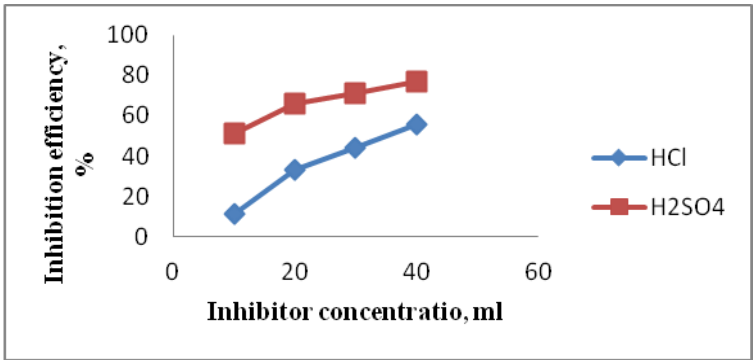


Figure 2 Plot of corrosion rate against inhibition efficiency of mild steel in IM H_2SO_4 and 1M HCl in presence of the inhibitors.

Table 3 Inhibition efficiency at various concentrations of pyrazole for the corrosion of mild steel in IM 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 inθ	C/θ	Corrosion Rate in mpy×10-3
HCl	blank(10 ml) HCl	0.009				0.0115
	HCl + 0.1 S	0.008	11.11	0.11	90.9091	0.01028
	HCl + 0.2 S	0.006	33.33	0.33	60.6061	0.0077
	HCl + 0.3 S	0.005	44.44	0.44	68.1818	0.00643
	HCl + 0.4 S	0.004	55.55	0.55	72.727	0.00514
H_2SO_4	Blank(10ml) H_2So_4	0.035				0.0449
	H $_2SO_4$ + 0.1 S1	0.017	19.61	0.51	51.43	0.0218
	H_2SO_4 + 0.2 S1	0.012	65.714	0.66	60.6061	0.01542
	H_2SO_4 + 0.3 S1	0.01	71.4	0.71	42.2535	0.0128
	H_2SO_4 + 0.4 S1	0.008	77.1428	0.77	51.948	0.01028

Effect of temperature and Kinetics thermodynamics

To investigate the mechanism of inhibition and to determine the activation energies of the corrosion process, the weight loss studies were carried out at various temperatures from 301-318K in 1M HCl and 1M H_2SO_4. The results are given in **Table 4**. The decrease in I.E with temperature may be attributed to desorption of the inhibitor molecules from the metal surface at higher temperature. But the values are not decreased very much which suggests that the adsorption-desorption equilibrium is not completely shifted towards desorption and still there remains the protective layer of the inhibitors on the surface. This shows that the compounds are effective even at 318K in both the acids. **Figure 3** represents the Arrhenius plots for the inhibitors in 1M HCl and 1M H_2SO_4 respectively. The slopes of the straight lines permit the calculation of Arrhenius activation energy Ea for the corrosion process. These types of inhibitors retard the corrosion process at ordinary temperatures whereas the efficiency is considerably decreased at elevated temperatures [25].

Table 4 Effect of temperature on inhibition efficiency of pyrazole at 0.01 ml concentration in IM H_2SO_4 and 1M HCl.

Medium	**Temperature (K)**	**Weight loss (mg)**	**Inhibition Efficiency %**	**Corrosion Rate (mpy)**
Blank HCl	301	0.036		0.0462
HCl + S	301	0.006	83.33	0.0077
Blank HCl	308	0.04		0.0475
HCl + S	308	0.005	86.5	0.00643
Blank HCl	318	0.037		0.0514
HCl + S	318	0.016	60	0.02056
Blank H_2SO_4	301	0.142		0.1824
H_2SO_4 + S	301	0.011	92.2	0.01413
Blank H_2SO_4	308	0.034		0.0436
H_2SO_4 + S	308	0.009	73.53	0.01157
Blank H_2SO_4	318	0.036		0.0462
H_2SO_4 + S	318	0.015	58.33	0.0193

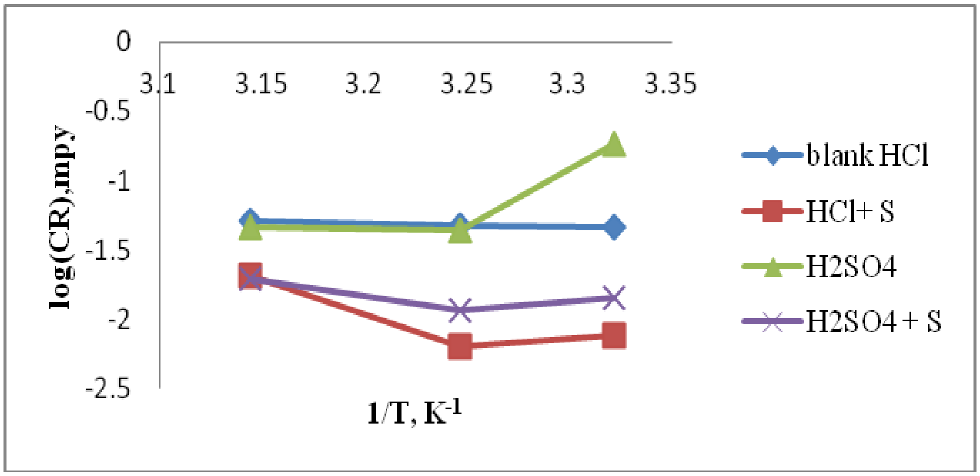


Figure 3 Arrhenius plot of corrosion rate of mild steel in IM H_2SO_4 and 1M HCl in presence and absence of the inhibitors.

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

$$\text{Log CR} = \log A - Ea/\,2.303\,RT \qquad (5)$$

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.

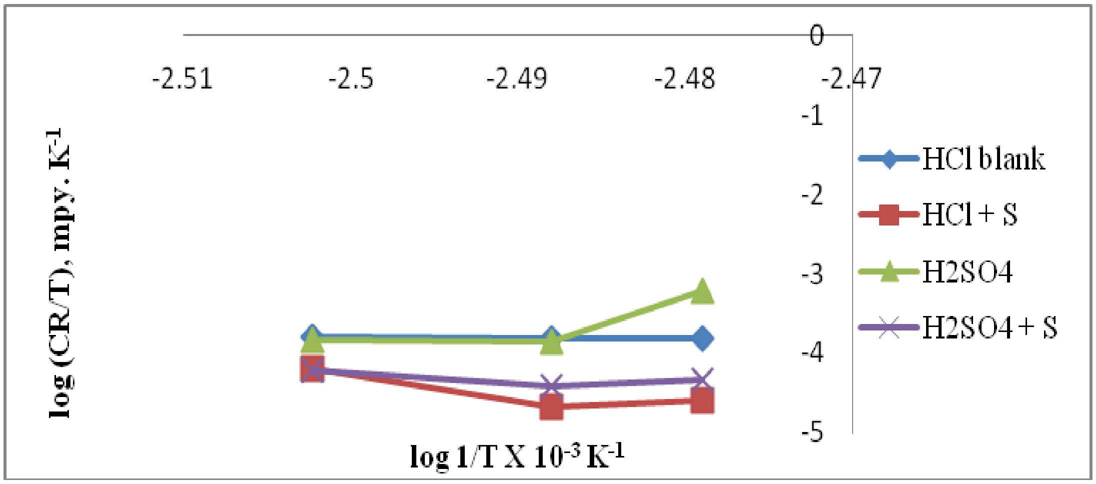


Figure 4 log (corrosion rate/T) – (1/T) curves for dissolution in 1M HCl and 1M H_2SO_4 in absence and presence of inhibitor.

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.

Adsorption isotherm

The effect of inhibition on the corrosion of metallic materials is mainly ascribed to the molecular adsorption of the corrosion inhibitor on the metal surface. Isotherms provide an idea of the adsorption and desorption processes and the interactions of metal-inhibitor molecules on the metallic surface. To understand the inhibition process of mild steel in sulphuric acid and hydrochloric acid, the experimental data were related to adsorption isotherms, which described the operative process between inhibitor-metal. Langmuir (Equation (6)).

$$K_{ads}C = \frac{\theta}{1-\theta} \qquad (6)$$

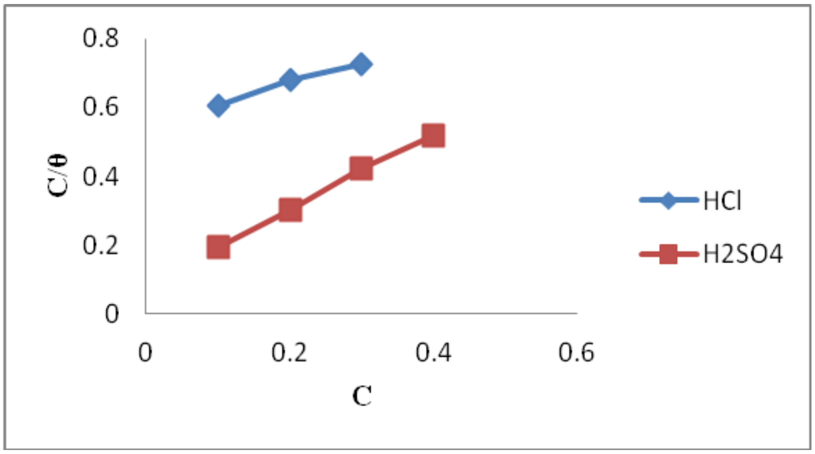


Figure 5 Langmuir adsorption isotherms after the addition of inhibitor used for carbon steel in 1 M HCl and 1M H_2SO_4

Tafel polarization tests

In iron or steel corrosion, electrochemical reactions may take place as follows [26]: At the anodic areas

$$Fe \longrightarrow Fe^{2+} + 2e^{-} \quad (7)$$

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	$2H + + 2e^{-} \longrightarrow H_2$
Oxygen reduction (acid solution)	$O_2 + 4 H{+}{+}4e^{-} \longrightarrow 2H_2O$
Oxygen reduction (neutral or basic solution)	$O_2 + 4H_2 O + 4e^{-} \longrightarrow 4OH^{-}$
Metal ion reduction	$M^{3+} + e^{-} \longrightarrow M^{2+}$
Metal deposition	$M^{+} + e^{-} \longrightarrow M$

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.

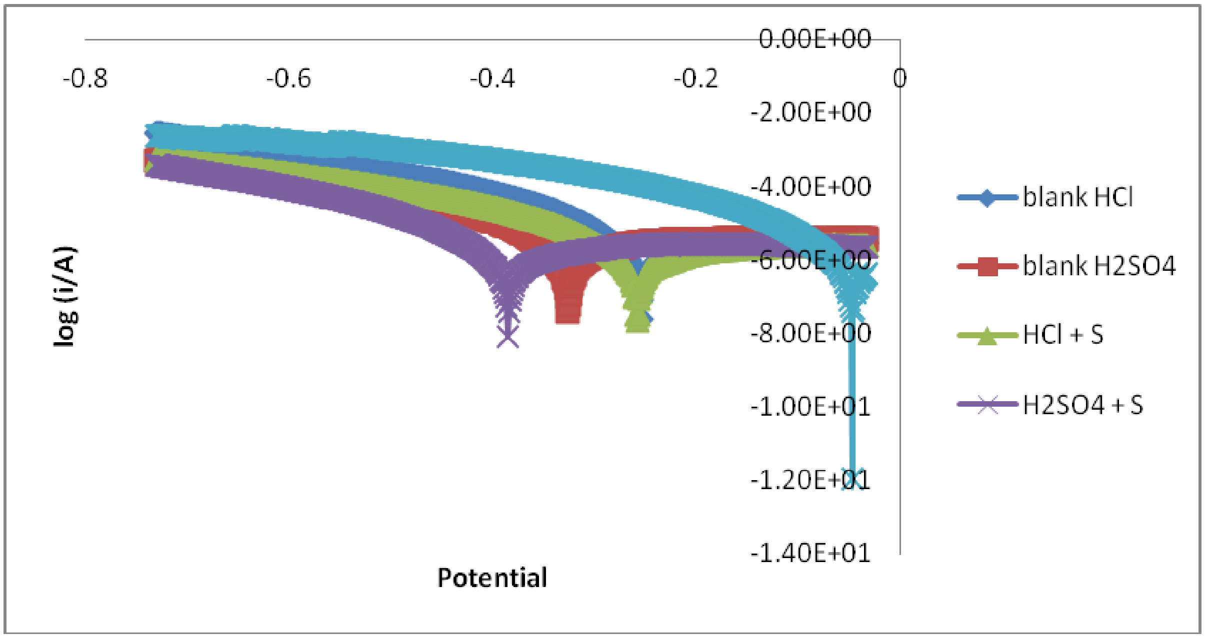


Figure 6 Potentio dynamic polarization curves for carbon steel in 1M H_2SO_4 and 1M HCl solution and after addition of inhibitor S.

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.

Synergistic effect

The synergistic effect provided by the addition of halide ions such as I^{-}, and Cl^{-} to the solution containing 1M H_2SO_4 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 cations. The positively charged propagated cations may be adsorbed by columbic attraction on the metal surface where halide ions are already adsorbed. This leads to more surface coverage and hence greater inhibition.

Table 5 Synergistic effect of 0.1N KI on the inhibition efficiency of inhibitors in 1M H_2SO_4 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×10-3
HCl	blank HCl	0.009				0.0115
	HCl+ S+ 0.1KI	0.005	44.44	0.44	22.95	0.00643
	HCl+ S+ 0.2KI	0.004	55.55	0.56	35.7143	0.00514
	HCl+ S + 0.3KI	0.003	66.67	0.67	44.776	0.003855
	HCl+ S+ 0.4KI	0.0035	61.11	0.61	65.574	0.0045
H_2SO_4	blank H2SO4	0.035				0.0449
	H_2SO_4+ S+ 0.1KI	0.012	65.71	0.66	45.4545	0.01542
	H_2SO_4+ S+ 0.2KI	0.014	60	0.60	66.67	0.01799
	H_2SO_4+S + 0.3KI	0.01	71.43	0.71	28.169	0.01285
	H_2SO_4+S+ 0.4KI	0.004	91.4	0.91	11.098	0.0038

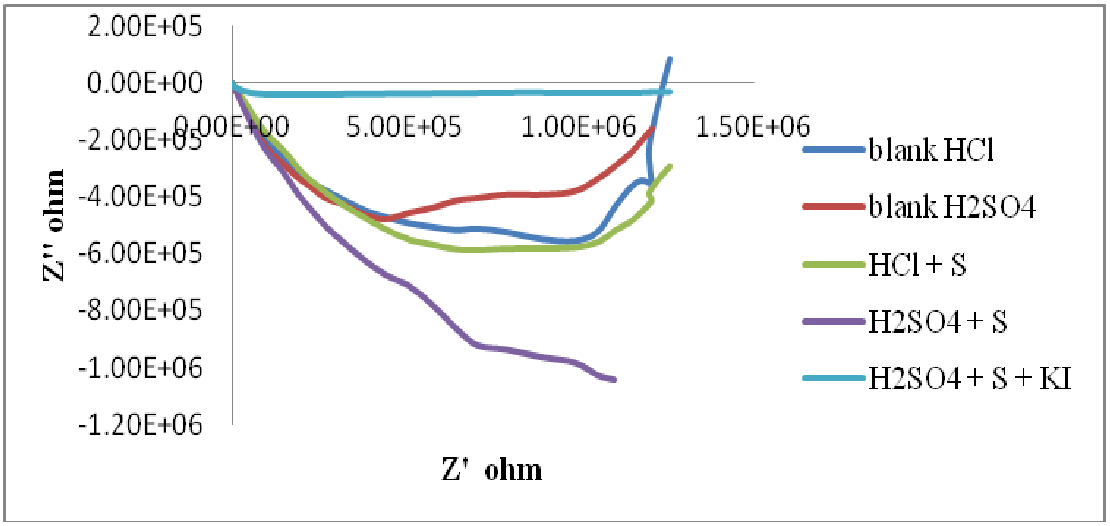


Figure 7 Nyquist diagram for mild steel in IM H_2SO_4 and 1M HCl in presence and absence of the inhibitor. Comparison of IE in 1M HCl and 1M H_2SO_4

The order of synergism of halide ions with the tested inhibitors has been found to be I^- > Cl^{-1}. The reason for better synergism with iodide ion is due to the large size and ease of polarisability of I^- ion, which facilitates chemisorptions on the iron surface.

Comparison of IE values of the inhibitors obtained by all the three methods in 1M HCl and 1M H_2SO_4 reveal that the inhibition efficiency is more for both the inhibitors at lower concentration in 1M HCl compared to that in 1M H_2SO_4. But the efficiencies are comparable at higher concentration in both the acids. Based on Cl^- interaction energy and induced charge data, reported that anions are not only adsorbing more strongly but inducing also greater negative charges to the corroding metal atoms. They have also reported that surface concentration of SO_4^{2-} ions should be low because of strong electrostatic repulsion operating between these divalent anions at the interface. The organic inhibitors get protonated as cations in acidic medium. The adsorptions of these cations are assisted by the already adsorbed Cl^- anions giving synergistic effect. In the synergetic effect shows the concentration of the inhibitors is increased more and more of the inhibitor molecules get adsorbed by planar adsorption of the neutral molecules through physisorption between the lone pairs of electrons on N and O atoms and P electrons of the aromatic ring in addition to the lateral ionic adsorption. Hence the surface is fully covered by inhibitor molecules in both the acids and hence I.E values are high.

Conclusion

- Pyrazole derivative exhibit excellent inhibition efficiency towards corrosion of mild steel in1M H_2SO_4 and 1M HCl solution.
- At lower concentration the inhibitors show better performance in HCl than in H_2SO_4 which may be due to the synergistic effect of the Cl^- ions.
- The optimum inhibition efficiency of these compounds was achieved at a concentration 0.2 mM.
- Inhibition Efficiency decreases with increase in temperature but increases with increase in concentration of inhibitors in both the acid.
- The inhibitors were adsorbed on the mild steel by physisorption mechanism.
- The adsorption of inhibitors on mild steel in 1M H_2SO_4 and 1M HCl obeys Langmuir adsorption isotherm.
- Potentio-dynamic polarization studies suggest that the inhibitors are mixed type cathodic in 1M HCl and anodic in 1M H_2SO_4.
- AC impedance study implies that the charge transfer process mainly controls the corrosion of steel.

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