

ISOXAZOLINE DERIVATIVES AS CORROSION INHIBITORS FOR MILD STEEL IN ACID MEDIA

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ABSTRACT

Inhibition of corrosion of mild steel in 1M H₂SO₄ by isoxazolines was studied using gravimetric, electrochemical techniques and scanning electron microscopy. The addition of all the isoxazolines to the corrosive medium reduced the corrosion rate. The effect of temperature on the corrosion behavior of mild steel was studied in the temperature range 303K - 333K for 1M H₂SO₄ with optimum concentration of the synthesized isoxazolines. Thermodynamic parameters were also calculated to know the mechanism of corrosion inhibition. Polarization studies showed that all the isoxazolines function as mixed inhibitors but predominantly act as anodic inhibitors. The percentage of iron in the corrodent solution was determined by atomic absorption spectroscopy. The protection of mild steel specimens by isoxazolines was further well supported by scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDX) analysis.

KEYWORDS: Corrosion Inhibition, Electrochemical Measurements, Isoxazolines, Mild Steel, Adsorption

INTRODUCTION

Corrosion is a serious environmental problem in the oil, fertilizers, metallurgical and other industries.¹⁻³ Valuable metals such as mild steel, aluminum, copper and zinc are prone to corrosion when they are exposed to an aggressive media.⁴ Mild steel is a common constructional material for many industrial units because of its excellent mechanical properties, low cost and availability in ease for fabrication of various reaction vessels such as cooling power tanks, pipelines etc.,⁵ Corrosion of mild steel has an enormous economic impact. The understanding of the corrosion problem and the solution to tackle this problem is an active field of research.

The use of inhibitor is an attractive and most practical method for the protection of metals in contact with corrosion medium. Inhibitors reduce the corrosion of metallic materials by controlling the metal dissolution and consumption.⁶ The action of inhibition of the corrosion of steel and iron in acidic media by organic compounds containing heteroatoms has been widely studied.⁷ Such compounds typically contain N, O or S in a conjugated system and function via., adsorption of the molecules on the metal surface creating a barrier to corrodent attack.

The most important aspect of inhibition normally considered by corrosion scientists is the relation between molecular structure and corrosion inhibition efficiency. Lorenz et al.,⁸ have classified the modes of inhibition effect of interface inhibitors into three categories:

- The geometric blocking effect of adsorbed inhibitive species on the metal surface.
- The effect of blocking the active sites on the metal surface by adsorbed inhibitive species.
- The electro catalytic effect of the inhibitor or its reaction products.

In 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 change in the average activation energy barriers on the anodic and cathodic reactions of the corrosion process.⁹

The present investigation aims to study the influence of isoxazolines on the corrosion of mild steel in 1M H₂SO₄. The study was carried out by gravimetric measurement, potentiodynamic polarization methods and electrochemical impedance techniques. The results from gravimetric measurements were confirmed by AAS. Synergistic effect of halide ions and surfactant effect of SLS and CTAB were evaluated by weight loss measurements. The amount of dissolved iron was estimated by atomic absorption spectroscopic method.

EXPERIMENTAL METHODS

Electrode Composition

Cold rolled mild steel specimen of size 1cm x 3cm x 0.08cm having composition 0.084% C, 0.369% Mn, 0.129% Si, 0.025% P, 0.027% S, 0.022% Cr, 0.011% Mo, 0.013% Ni and the remainder iron were used for weight loss measurements. For electrochemical methods, a mild steel rod of same composition with an exposed area of 0.785 cm² was used. The specimens were polished with 1/0, 2/0, 3/0 and 4/0 grades of emery sheets and degreased with trichloroethylene and dried using a drier. The plates were kept in a desiccator to avoid the absorption of moisture.

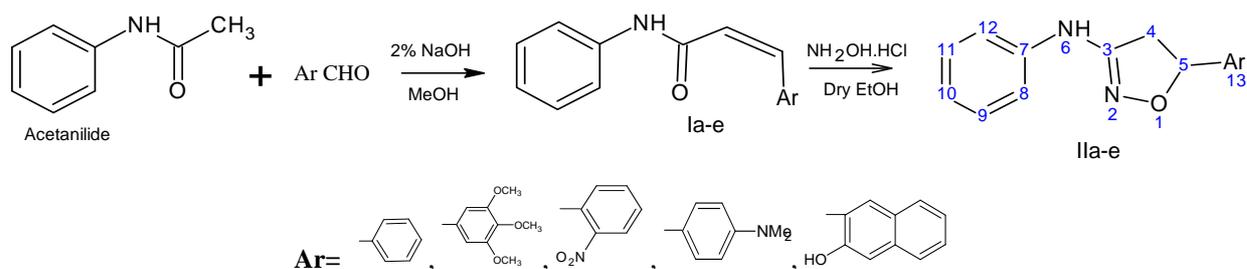
Synthesis of Inhibitors

- **Synthesis of Chalcones (I_{a-e})**

Chalcones were prepared by reacting a mixture of acetanilide (0.05mol), aromatic aldehyde (0.05mol), aqueous sodium hydroxide (10%, 5ml) and methanol (50ml). The reaction mixture was stirred for 10 hours at room temperature using magnetic stirrer. Then, it was refluxed for further 6 hrs on a water bath. After completion of the reaction an excess of solvent was removed by distillation and the resultant viscous mass was poured into ice water (100ml) with vigorous stirring and left overnight for complete precipitation. The resultant solid product was filtered, washed with cold water, dried and recrystallized from ethanol.¹⁰

Synthesis of Isoxazolines (II_{a-e})

Isoxazolines were prepared by reacting a mixture of purified chalcones (0.01mol), hydroxylamine hydrochloride (0.01mol) and a solution of sodium hydroxide (0.01mol) in dry ethanol (50ml) by refluxing for 6 hrs on a water bath. After completion of the reaction, an excess of the solvent was removed by distillation and the resultant mass was poured into ice water (100ml) with vigorous stirring. It was cooled overnight. The resultant solid product was filtered, washed with sufficient cold water, dried and purified by recrystallization from acetone.¹⁰ (**Scheme 1**)



Scheme-1

3-Phenylamino-5-Phenylisoxazoline (ISO 1) II_a: Yield: 92%, Colour: dirty white, IR Spectrum (γ/cm^{-1}): 3276.35 (NH); 1588.44 (C=N); 1733.26 (C=O); 1207.07 (C-N); 1312.11 (C-O-N str); 1455.71 and 1490 (Aromatic $>\text{C}=\text{C}<$ str)

3-Phenylamino-5-(3',4',5'-Trimethoxyphenyl)Isoxazoline (ISO 2): Yield: 85%, Colour: grey, IR Spectrum (γ/cm^{-1}): 3298.42 (NH); 1597.13 (C=N); 1746.62 (C=O); 1219.06 (C-N); 1327.08 (C-O-N str); 1445.71 and 1500 (Aromatic $>\text{C}=\text{C}<$ str)

3-Phenylamino-5-(2'-Nitrophenyl)Isoxazoline (ISO 3) : Yield: 82% Colour: brown, IR Spectrum (γ/cm^{-1}): 3328.14 (NH); 1600.13 (C=N); 1737.14 (C=O); 1235.86 (C-N); 1336.38 (C-O-N str); 1429.13 and 1486.96 (Aromatic $>\text{C}=\text{C}<$ str)

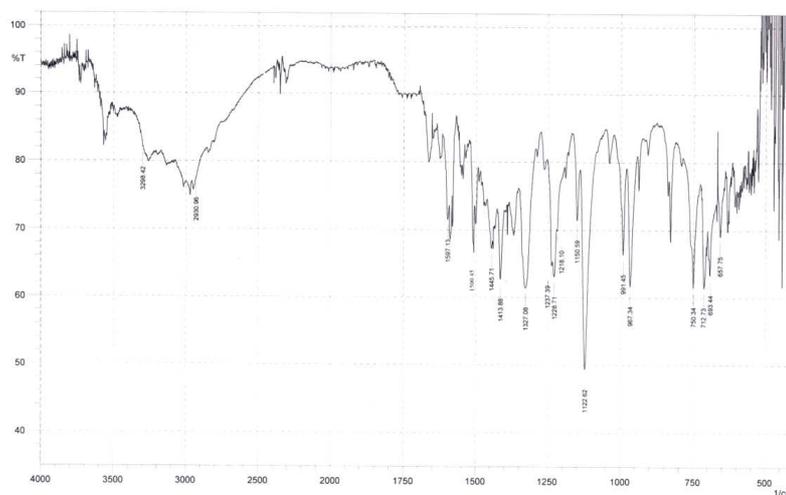


Figure 1

3-Phenylamino-5-(4'-Dimethylaminophenyl)Isoxazoline (ISO 4): Yield: 83%, Colour: yellow, IR Spectrum (γ/cm^{-1}): 3810.86 (NH); 1589.94 (C=N); 1738 (C=O); 1223.25 (C-N); 1320.33 (C-O-N str); 1432.22 and 1501.26 (Aromatic $>\text{C}=\text{C}<$ str)

3-Phenylamino-5-(2'-Hydroxynaphthyl)Isoxazoline (ISO 5): Yield: 80%, Colour: yellow, IR Spectrum (γ/cm^{-1}): 3279.77 (NH); 1579.73 (C=N); 1720.27 (C=O); 1209.25 (C-N); 1317.15(C-O-N str); 1454.36 and 1519.38 (Aromatic $>\text{C}=\text{C}<$ str)

Non-Electrochemical Measurements

Weight Loss Method

The simplest and most accurate method for estimating the corrosion rate is weight loss analysis.

The initial weight of the polished specimen was taken. The solutions were taken in 100ml beakers and the specimens were suspended in triplicate into the solution using glass hooks. Care was taken to ensure the complete immersion of the specimen. After a period of three hours, the mild steel samples were taken out, washed with distilled water, dried and weighed to the accuracy of four decimals. From the initial and final mass of the specimen, (i. e before and after immersion in the solution) the loss in weight was calculated. The experiment was repeated for various concentrations of the isoxazolines (ISO 1- ISO 5).

The inhibition efficiency, corrosion rate and surface coverage were calculated from the weight loss results using the formulas,

$$\text{Inhibition efficiency (\%)} = \frac{W_b - W_i}{W_b} \times 100$$

where, W_b = Weight loss without inhibitor; W_i = Weight loss with inhibitor.

$$\text{Corrosion Rate (mpy)} = \frac{534 \times \text{Weight loss in g}}{\text{Density} \times \text{Area (cm}^2\text{)} \times \text{Time in hrs}}$$

$$\text{Surface Coverage } (\theta) = \frac{W_b - W_i}{W_b}$$

Where, W_b = Weight loss without inhibitor; W_i = Weight loss with inhibitor.

In order to investigate the effect of temperature on the inhibitor performance, the above procedure was carried out in the different temperature range i.e., 303K-333K with one hour immersion time, using a thermostat, with the inhibitor concentration of 10mM.

Activation energy (E_a), Free energy of adsorption (ΔG^0), Enthalpy and Entropy (ΔH^0 & ΔS^0) were calculated using the formula,

- $E_a = 2.303 \times 8.314 \times \text{Slope (J)}$

- $K = \frac{1}{55.5} \exp \left[\frac{\Delta G_{ads}^0}{RT} \right]$

$$K = \frac{\theta}{C(1 - \theta)} \quad [\text{From Langmuir Eqn}]$$

Where, θ = Surface coverage of the inhibitor; C = Concentration of the inhibitor in mM/100ml.

Therefore, $\Delta G_{ads}^0 = -RT \ln(55.5K)$

- $\log \left(\frac{CR}{T} \right) = \log \left(\frac{R}{Nh} \right) + \frac{\Delta S_{ads}^0}{2.303R} - \frac{\Delta H_{ads}^0}{2.303RT}$

Where R is the gas constant, T is the temperature, N is the Avogadro's number and h is the Planck's constant. A plot of $\log(CR/T)$ versus $1/T$ should produce a straight line with slope and intercept equal to $\frac{\Delta H_{ads}^0}{2.303R}$ and $\log \left(\frac{R}{Nh} \right) + \frac{\Delta S_{ads}^0}{2.303R}$ respectively.

Atomic Absorption Spectrophotometric Studies

The weight loss can also be determined by the amount of metal dissolved in the solution using atomic absorption spectroscopy (AAS)

Atomic Absorption Spectrophotometer (model GBC 908, Australia) was used for estimating the amount of dissolved iron in the corrodent solution containing various concentrations of inhibitors in 1M H_2SO_4 after exposing the mild steel specimens for 3 hrs. From the amount of dissolved iron, the inhibition efficiency was calculated.

$$\text{Inhibitor efficiency (\%)} = \frac{B - A}{B} \times 100$$

where A and B are the amount of dissolved iron in presence and absence of inhibitor.

Electrochemical Techniques

The electrochemical impedance measurements were carried out for mild steel in acidic media using computer controlled potentiostat. (IVIUMCompactstat Potentiostat/Galvanostat). After immersion of the specimen prior to the impedance measurement, a stabilization period of 30 minutes was observed for E_{oc} to attain a stable value. The impedance measurements were made at corrosion potentials over a frequency range of 10 KHz to 0.01Hz with a signal amplitude of 10mV.

The real part (Z') and the imaginary part (Z'') were measured at various frequencies. A plot of Z' Vs Z'' were made. From the plot, the charge transfer resistance (R_t) and double layer capacitance (C_{dl}) were calculated.

Where, $R_{t(inh)}$ = charge transfer resistance in the presence of inhibitor; $R_{t(blank)}$ = charge transfer resistance in the absence of inhibitor.

Polarization measurements were made after EIS studies in the same cell set up for a potential range of -200 mV to +200 mV with respect to open circuit potential at a sweep rate of 1mV/sec. From the plot, the inhibition efficiency, Tafel slopes corrosion potentials and corrosion current were calculated using IVIUM software.

$$\text{Inhibition Efficiency (\%)} = \frac{I_{corr(blank)} - I_{corr(inh)}}{I_{corr(blank)}} \times 100$$

Where $I_{corr(blank)}$ and $I_{corr(inh)}$ are the corrosion current density values without and with inhibitors respectively.

Surface Morphology

Scanning Electron Microscope-Energy Dispersive X-Ray Spectroscopy (SEM-EDX)

Scanning electron microscopy (SEM) was used to study the surface morphology of the mild steel specimen. The surface morphology of the samples, after 3 hour immersion in 1M H_2SO_4 solutions in presence of selected concentration of various inhibitors studied, was performed on Medzer biomedical research microscope.

Surface Examination Study

Mild steel specimens were immersed in selected concentrations of the inhibitors for duration of 3 hours. After 3 hours, the specimens were taken out and dried. The surface of the metal specimen was analyzed by Fourier transform infrared spectra using FTIR-Affinity (Shimadzu).

RESULTS AND DISCUSSIONS

Non-Electrochemical Methods

Weight Loss Measurements

The gravimetric method is probably the most widely used method of inhibition assessment. The simplicity and reliability of the measurements offered by weight loss method is such that the technique forms the baseline method of measurement in many corrosion monitoring programmes.

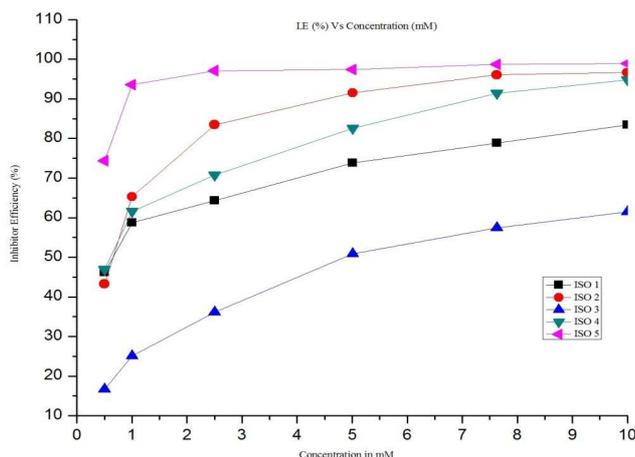


Figure 2: Plot of Inhibition Efficiency (%) Vs Concentration (mM) for the Inhibition of Corrosion of Mild Steel in 1M H₂SO₄

Weight loss measurements were carried out at $\pm 30^{\circ}\text{C}$ for different concentrations (0.5-10mM) of isoxazolines after immersion in 1M H₂SO₄ for 3 hours. From the weight loss, the inhibition efficiency (IE), corrosion rate and surface coverage (θ) were calculated and the results are presented in **Table 2** and depicted in **Figure 2**. The values in **Table 2** reveal that the isoxazolines efficiently inhibit the corrosion of mild steel in 1M H₂SO₄.

The corrosion rate decreased considerably with an increase in concentration of inhibitor. This is due to the presence of heteroatoms like nitrogen, oxygen and aromatic rings. The extent of inhibition depends upon the nature and mode of adsorption of inhibitors on the metal surface. The adsorption is assumed to be a quasi-substitution process between water molecules on the surface and the inhibitor.

The isoxazolines are adsorbed on the metal surface by flat orientation. Increase in percentage inhibition efficiency with an increase in the concentration of the inhibitors, suggest that the number of molecules adsorbed increased over the mild steel surface blocking the active sites of acid attack and thereby protecting the metal from corrosion. At highest concentration of 10mM of isoxazolines, the % IE attained was above 90% which confirmed that isoxazolines were very effective inhibitors. The high percentage inhibition efficiency of isoxazolines may be attributed to the presence of a number of anchoring sites namely $-\text{NH}$, lone pair of electrons on N, O and the π bonds of the benzene and isoxazoline rings.

Table 1: Inhibition Efficiencies of Various Concentrations of Inhibitors for the Corrosion of Mild Steel in 1M H₂SO₄ Obtained by Weight Loss Measurements at $30\pm 1^{\circ}\text{C}$

Name of the Inhibitor	Concentration (mM)	Weight Loss (g)	Inhibition Efficiency (%)	Corrosion Rate (mpy)	Surface Coverage (θ)
Blank	-	0.2059	-	13.34	-
ISO 1	0.5	0.1108	46.18	7.18	0.4618
	1	0.0745	63.81	4.83	0.6381
	2.5	0.0734	64.35	4.76	0.6435
	5	0.0538	73.87	3.49	0.7387
	7.5	0.0436	78.83	2.89	0.7883
10	0.0342	83.39	83.39	2.22	0.8339
ISO 2	0.5	0.1168	43.27	7.57	0.4327
	1	0.0714	65.32	4.63	0.6532
	2.5	0.0546	73.48	3.54	0.7348

	5	0.0175	91.50	1.13	0.9150
	7.5	0.0081	96.06	0.52	0.9606
	10	0.0069	96.64	0.45	0.9664
ISO 3	0.5	0.1716	16.65	11.12	0.1665
	1	0.1528	25.78	9.90	0.2578
	2.5	0.1315	36.13	8.52	0.3613
	5	0.1011	50.89	6.55	0.5089
	7.5	0.0877	57.40	5.68	0.5740
	10	0.0669	67.50	4.33	0.6750
ISO 4	0.5	0.1558	46.52	10.09	0.4652
	1	0.0903	56.14	5.85	0.6487
	2.5	0.0723	64.87	4.68	0.5614
	5	0.0359	82.56	2.33	0.8256
	7.5	0.0177	91.40	1.15	0.9140
	10	0.0108	94.75	0.70	0.9475
ISO 5	0.5	0.0327	74.40	2.12	0.7440
	1	0.0246	88.05	1.59	0.8805
	2.5	0.0059	97.13	0.38	0.9713
	5	0.0033	98.39	0.21	0.9839
	7.5	0.0027	98.68	0.17	0.9868
	10	0.0022	98.93	0.14	0.9893

Effect of Temperature

The effect of temperature on the corrosion of mild steel in the presence and absence of inhibitors (ISO1-ISO5) at 10mM concentration in 1M H₂SO₄ was studied by weight loss method. The values of inhibition efficiency and corrosion rate are presented in **Table 3**. The inhibition efficiency decreased with increase in temperature.

Table 2: Inhibition Efficiencies at 10mM Concentration of Inhibitors for the Corrosion of Mild Steel in 1M H₂SO₄ obtained by Weight Loss Measurements at Higher Temperature

Name of the Inhibitor	Temperature (K)	Weight Loss (g)	Inhibition Efficiency (%)	Corrosion Rate (g/cm/hr)	Surface Coverage (θ)
ISO 1	303	0.0190	72.30	3.69	0.7230
	313	0.0741	56.36	14.40	0.5636
	323	0.1335	52.65	25.95	0.5265
	333	0.2519	35.85	48.96	0.3585
ISO 2	303	0.0038	94.46	0.74	0.9446
	313	0.0154	90.93	2.99	0.9093
	323	0.0524	81.41	10.18	0.8141
	333	0.1415	63.96	27.50	0.6396
ISO 3	303	0.0023	96.64	0.45	0.9664
	313	0.0063	96.28	1.22	0.9628
	323	0.0138	95.10	2.68	0.9510
	333	0.0761	80.62	14.79	0.8062
ISO 4	303	0.0114	83.38	2.22	0.8338
	313	0.0312	81.62	6.06	0.8162
	323	0.0626	77.80	12.17	0.7780
	333	0.1216	69.03	23.63	0.6903
ISO 5	303	0.0030	95.62	0.58	0.9562
	313	0.0211	87.57	4.10	0.8757
	323	0.0784	72.19	15.24	0.7219
	333	0.2492	36.54	48.43	0.3654

The temperature increases the rate of all electrochemical processes and influences adsorption equilibrium and kinetics as well. Weight loss increases with temperature in the absence and presence of inhibitor. Adsorption and desorption of inhibitor molecules continuously occur at the metal surface and an equilibrium exists between two processes at a particular temperature. With increase of temperature, the equilibrium between the adsorption and desorption processes

is shifted to a higher desorption rate than adsorption until equilibrium is again established at a different value of equilibrium constant. This explains the lower inhibition efficiency at higher temperature.

The relationship between the corrosion rate (CR) of mild steel and temperature can be expressed by Arrhenius equation

$$C_R = K \exp\left(\frac{-E_a}{RT}\right) \quad 1$$

Where E_a is the the activation energy, R is the universal gas constant, K is the pre-exponential constant and T is the absolute temperature. Using equation 1 and from a plot of $\log C_R$ Vs $1000/T$ **Figure 4** the values of E_a and K at 10mM concentration of the isoxazolines were computed from slopes and intercepts respectively and the values are given in **Table 4**

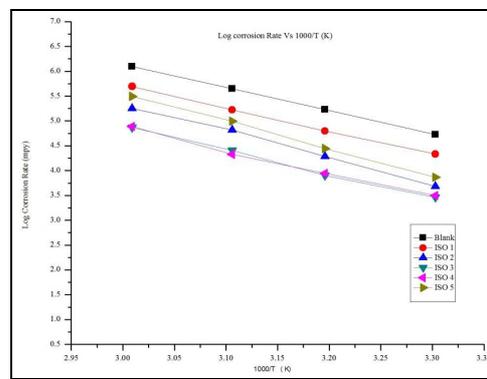


Figure 3: Arrhenius Plot of Corrosion Rate of Mild Steel in 1M H₂SO₄ Solution in Absence and Presence of Inhibitors

From **Table 4** it is evident that the inhibitive additives cause a rise in activation energy value when compared to the blank solution. The increase of E_a decelerated the corrosion rate of steel. The large increase in the activation energy of the corrosion process in the presence of the inhibitor may be attributed to the slow rate of inhibitor adsorption on the metal surface at higher temperature as reported by Hoar and Holliday.¹²

But, Riggs and Hurd¹³ explained that, the increase in the activation energy of corrosion at higher levels of inhibition arises from a shift of the net corrosion reaction from that on the uncovered part on the metal surface to the covered one. Schmid and Huang¹⁴ and Hegazy¹⁵ found that, the organic molecules inhibit both the anodic and cathodic partial reactions on the electrode surface and a parallel reaction takes place on the covered area, but the reaction rate on the covered area is substantially less than on the uncovered area. This is in agreement with the results of this work as represented in **Table 4**.

The values of enthalpy of activation ΔH° and entropy of activation ΔS° were obtained from the transition state equation [16].

$$C_R = \frac{RT}{Nh} \exp\left(\frac{\Delta S^\circ}{R}\right) \exp\left(-\frac{\Delta H^\circ}{RT}\right) \quad 2$$

Where h is the Planck's constant, N is the Avogadro number, R is the universal gas constant, T is the absolute temperature, ΔH° is the enthalpy of activation and ΔS° is the entropy of activation. A plot of $\log C_R/T$ as a function of $1000/T$ (Figure 4) was made for mild steel corrosion in 1M H_2SO_4 in the presence and absence of isoxazolines. Straight lines were obtained with slope $\Delta H^\circ/2.303R$ and intercept $[\log(R/Nh) + (\Delta S^\circ/2.303R)]$ from which the values of ΔH° and ΔS° were computed and listed in Table 4. Examination of these data reveals that the ΔH° values for dissolution reaction of mild steel in 1M H_2SO_4 in the presence of the inhibitors are higher (67-120 kJ/mole) than that in the blank (42 kJ/mole).

Table 3: Kinetics/Thermodynamic Parameters of Mild Steel Corrosion in 1M H_2SO_4

Name of the Inhibitor	E_a (KJ)	ΔH° kJ/mole	ΔS° kJ/mole	ΔG_{ads}° at Various Temperatures (KJ)			
				303	313	323	333
BLANK	62.61	-45.81	-0.87	-	-	-	-
ISO 1	81.18	-67.70	-0.81	-6.73	-5.12	-4.88	-3.12
ISO 2	101.47	-98.84	-0.72	-11.46	-10.45	-8.56	-6.33
ISO 3	94.20	-91.59	-0.75	-12.77	-12.90	-12.56	-8.69
ISO 4	65.29	-62.93	-0.83	-8.38	-8.33	-7.96	-6.96
ISO 5	122.15	-119.97	-0.65	-12.08	-9.54	-7.16	-3.21

The negative values of ΔH_{ads}° mean that the dissolution process in an exothermic process.¹⁷ The exothermic process is attributed to either physical or chemical adsorption or mixture of both,¹⁸ whereas endothermic process corresponds to chemisorption.¹⁹ In an exothermic process, physisorption is distinguished from chemisorption by considering the absolute value of ΔH_{ads}° . For physisorption process the value of ΔH_{ads}° is lower than 40KJ/mole. while for that of chemisorption it approaches 100kJ/mole.²⁰ In the present study ΔH_{ads}° is greater than 40KJ/mole which confirms that chemisorption is favoured.

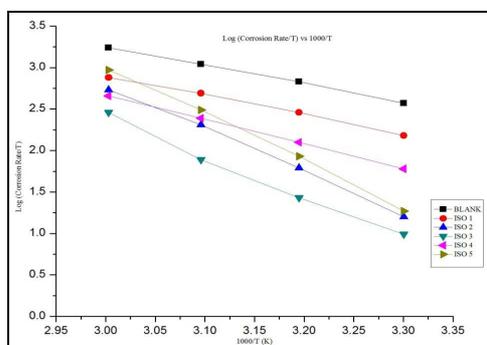


Figure 4: Arrhenius Plot of Log(Corrosion Rate/T) vs 1000/T

The negative values of ΔS_{ads}° implies that the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex.²¹ The negative values of standard free energy of adsorption ΔG_{ads}° confirms the spontaneity of the adsorption process. in 1M H_2SO_4 solution in absence and presence of inhibitors.

Generally, values of ΔG_{ads}° upto -20 kJ/mol are consistent with physisorption while around -40 kJ/mol or more is associated with chemisorption.²² In the present study ΔG_{ads}° values are below -20kJ/mole confirming physisorption. But ΔH° values confirm chemisorption. This indicates that adsorption of the inhibitors is neither physisorption or chemisorption but it is a complex mixed type.

Adsorption Isotherm

Adsorption isotherms are very important in determining the mechanism of organoelectrochemical reaction.²³ The most frequently used isotherms are Langmuir, Frumkin, Hull de-Boer, Parsons Temkin, Flory Huggin, Freundlich, Dhar-Flory-Huggin, kinetic/thermodynamic model of El-Awady et al., and Bockris Swinkels. All these isotherms are of the general form

$$f(Q, x) \exp(-2\alpha Q) = k_{ads} c \quad 3$$

Where $f(Q, x)$ is the configurational factor which depends upon the physical model and the assumptions underlying the derivation of the isotherm, Q the surface coverage, C the inhibitor concentration in the electrolyte, x the size factor ratio, a the molecular interaction factor and k the equilibrium constant of the adsorption process. In this work, Langmuir adsorption isotherm was found to be suitable for the experimental findings. The isotherm is described by the following equation.

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad 4$$

$$\text{With } K_{ads} = \frac{1}{55.5} \exp\left(-\frac{\Delta G_{ads}^0}{RT}\right) \quad 5$$

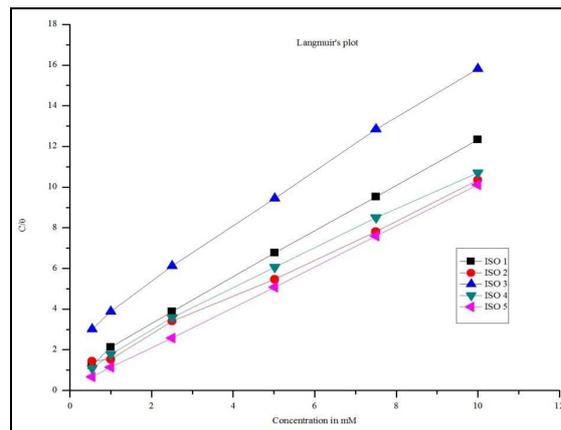


Figure 5: Langmuir Plot of Inhibitors in 1M H₂SO₄

Where 'C' is the inhibitor concentration, K_{ads} is the adsorption equilibrium constant and ΔG_{ads}^0 is the standard free energy of adsorption. Though the plot of C/θ versus C is linear (Figure 5), the deviation of the slopes from unity (for ideal Langmuir Isotherm) can be attributed to the molecular interaction among the adsorbed inhibitor species, a factor which was not taken into consideration during the derivation of the Langmuir equation. The fit of the experimental data to this isotherm provides evidence for the role of adsorption in the inhibitive effect of isoxazolines.

Atomic Absorption Spectrophotometric Studies

The amount of iron dissolved in the presence of isoxazolines when mild steel specimens were exposed to 1M H₂SO₄ were calculated and presented in Table 6. It has been found that the amount of dissolved iron in the corrodent solution decreases with increase in concentration of the inhibitors and there is good agreement between values of percentage inhibition efficiency calculated from weight loss and AAS technique.

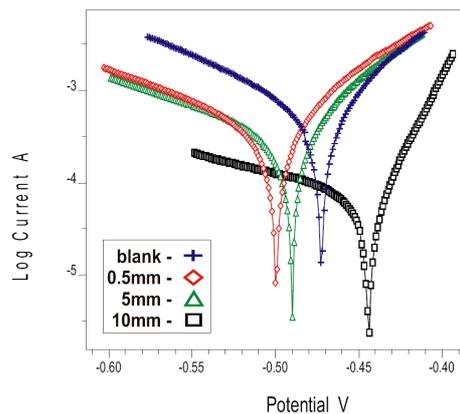
Table: 4 Amount of Dissolved Iron Present in the Corrosive Solution with and without Inhibitors in 1M H₂SO₄ Measured Using Atomic Absorption Spectroscopy

Name of the Inhibitor	Inhibitor Concentration	Amount of Iron Content (mg/l)	Inhibition Efficiency (%)
Blank	-	1304.96	-
ISO 2	0.5	776.3	40.55
	10	129.5	90.07
ISO 5	0.5	364.6	72.06
	10	93.57	92.82

Electrochemical Measurements

Potentiodynamic Polarization Curves

The polarization behaviour of mild steel in 1M H₂SO₄ containing different concentrations of isoxazoline (ISO 5) are shown in **Figure 6**. Electrochemical parameters extracted from these curves are given in **Table 7**. From the figures it is clear that the values of (I_{corr}) of mild steel in the inhibited solution were smaller than those for the inhibitor-free solution. The addition of the isoxazolines induce a decrease in both cathodic and anodic currents confirming that the addition of the isoxazolines have hindered the acid attack on the steel electrode.

**Figure 6: Polarization Curve for Mild Steel Recorded in 1M H₂SO₄ for Selected Concentrations of Inhibitor (ISO 5)**

Further inspection of the figures reveal that in the cathodic range, the cathodic current density is less sensitive to isoxazolines, while in the anodic range, a significant decrease in the anodic current densities lead to a shift of the corrosion potential (E_{corr}) toward more positive direction.²⁴ Hence it can be concluded that these inhibitors are mixed type but dominantly act as anodic inhibitors for mild steel in 1M H₂SO₄. The above results are further confirmed by the change in both cathodic and anodic Tafel slope values (b_c & b_a) relative to blank.

Table 5: Corrosion Parameters for Mild Steel with Selected Concentrations of the Inhibitors in 1M H₂SO₄ by Potentiodynamic Polarization Method

Name of the Inhibitor	Inhibitor Concentration (mM)	Tafel Slopes (mV/decade)		E_{corr} (mV)	I_{corr} (μ A/cm ²)	Inhibition Efficiency (%)
		b_a	b_c			
Blank		52	112	-467.4	1567	-
ISO 1	0.5	31	121	-480.2	623.0	60.24
	5	44	147	-472.0	549.7	64.92
	10	45	155	-451.2	384.4	75.46

ISO 2	0.5	57	120	-483.5	407.4	74
	5	53	127	-477.8	328.2	79.05
	10	40	144	-462.3	230.7	85.27
ISO 3	0.5	57	120	-491.3	675.5	56.89
	5	56	125	-489.1	561.8	64.14
	10	48	140	-475.2	447.5	71.44
ISO 4	0.5	52	114	-481	437.2	72.09
	5	41	129	-463.8	345.5	77.95
	10	39	165	-457.9	332.5	78.78
ISO 5	0.5	75	131	-502.7	416	73.45
	5	64	153	-491.4	360.4	77
	10	28	232	-437.1	85.9	94.5

Electrochemical Impedance Spectroscopy (EIS) Measurements

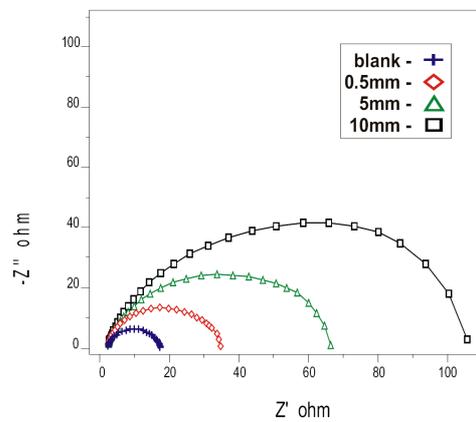


Figure 7: Nyquist Diagram for Mild Steel in 1M H₂SO₄ for Selected Concentrations of Inhibitor (ISO 5)

Nyquist plots of the isoxazoline (ISO 5) in 1M H₂SO₄ in the absence and presence of various concentrations are given in **Figure 7**. The impedance spectra shows a single semicircle and the diameter of the semicircle increases with increasing inhibitor concentration. The impedance spectra consist of one capacitive loop at high frequency which is attributed to charge transfer of the corrosion process.²⁵ Various parameters such as charge transfer resistance (R_{ct}), double layer capacitance (C_{dl}) and inhibition efficiency obtained from impedance measurements are shown in **Table 8**. R_{ct} values were calculated from the difference in impedance at lower and higher frequencies as suggested by Tsuru et al.,²⁶ C_{dl} values were calculated from the frequency at which the imaginary component of impedance was maximum (f_{max}) using the reaction

$$C_{dl} = \frac{1}{2\pi f_{max} R_{ct}}$$

The R_{ct} values increased and C_{dl} values decreased with concentration. The decrease in C_{dl} values indicate that the inhibitors function by adsorption at the metal/solution interface by gradual displacement of water molecules leading to a protective film.

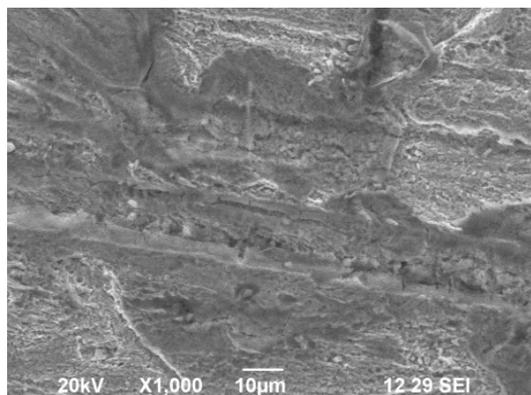
The decrease in C_{dl} may be due to in local dielectric constant and/or an increase in the protective layer thickness at the electrode interface.²⁷

Table 6: A. C.-Impedance Parameters for Mild Steel for Selected Concentrations of the Inhibitors in 1M H₂SO₄

Name of the Inhibitor	Inhibitor Concentration (mM)	R _t (ohm cm ²)	C _{dl} (μ F cm ⁻²)	Inhibition Efficiency(%)
BLANK		11.06	27.8	-
ISO 1	0.5	22.6	22.7	51.06
	5	24.31	p22.5	54.5
	10	37.19	21.9	70.26
ISO 2	0.5	34.16	32.4	67.62
	5	50.31	31.7	78.01
	10	67.54	27.1	83.62
ISO 3	0.5	17.01	35.9	34.97
	5	21.50	35.2	48.55
	10	32.67	33.8	66.14
ISO 4	0.5	34.77	30.7	68.19
	5	49.21	28.6	77.52
	10	59.31	33.3	81.35
ISO 5	0.5	26.26	22.7	57.88
	5	51.55	20.5	78.54
	10	80.34	15.2	86.23

Scanning Electron Microscope-Energy Dispersive X-Ray Spectroscopy (SEM-EDX)

Figure 8-9 shows the SEM micrographs of different slides of mild steel after immersion in the aqueous solution in the absence and presence of inhibitors (ISO 5). The exposure of mild steel sample to 1M H₂SO₄ for 3 hours results in an aggressive attack of the corroding medium on the mild steel surface, strongly damaging the surface **Figure 8**. SEM image of inhibited mild steel specimen **Figure 9** reveals that a good protective adsorbed film is formed on the specimen surface which suppresses the rate of corrosion being responsible for the inhibition.

**Figure 8: (Blank)****Figure 9: (ISO 5)****Figure 8 & 9: Scanning Electron Microscopy Photographs in the Absence and Presence of Inhibitors**

The EDX spectra were used to determine the elements present on the surface of mild steel in the uninhibited and inhibited 1M H₂SO₄. The EDX analysis of uninhibited mild steel plate indicate the presence of only Fe and oxygen confirming that passive film on the mild steel surface contained only Fe₂O₃. **Figure 10 & Figure 11** portrays the EDX analysis of mild steel in 1M H₂SO₄ in the presence of isoxazoline (ISO 5). This EDX spectra shows additional lines due to C, O and N. This spectra confirms the presence of the isoxazolines molecules on mild steel surface.²⁸ A comparable elemental distribution is shown in **Table 11**.

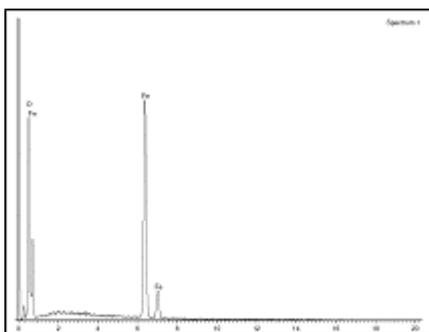


Figure 10: EDX Analysis for Mild Steel in 1M H₂SO₄ in Absence of Inhibitor

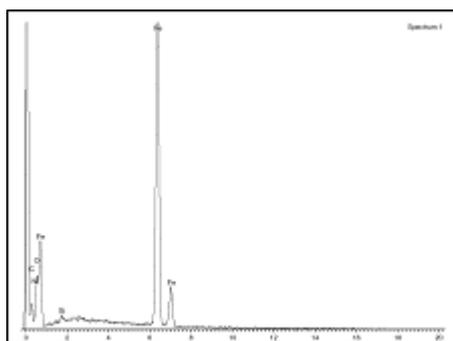


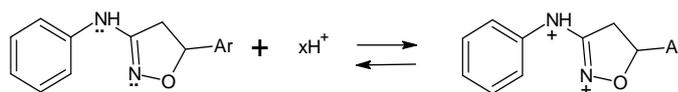
Figure 11: EDX Analysis for Mild Steel in 1M H₂SO₄ in Presence of Inhibitor (ISO 5)

Table 7: Surface Compositions (Weight %) of Mild Steel after 3 Hours of Immersion in 1M without and with the Optimum Concentrations of the Studied Inhibitors

(Mass %)	Fe	C	N	O	Si
Blank	66.20	-	-	33.80	-
ISO 5	58.56	15.91	10.08	15.02	0.43

Mechanism of Inhibition by Isoxazolines

In the present work, isoxazolines contain two nitrogen atoms which can be protonated in an acid medium. Thus they become cations, existing in equilibrium with the corresponding molecular form.



The protonated ion, could be attached to the mild steel surface by means of electrostatic interaction between SO_4^{2-} and the protonated isoxazolinium ion since mild steel surface has positive charge in H₂SO₄ medium.²⁹ explained

based on the assumption that in the presence of SO_4^{2-} , the negatively charged SO_4^{2-} would be attached to positively charged surface thereby the protonated ion may also get adsorbed onto the metal surface.

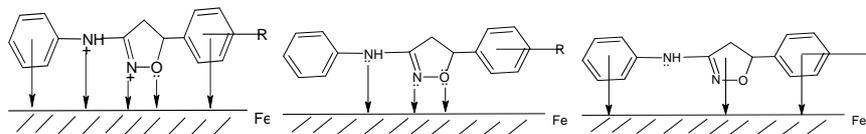


Figure 12

Figure 13

Figure 14

Figure 12, 13 & 14: Represent Schematic Diagram of Adsorption of Isoxazolines on Mild Steel Surface

FT-IR Studies

The mode of bonding of the isoxazolines to the mild steel surface was elucidated by comparing the IR spectra of the pure compounds with the IR spectra of the inhibited plates.

In the FTIR spectrum of the inhibited plates (ISO 2) (Figure 15) the band around $3200\text{--}3300\text{cm}^{-1}$ is attributed to N-H stretching vibrations have become weak (compared with the IR spectra of the isoxazolines) with reduced intensity which may be due to protonated NH group³⁰ and also confirming the adsorption of these compounds on mild steel surface via the protonated NH group.

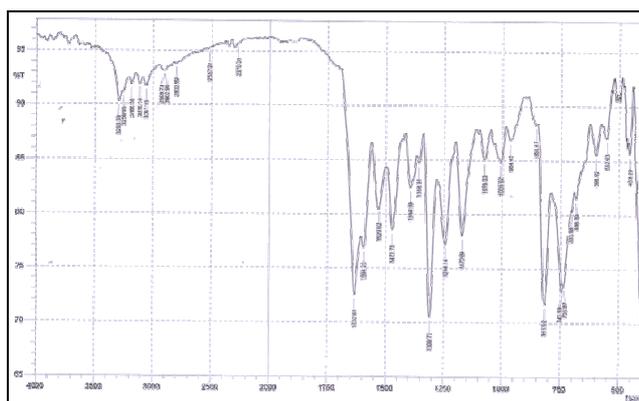


Figure 15: IR Spectrum of Mild Steel Plate Immersed in 1M H_2SO_4 Containing ISO 2

In comparison to the IR spectrum of the inhibitors, it is evident that the ν NH, ν C=N, ν C-O-N stretching frequency have shifted to a considerable extent confirming that these electron centers are involved in the sharing of electrons with the metal. Moreover the C=C stretching frequency of the aromatic ring have shifted drastically to the extent of $20\text{--}30\text{cm}^{-1}$ in comparison to the IR spectrum of inhibitors confirming the participation of the C=C in the adsorption process. Furthermore, the intensity of these stretching frequencies have decreased which implies that the isoxazolines are co-ordinated to Fe^{2+} resulting in the formation of a Fe^{2+} -inhibitor complex on the metal surface.³¹

Evaluation IE of Isoxazolines: Chemical Structure and Corrosion Inhibition of Fe

The inhibition efficiency of the isoxazolines follows the order



The inhibition efficiency of the investigated compounds depends on many factors, which include the number of adsorption active centres in the molecule and their charge density, molecular size, mode of adsorption, heat of hydrogenation and formation of metallic complexes.

ISO 5 has the highest percentage inhibition efficiency (98%). This may be due to the presence of a naphthyl ring. The -OH group in ortho position in the naphthyl ring is expected to form intramolecular hydrogen bond with lone pair of electrons on oxygen of isoxazoline ring leading to the less availability of lone pair of electron on oxygen for electrostatic interaction with metal due to ortho effect. In contradiction the high inhibition efficiency of ISO 5 indicates that -OH group is not in the same plane as naphthyl ring and does not make any contribution to adsorption. ISO 2 has almost equal IE of about 96% which may be attributed to the presence of three methoxy group (p-OCH₃, $\sigma = -0.27$) respectively. They are all electron donating groups with negative Hammett constant which enhance the electron density on the molecule. As the number of electron donating groups on the benzene ring increases percentage inhibition efficiency also increases.

ISO 4 is expected to show very high inhibition efficiency (Hammett constant $\sigma = -0.83$) but it is slightly less than expected. This may be due to the perpendicular orientation of -NMe₂ with respect to benzene ring thus preventing the exactly flat orientation of the molecule onto the mild steel surface. ISO 3 may be attributed to the strong electron withdrawing nature of the NO₂ group which reduces the electron density on the molecule and thereby result in a decrease in protection efficiency.

CONCLUSIONS

1. All the isoxazolines studied are found to perform well as a corrosion inhibitor in 1M H₂SO₄ and the inhibiting efficiency values of the examined isoxazolines follows the order:



2. The adsorption of the compounds on metal surface is found to obey Langmuir adsorption isotherm.
3. The inhibition efficiency obtained from the atomic absorption spectrophotometric studies was found to be in good agreement with that obtained from the conventional weight loss method.
4. The activation energy is higher for the inhibited acids than for uninhibited acids showing the temperature dependence of inhibition efficiency.
5. The negative values of standard free energy of adsorption ΔG_{ads}° confirm the spontaneity of the adsorption process.
6. Polarization studies showed that all the isoxazolines function as mixed inhibitors but predominantly act as anodic inhibitors.
7. SEM reveals the formation of a smooth, dense protective layer in presence of an effective inhibitor.

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