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CORROSIVE INHIBITIVE EFFECT OF PYRAZOLE COMPOUNDS TOWARDS THE CORROSION OF MILD STEEL IN ACIDIC MEDIUM

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ABSTRACT

The inhibitive effect of compound (1-acetyl-4, 5-dihydro-5-Bromophenyl-3-(thiophen-2yl) pyrazoles) on mild steel in 1M H_2SO_4 and 1M HCl was investigated by weight loss, Potentiodynamic polarization and electro chemical impidence studies. The synthesized compound of 1-acetyl-4, 5-dihydro-5-Bromophenyl-3-(thiophen-2yl) pyrazoles was characterized by FTIR, ^{1}H NMR, ^{13}C NMR and mass. The purity of the compound confirmed by TLC. The corrosion inhibition rate was increased with increasing the concentration of our synthesized inhibitor (1-acetyl-4, 5-dihydro-5-Bromophenyl-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 Langmuir adsorption isotherm.

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

INTRODUCTION

Corrosion is the cancer of metals due to thermodynamic instability[1]. One of the most economical and practical preventive maintenance methods for minimizing and controlling corrosion in product pipelines, vessels, etc., is to treat the corrosive environment with chemical inhibitors[2,3]. The chemical corrosion inhibitors (CIs) allow decreasing the rate of corrosion process. In the oil and chemical industry, inhibitors have always been considered to be the first line of defence against corrosion[4], especially in acidic media[5-7]. The addition of Inhibitors can effectively protect the metal from acid attack; as a result, there have been developed different families of chemical compounds as inhibitors. A number of organic compounds are used as corrosion inhibitors for steel in acidic environments[8].Among this class of organic compounds are pyridines,[9-11] imidazolines,[12,13] thiazine[14], 1, 3-azoles[15,] and other groups. Nevertheless, the environmental protection standards, cost, toxicity and availability of corrosion inhibitors require continuous efforts to synthesis a new chemicals.[16,17]

Nowadays most important considerations in industry are reduction of overall costs by protection and maintenance of materials used. The protection of corroding metal surface prevents the waste of resources and money during the industrial applications and is vital to extend the equipment’s lifetime[18]. Mild steel is extensively used in different industries in the merit of its good structural properties, good mechanical workability and low cost. Corrosion can be minimized using suitable preventive measures, and several techniques have been developed[19-23] to control corrosion. Corrosion inhibition of mild steel in acid solutions has become one of the most urgent and severe challenges in acid pickling process [24-26]. Mild steel is exposed to the action of acid in industrial processes in which acids have important functions, for example in oil well acidification, acid pickling, acid cleaning, and acid decaling. Use of inhibitors is one of the best methods of protecting metals against corrosion[27, 28]. Corrosion inhibitors are compounds that are added in small quantities to an environment to prevent corrosion of metals[29]. Most of the efficient acid inhibitors are organic compounds containing nitrogen, sulphur and/or oxygen atoms in their molecule[30-32].

EXPERIMENTAL

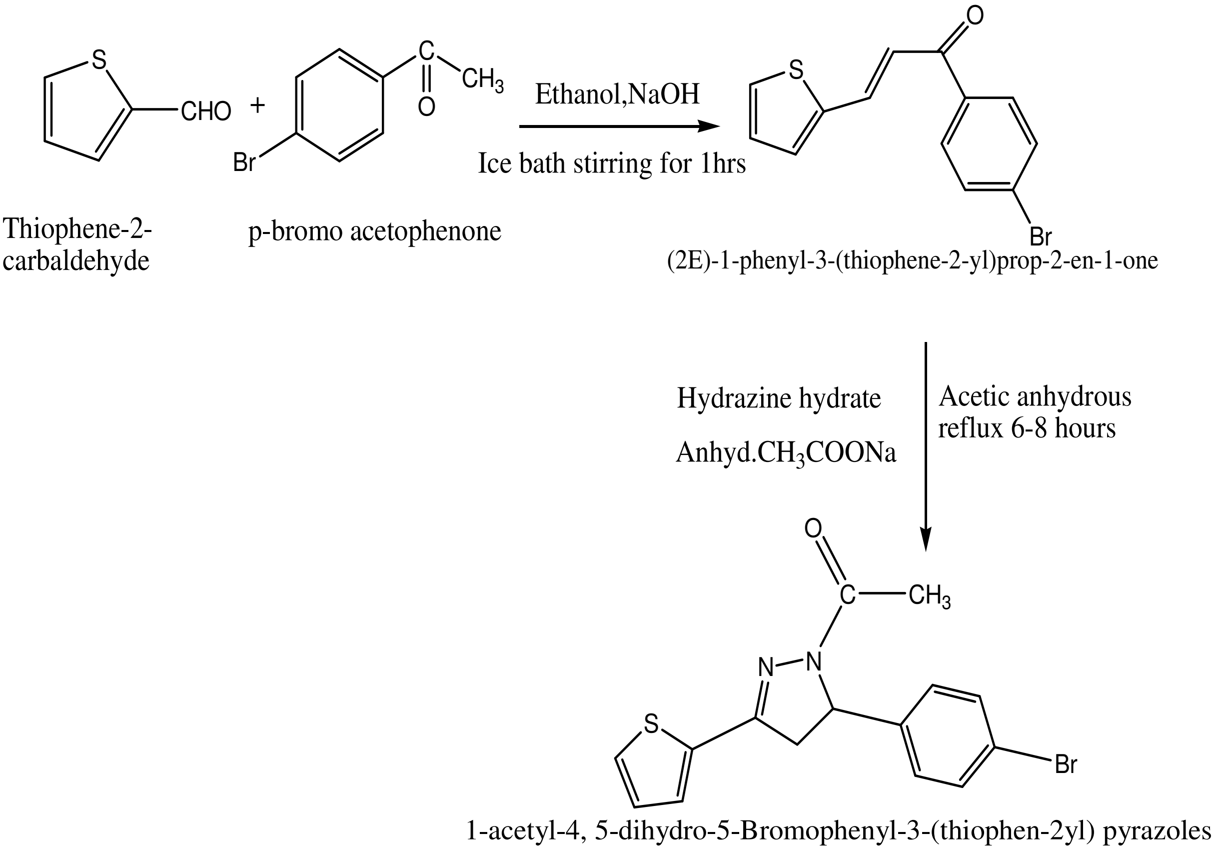
Composition of Mild steel strips

The Composition of Mild steel strips is as follows-

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 solution 1M 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 1/0, 2/0, 3/0 and 4/0 grades to remove adhering impurities. At the end they were cleaned with double distilled water and acetone.



Scheme-1

Measurements and Equipments

The compounds were synthesised and characterized by ^1H, ^{13}C NMR and IR spectroscopy. Melting points (uncorrected) were determined using a Guna melting point apparatus. FT-IR spectra were carried out on a Perkin-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.
The aim of this study is to investigate the inhibitive property of organic compound namely 1-acetyl-4, 5-dihydro-5-Bromophenyl-3-(thiophen-2yl) pyrazoles on the corrosion of the mild steel in 1M H_2SO_4 and 1M HCl medium. The chemical structures of the compound were studied by IR, ^{1}H and ^{13}C NMR spectroscopy.

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 etylacetate (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[33].

1-acetyl-4, 5-dihydro-5-Bromophenyl-3-(thiophen-2yl) pyrazoles

Yield 70%; M.P 100°C; Molecular Formula $C_{15}H_{15}N_2SOBr$; %Calcd. (Found); C%= 51.42 (51.47), H% =4.28 (4.31), N% = 7.8 (8.0) S%=9.16 (9.21). M/z (M) +:350,352.
FT-IR (KBr, cm^{-1}): 3066.11 cm^{-1}(Aromatic CH stretching), 2885.51cm^{-1} (Aliphatic CH stretching), 1658.78 cm-1(Amide C=O stretching), 1417.68 cm-1(C=N Stretching), 642.3, 709.8, 763.81 cm-1(Aromatic ring stretching)
^{1}H NMR ($CDCl_3$, δ ppm, 400 MHz) 3.33(dd, H4a), 3.71(dd, H4e), 5.93(dd, H5a), 2.41(acetyl methyl groups), 7.64-6.93(Aromatic protons and thiophene protons)
^{13}C NMR ($CDCl_3$, δ ppm,100 MHz)55.44 (C-5 of pyrazole moiety),41.89 (C-4 of pyrazole moiety), 152.78 (C-3 of pyrazole moiety), 21.97 (acetyl methyl carbon), 168.94 (amide cabonyl carbon),128.04-124.67 (Aromatic and thiophenecarbons)144.09,132.01,130.25(Ipso carbon).
Mechanism is as per given in Scheme-2.

Corrosion prevention by inhibitors

A corrosion inhibitor is a substances that when added in small amounts to a corrosive medium, reduces its corrosivity. Corrosion inhibitors function by interfering with either the anodic or cathodic reactions or both. Many of these inhibitors are organic compounds. It is generally assumed that corrosion inhibition performed by adsorption of the additives (ion or neutral polar molecules) to the metal-solution interface. It is known that the potential difference between a metal electrode and the solution is due to a non-uniform distribution of electric charges at the interface.
The interaction of ions or neutral molecules at the electrical double layer, changes its properties and structures. The water molecules pre adsorbed at the metal surface in contact with the aqueous solution are involved in the successive adsorption processes. According to Bockris[34], the adsorption of an organic substance at the metal-solution interface may be written according to the following displacement reaction.

$$Org(sol) + n\,H_2O \rightarrow Org(ads) + \;nH_2O \qquad (1)$$

Where, n is the number of water molecules removed from the metal surface for each molecule of inhibitor adsorbed. According to Bockris, n is assumed to be independent of coverage or charge of the electrode. Clearly, the value of n will depend on the cross-section area of the organic molecules with respect to that of the water molecule. Adsorption of organic molecule occurs because the interaction energy between the metal surface and the inhibitor is higher than the interaction energy between the metal surface and the water molecules.

Lorenz and Mansfeld[35] classified the modes of inhibition effect of interface inhibitors into three categories: that caused by (i) the geometric blocking effect of adsorbed inhibitive species on the metal surface (ii) the effect of blocking the active sites on the metal surface by adsorbed inhibitive species (iii) the electrocatalytic effect of the inhibitor or its reaction products. It has been discussed[36] in the case of the first mode the inhibition effect comes from the reduction of the reaction area on the surface of the corroding metal, whereas for the other two modes the inhibition effects are due to the changes in the average activation energy barriers of the anodic and cathodic reactions of the corrosion process. Thus, the electrochemical behaviour and the interpretation of the measured electrochemical data will not the same for all the modes. There are many factors affect the inhibition efficiency of the organic compounds in acidic media.

The effect of the structure of organic compounds on their inhibiting properties

Most organic inhibitors contain at least one polar group with an atom of nitrogen, sulphur, or in some cases selenium and phosphorus. According to Hackerman[37], 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.

Hackerman et al[38,39] have been studied the adsorption of organic substances with a long hydrocarbon chain from organic solvents. Theses 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 10 ml of inhibitor. At the end of the testing period, the specimens were cleaned and finally its weight loss was recorded. The corrosion rate (V_{corr} mm/year), inhibition efficiency ($IE_{w,}$ %) and surface coverage (θ) were determined by the following equations-

$$v_{corr} = (8.76 \text{ X } 10^4 \text{ W}) / \text{ATD} \quad (2)$$

$$\phi = (v_{corr,0} - v_{corr,i}) / v_{corr,0} \quad (3)$$

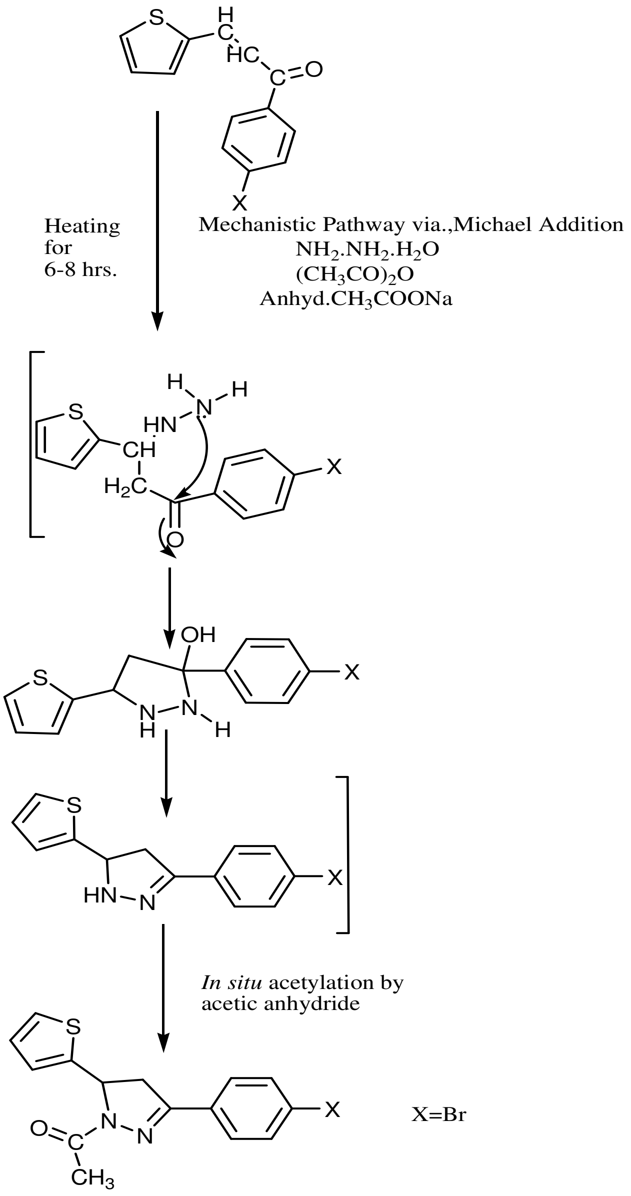
$$(I.E_w, \%) = [(v_{corr,0} - v_{corr,i}) / v_{corr,0}] \text{ X } 100 \quad (4)$$

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 stat 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}.



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

This was followed by the cathodic and anodic polarization curves in the potential range of -250 mV to E_{ocp}, and from to +250 mV at the same scans rate[40]. The inhibition efficiencies were determined from the measured polarization resistance values as:

$$[(IE]_{Rp},\%) = \frac{R^i_p - R^0_p}{R^i_p} \times 100 \qquad (5)$$

Where R^o_p and R^i_p 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:

$$(IE_T\,\%) = \frac{i^0{}_{corr} - i^i{}_{corr}}{i^0{}_{corr}} \times 100 \qquad (6)$$

Where i^i_{corr} and i^o_{corr} are the corrosion current densities values with and without inhibitor, respectively.

Synergistic effect

The synergistic effect was studied in the presence of 0.1 N KCl and KI to the steel specimen immersed for hours in 1M H_2SO_4 and 1M HCl containing various concentration of the inhibitor. The weight loss method procedure was followed to study the synergistic effect.

RESULTS AND DISCUSSION

Structural elucidation of synthesized organic compound

1-acetyl-4, 5-dihydro-5-bromophenyl-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, in situ acetylation occurs in the course of the reaction due to solvent, acetic anhydride under the reaction conditions. An array of 1-acetyl-4, 5-dihydro-5-bromophenyl-3-(thiophen-2yl) pyrazoles is synthesized under classical thermal method. The structures of the synthesized 1-acetyl-4, 5-dihydro-5-bromophenyl-3-(thiophen-2yl) pyrazoles is confirmed by FT-IR,MS.^{1}HNMR and ^{13}C NMR spectral studies and elemental analysis.

FT-IR spectrum of compound 1-acetyl-4,5-dihydro-5-bromophenyl-3-(thiophen-2yl) pyrazoles shows characteristic absorption frequencies at 3066.11 cm^{-1} due to aromatic CH stretching vibration. The absorption bands at 2885.51 cm^{-1} is 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. 642.3, 709.8, 763.81 cm^{-1}(Aromatic ring stretching). The absence of carbonyl band clearly supported for the formation of bromo pyrazole, besides the disappearance of NH stretching vibration, which conforms the situ acetylation reaction due to acetic anhydride solvent.

Elemental analysis of (C_{cal} 51.47, C_{obs} 51.42 ; H_{cal} 4.31 , H_{obs} 4.28; N_{cal} 8.0, N_{obs} 7.8; S_{cal} 9.21 , S_{obs} 9.16 are consistent with the proposed molecular formula($C_{15}H_{16}N_2SOBr$) of 1-acetyl-4,5-dihydro-5-bromophenyl-3-(thiophen-2yl) pyrazoles .

In the H^1 NMR spectrum of compound, 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 3.71 ppm. The doublet of doublet at 5.93 ppm (J4a, 5a=17.5 Hz and J4a, 4e=4.0 Hz) is assigned to H-4a proton of the pyrazoline moiety. Likewise, the doublet of doublet at 3.71 ppm (J4e, 4a =17.5 and J4e, 5a =11.5 Hz) is assigned to H-4e proton of the pyrazoline moiety. Similarly, the methane 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 5.93 ppm (J5a, 4a= 11.5Hz and J5a, 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 6.93-7.64 ppm.

In the ^{13}C NMR spectrum of 1-acetyl-4, 5-dihydro-5-bromophenyl-3-(thiophen-2yl) pyrazoles, ^{13}C resonance at 55.44 ppm is assigned to C-5 of pyrazole moiety. The 13C resonance observed at 41.89 ppm is due to C-4 of pyrazole moiety. The 13C resonance observed at 152.78 ppm is assigned to C-3 of pyrazole moiety. The aromatic carbons are observed in the region of 124.67-128.04 ppm. The ^{13}C resonance observed at 21.97 ppm is due to acetyl methyl carbon. The remaining ^{13}C signal at 144.09, 132.01, and 130.25 is due to ipso carbon.

The compound gave significantly stable molecular ion peaks with a relative abundance ranging from 55.2%. The common possible fragmentation pattern involves some rearrangement with the removal of smaller molecules viz. CO, CH_3 etc. The satisfactorily elemental analysis further supports structure of the products, as-

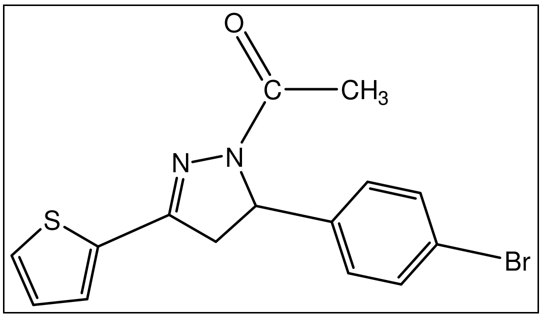


Fig-1: Structure of the inhibitor.

Weight loss measurements

The inhibition efficiency with different concentration of the inhibitor (S) on the mild steel in 1M HCl and H_2SO_4 has been evaluated by weight loss measurements and the results are summarized in Table-1. The data revels that inhibition efficiency increases with increase in concentration of the inhibitor 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.

Effect of temperature

The corrosion rate of carbon steel exposed to 1 M H_2SO_4 at 28°C, 35°C and 45°C as a function of inhibitor concentration is shown in Fig.2.In this figures , it is observed that at 28°C, 35^0C and 45^0C, the corrosion rate of carbon steel decreased as the concentration of inhibitor was added. The corrosion rate of carbon steel exposed to 1 M HCl at 28°C, 35°C and 45°C as a function of inhibitor concentration is shown in Figs.1.In this figures , it is observed that at 28°C,35^0C and 45^0C, the corrosion rate of carbon steel decreased as the concentration of inhibitor was added.

This behaviour could be attributed to an adding the inhibitor to the solution at the acid solution and increases in the temperature, the corrosion rate should be decreased. The values Corrosion Rate and of IE_w (%) obtained from weight loss tests at different temperatures are summarized in Table-1.

Adsorption isotherm

The adsorption of inhibitor molecules on the corroding surfaces generally does not reach the real equilibrium and tends to a steady state. It is therefore reasonable to consider quasi-equilibrium adsorption in thermodynamic by using the appropriate adsorption isotherm.

Corrosion inhibition of carbon steel in sulphuric acid solution and hydrochloric acid solution can be explained in terms of molecular adsorption, which is influenced by the chemical structure and charge distribution of inhibitor[41]. The process of inhibitor on metal surface can be described by different isotherms, from which Langmuir is the simplest and it is based on the assumption that all adsorption sites are equivalent and the particle binding occurs independently from nearby sites being occupied or not[42,43]. In order to obtain adsorption isotherm, the surface coverage values (θ) for the inhibitors were obtained from the weight loss measurements at different medium of 1M HCl and 1M H_2SO_4 solution at (301-318 K), based on the following models-

Temkin isotherm $k_{ads}C = \exp(f.\theta)$ (9)

Langmuir isotherm $$k_{ads}\,C = \frac{\theta}{(1-\theta)} \quad (10)$$

Frumkin isotherm $k_{ads}C = \frac{\theta}{(1-\theta).\exp(-2f.\theta)}$ (11)

Freundluich isotherm $k_{ads}\,C = \theta$ (12)

Where k_{ads} is the equilibrium constant of the adsorption process, C is the inhibitor concentration and is the factor of energetic in homogeneity. The best fitting to the adsorption inhibitor behaviour was provided by Langmuir shown in (Fig 3). To obtain the adsorption isotherm, the degree of surface coverage (θ) was calculated for various concentrations of pyrazole from the weight loss data and listed in Table-1.

Table-1: 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	0.003	66.67	0.66	15.1516	0.0038
	HCl + 0.2 S	0.002	77.78	0.78	25.64	0.00257
	HCl + 0.3 S	0.004	55.55	0.55	54.55	0.008995
	HCl + 0.4 S	0.006	33.33	0.33	121.2	0.00514
H_2SO_4	blank(10 ml)H_2So_4					0.0449
	$H\ _2SO_4$ + 0.1 S	0.006	82.8	0.83	12.048	0.0077
	H_2SO_4 + 0.2 S	0.004	88.57	0.89	22.472	0.00514
	H_2SO_4 + 0.3 S	0.008	77.1428	0.77	38.961	0.01028
	H_2SO_4 + 0.4 S	0.012	65.7142	0.66	60.6061	0.01542

Table-2: Effect of temperature on inhibition efficiency of pyrazole at 0.01 ml concentration in IM 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	0.0115
Blank HCl	308	0.04		0.0475
HCl + S	308	0.009	77.5	0.0115
Blank HCl	318	0.037		0.0514
HCl + S	318	0.008	78.3	0.0102
Blank H_2SO_4	301	0.142		0.1824
H_2SO_4 + S	301	0.11	92.2	0.0141
Blank H_2SO_4	308	0.034		0.0436
H_2SO_4 + S	308	0.009	73.5	0.0115
Blank H_2SO_4	318	0.036		0.0462
H_2SO_4 + S	318	0.009	75	0.01028

Table 3: Synergistic effect of 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(10ml) 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	0.0029	67.77	0.68	44.12	0.0037
	HCl+ S+ 0.4KI	0.0032	64.44	0.64	62.5	0.0041
H_2SO_4	Blank(10ml) H2SO4	0.035				0.0449
	H2SO4+ S+ 0.1KI	0.003	91.4	0.91	11.098	0.0038
	H2SO4+ S+ 0.2KI	0.0089	74.57	0.75	26.66	0.01105
	H2SO4+S + 0.3 KI	0.0056	84	0.84	35.7	0.0072
	H2SO4+S+ 0.4KI	0.0044	88	0.88	45.45	0.0054

Note: S - Inhibitor

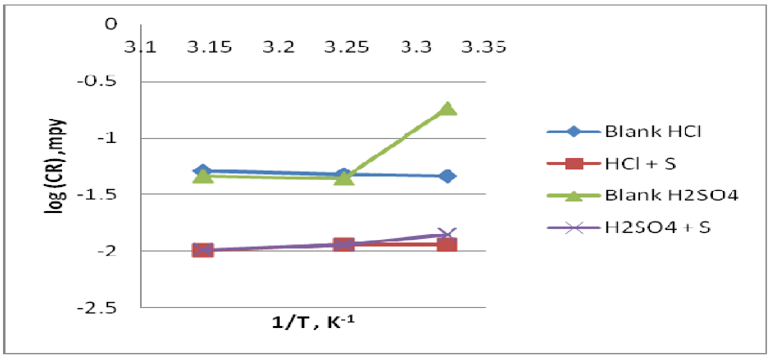


Fig.-2: Arrhenius plot of corrosion rate of mild steel in IM H2SO4 and 1M HCl in presence and absence of the inhibitors

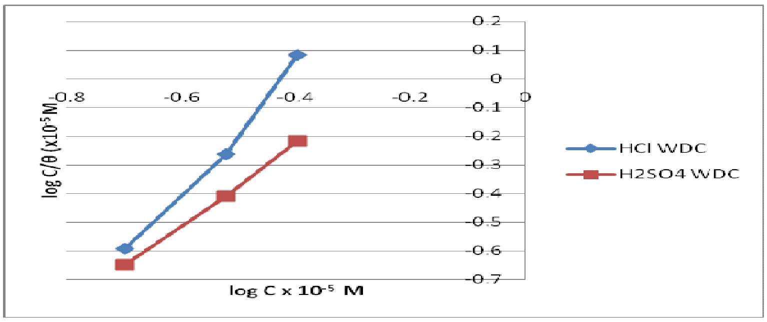


Fig.-3: Langmuir adsorption isotherms after the addition of inhibitor used for carbon steel in 1 M HCl and 1M H_2SO_4 .

Potentiodynamic polarization tests

The values of electrochemical parameters, i.e., corrosion current density i_{corr}), corrosion potential (E_{corr}), Tafel slops (β_c) and inhibitor efficiency (IE_T,%) obtained as function of different are measured.(but not shown).

Electrochemical nature of steel corrosion

In iron or steel corrosion, electrochemical reactions may take place as follows:

At the anodic areas

$$Fe \quad \rightarrow \quad Fe^{2+} + 2e^{-} \qquad (13)$$

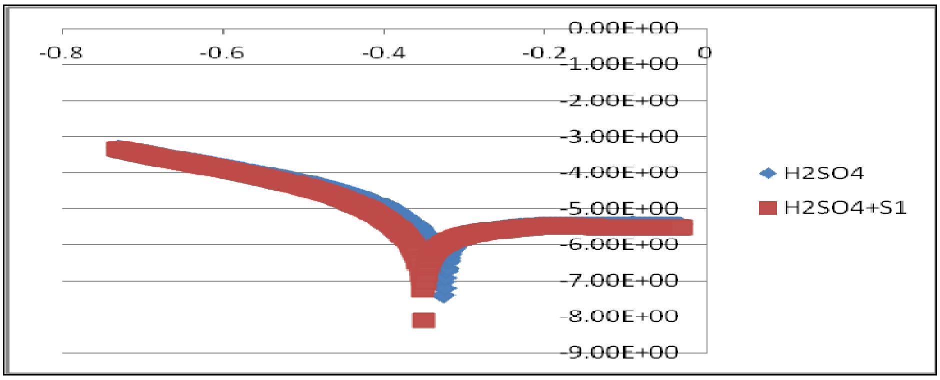


Fig.-4: Potentiodynamic polarization curves for carbon steel in 1M H_2SO_4 solution and after addition of inhibitor S.

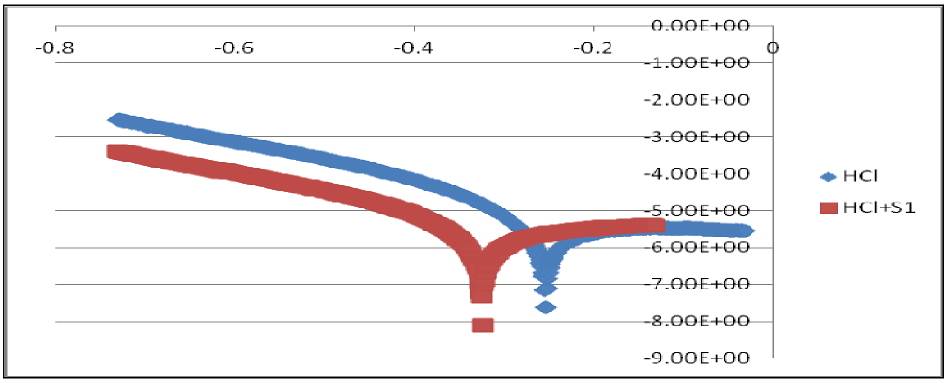


Fig.-5: Potentiodynamic polarization curves for carbon steel in 1M HCl solution and after addition of inhibitor S.

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

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 H_2SO_4 at different concentrations of inhibitors was studied using weight loss measurements. Plots of log k (corrosion rate) against 1/T (Figure 6), 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 (E_a^*). Activation parameters for corrosion of iron in 1M HCl and 1M H_2SO_4 were calculated from Arrhenius type plot:

$$K = A \exp^{(-Ea^*/RT)} \tag{14}$$

and transition state type equation:

$$k = RT/Nh \exp^{(\Delta S^*/R)} - \exp^{(-\Delta H^*/RT)} \tag{15}$$

The almost similar values of ΔEa* 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-14.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.

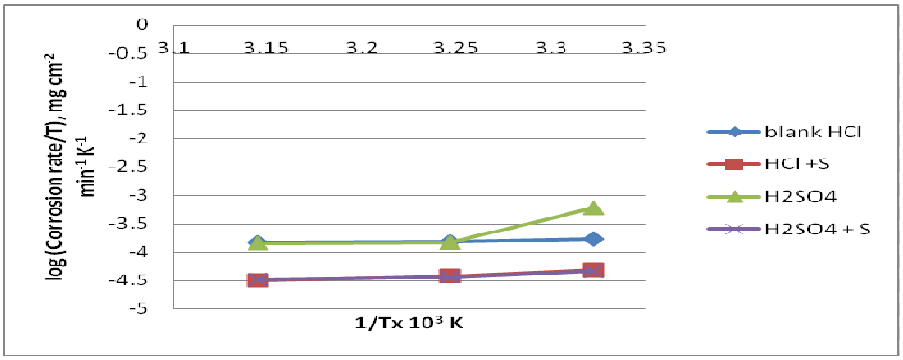


Fig.-6: log (corrosion rate/T) – (1/T) curves for dissolution in 1M HCl and H_2SO_4 in absence and presence of inhibitor.

The synergistic effect

Organic cations do not always alter the kinetics of the electrode processes. If salts of organic bases are added to 1 M HCl, there will be a significant change in the rate of hydrogen reduction, as well as in the ionization of iron. In 1 M H_2SO_4 these same organic cations have only a slight effect. This is because organic cations are not strongly adsorbed on the iron surface; the surface of the iron can be assumed to be positively charged in sulphuric acid, so that ions of like charges are weakly adsorbed. However, if halide ions are introduced into the solution, the situation is changed. The mechanism of action of anion-active substances is connected with the fact that adsorbed anion-active substances create connecting bridges between metal atoms and organic cations. It was assumed that many organic inhibitors in acidic electrolytes become protonated, changing into cations according to the equations[40] [Equations-16 to 20]:

$$R_2As + H^+ \rightarrow [R_2AsH]^+ \tag{16}$$
$$R_3P + H^+ \rightarrow [R_3PH]^+ \tag{17}$$
$$R_3N + H^+ \rightarrow [R_3NH]^+ \tag{18}$$
$$R_2S = O + H^+ \rightarrow [R_2SOH]^+ \tag{19}$$
$$(RNH_2)\ C{=}\ S + H^+ \rightarrow [(RNH)_2\ C = SH]^+ \tag{20}$$

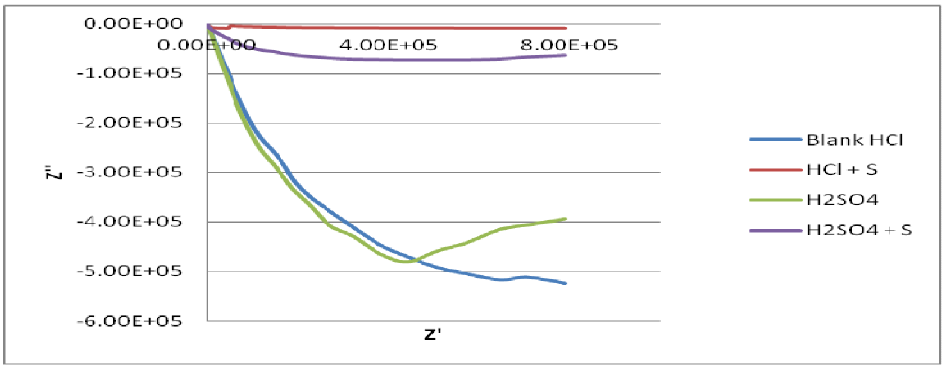


Fig.-6: Nyquist diagram for mild steel in IM H_2SO_4 and 1M HCl in presence and absence of inhibitor.

The adsorption of these cations is facilitated in the presence of halide ions, which form intermediate bridges the negative ends of the halogen-metal dipoles being oriented toward the solution. Halide ions are found[44] to enhance the inhibitive effect of several nitrogen containing compounds of mild steel in acidic solutions. The synergistic influence caused by iodide ions on the inhibition of corrosion of mild steel in H_2SO_4 in the presence of 1-acetyl-4,5-dihydro-5-Bromophenyl-3-(thiophen-2yl) pyrazole has been studied using potentiodynamic polarization, linear polarization and a.c. impedance technique. The addition of iodide ions enhances the inhibition efficiency to a considerable extent. This is due to the synergistic effect of 1-acetyl-4, 5-dihydro-5-Bromophenyl-3-(thiophen-2yl) pyrazole is adsorbed by columbic interaction on the metal surface, where iodide ions are already adsorbed and thus reduces the corrosion rate.

CONCLUSIONS

1. The compound 1-acetyl-4, 5-dihydro-5-Bromophenyl-3-(thiophen-2yl) pyrazole was synthesized by convectional method (Michael addition) using NaOH catalyst.
2. The melting point of the 1-acetyl-4, 5-dihydro-5-Bromophenyl-3-(thiophen-2yl) pyrazole = 100°C
3. Structure of the synthesized compound 1-acetyl-4, 5-dihydro-5-Bromophenyl-3-(thiophen-2yl) pyrazole was characterized by FTIR, ^{1}H NMR, ^{13}C NMR and Mass spectroscopy.
4. The ability of the synthesized compound on to the corrosion inhibition was checked by 1M HCl and 1M H_2SO_4 medium on mild steel by both weight loss and polarisation studies
5. Pyrazole act as good corrosion inhibitors for mild steel in 1M H_2SO_4 and 1M HCl.
6. The rate of corrosion was decreases with increase in concentration of the inhibitor.
7. The rate of the corrosion was decreases with increases in temperature.
8. The adsorption of the inhibitors obey Langmuir's adsorption isotherm.
9. Addition of halide ions (synergetic effect) leads to pronounced increase in inhibition efficiency in which columbic attraction prevails.
10. The kinetics thermodynamics value shows that the mechanism was endothermic.
11. The Tafel slopes obtained from potentiodynamic polarization studies indicates that the inhibitors behave as mixed type.

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