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Study of N-(3-chloro-2-phenyl)-4-oxozetiden-1-yl)-isonicotinamide as a corrosion inhibitor of mild steel in acidic environment

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This study investigates the efficacy of synthesized inhibitor, N-(3-chloro-2-phenyl)-4-oxozetiden-1-yl)-isonicotinamide (CPOI), in mitigating mild steel corrosion in a 15% HCl solution. Various methodologies, including weight loss measurements, potentiodynamic polarization, and electrochemical impedance spectroscopy have been employed to evaluate CPOI effectiveness. The results show a positive correlation between inhibitor concentration and corrosion inhibition efficiency, with Tafel plot analysis suggesting mixed-type inhibition. Additionally, the influences of temperature variation on corrosion rate and associated thermodynamic parameters have been examined. CPOI demonstrates significant proficiency as a mild steel corrosion inhibitor in acidic environments, attributed to its adsorption behaviour following Langmuir adsorption isotherm. Observations from atomic force microscopy and field emission scanning electron microscopy confirm the presence of adsorbed protective film on mild steel surfaces.

Keywords: Acidic environment, Corrosion inhibitor, Isonicotinamide, Mild steel, Polarization

Introduction

Acidic solutions find extensive use in diverse industrial applications, such as acidifying oil wells, pickling with acids, and carrying out acidic cleaning procedures[1]. The use of acid solutions often leads to substantial corrosion of metals. Stimulating oil production through acidification of petroleum wells is a highly significant technique. Employing chemical inhibitors to counteract the corrosive conditions is a practical and cost-effective preventive care approach for minimizing and managing corrosion in pipelines, vessels, and other equipment[2,3]. It is required to effectively cover the surface with either an organic or inorganic inhibitor material to manage metal corrosion. This protective layer acts as a barrier, physically separating the metal from the corrosive environment[4, 5]. Based on the findings mentioned in reports[6, 7], it has been observed that 3-nitroacetophenone (3-NA) and 4-aminoacetophenonepyridine 2-aldehyde (4AAPA) demonstrate corrosion inhibition properties on mild steel when exposed to a 1 N hydrochloric acid (HCl) solution. Heterocyclic organic compounds with distinctive molecular structures, encompassing elements such as sulphur, phosphorus, oxygen, nitrogen, and aromatic rings, exhibit exceptional effectiveness and efficiency as metal inhibitors in acidic environments[8–10]. Because of their utilization in various industries, a wide array of organic compounds containing hetero atoms have been synthesized or chosen specifically as inhibitors[11]. The scientific literature extensively documents the corrosion inhibition achieved through the utilization of heterocyclic compounds containing nitrogen[12–16]. Heterocyclic compounds that incorporate both nitrogen and sulfur as opposed to compounds containing solely nitrogen or sulfur have shown to be more commonly superior inhibitors of corrosion[17–21]. Moreover, numerous preventive strategies have been implemented, and among them, the use of organic compounds containing nitrogen, oxygen, and sulfur has become widely adopted[22–26]. These compounds have the ability to either establish robust coordination bonds with metal atoms or generate inert surface films[27]. The adsorption characteristics of inhibitor molecules are influenced by factors such as the surface condition and the presence of an excessive charge on the metal surface[28].

The aim of the present work is to study of the corrosion inhibition performance of various concentrations of N-(3-chloro-2-phenyl)-4-oxozetiden-1-yl)-isonicotinamide (CPOI) on mild steel in 15% hydrochloric acid (HCl) solution. To evaluate the effectiveness of different concentrations of the compound in mitigating mild steel corrosion, an investigation was conducted using weight loss measurements, electrochemical techniques, AFM and FE-SEM. The study aimed to determine the inhibitory capabilities of these compounds and delve into the mechanism underlying the interaction between the inhibitor molecules and the mild steel surface.

Experimental Section

Mild steel samples

The corrosion experiments involved mild steel samples obtained from the Research & Development Centre for Iron and Steel, Steel Authority of India Limited, Ranchi and the composition is shown in Table 1.

To conduct weight loss measurements, the mild steel coupons were mechanically cut into dimensions of 6.0 cm × 2.5 cm × 0.1 cm, while for electrochemical measurements, they were cut into dimensions of 1.5 cm × 1.5 cm × 0.1 cm. The working electrode (WE) had an exposed surface area of 0.785 cm^2. To prepare the specimens, emery papers with various grain sizes up to 1200 grit were used, followed by polishing with Al_2O_3 particles (initially 1 µm, then 0.3 µm in particle size). Afterwards, the electrodes were cleaned under a thorough cleaning process using distilled water and acetone. They were carefully dried and then placed in desiccators to ensure their preservation and safeguard against any potential contaminants.

Table 1 — Composition of mild steel

Sample	wt (%)						
	C	Mn	Si	S	Pb	Cr	Fe
Mild Steel	0.14	0.98	0.033	0.018	0.026	0.02	Balance

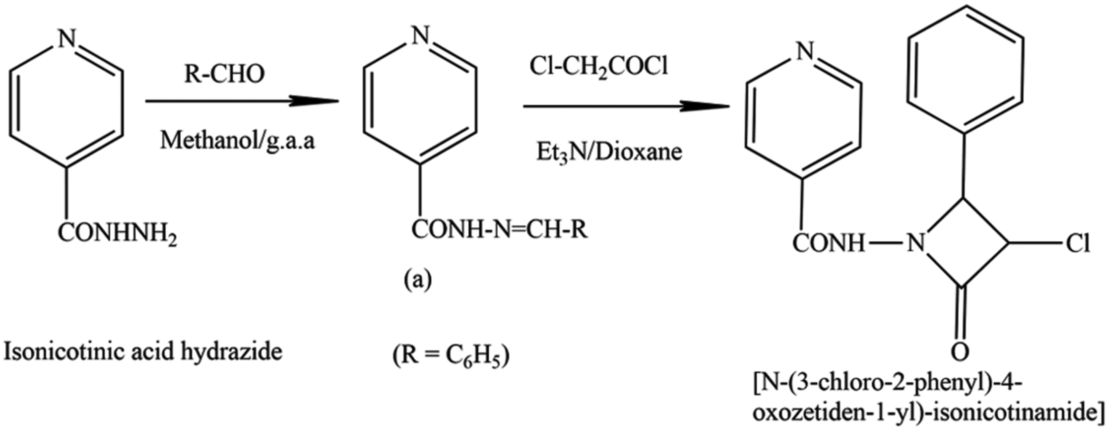
Test Solution

To create the electrolytic solutions, double-distilled water and analytical reagent-grade 37% hydrochloric acid (Ramkem) were utilized. The inhibitor concentration employed in the study ranged from 100 to 300 parts per million (ppm). To perform weight loss measurements and electrochemical studies, the electrolytic solution was employed in volumes of 500 mL and 250 mL, respectively, to ensure accurate data collection and analysis.

Synthesis of corrosion inhibitors

The synthesis of N-(3-chloro-2-phenyl)-4-oxozetiden-1-yl)-isonicotinamide (CPOI) is depicted in Scheme 1, following the reported procedure[29]. To begin the experiment, a methanol solution containing isonicotinic acid hydrazide (0.1 mol) and substituted benzaldehyde (0.1 mol) was prepared. A few drops of glacial acetic acid were added to the mixture, and the resulting solution was refluxed for 5-6 h using a water bath. After cooling, the liquid was poured onto crushed ice, and recrystallization was carried out employing methanol. The resulting product from this step was N'-benzylideneisonicotinohydrazide.

To synthesize CPOI, N'-benzylidene-isonicotinohydrazides (0.01 mol) in dioxane (20 mL) were added to a well-stirred mixture of chloroacetyl chloride (0.012 mol) and triethylamine (Et_3N) (0.012 mol) in dioxane (10 mL) at a temperature



Scheme 1 — Synthetic route of inhibitor CPOI range of 0-5 °C. The reaction mixture obtained was stirred for 8 h, left at room temperature for two days, and subsequently treated with cold water. The resulting solid was filtered, washed with water, and recrystallized from methanol. Thin layer chromatography (TLC) was used to check the purity of the synthesized compounds.

Weight loss studies

Metal coupons made of mild steel, measuring dimensions of 6.0 cm × 2.5 cm × 0.1 cm were placed in 15% HCl solution in the absence and presence of different inhibitor concentrations (100 to 300 ppm). The weight loss experiments were conducted in 500 mL of test solutions between temperatures of 303 K to 333 K, with the coupons fully immersed in the solution. After a six-hour immersion period, the mass of the metal coupons decreased. The purpose of this experiment was to assess the corrosion of the coupons by measuring the weight loss they experienced. The equations for calculating the corrosion rate (CR), surface coverage (θ), and inhibition efficiency (η) are expressed as follows[30, 31]:

$$\mathrm{CR}\left(\mathrm{mmy}^{-1}\right) = \frac{8.76 \times 10^4 \times W}{D \times A \times t} \quad \ldots(1)$$

where, A = area of mild steel (cm^2) in acidic solution, W = weight loss (g), t = exposure time (h), and D = density of mild steel (g cm^{-3})

$$\theta = \frac{\mathrm{CR_0}-\mathrm{CR_i}}{\mathrm{CR_0}} \quad \ldots(2)$$

$$\eta(\%) = \frac{\mathrm{CR_0}-\mathrm{CR_i}}{\mathrm{CR_0}} \times 100 \quad \ldots(3)$$

Where, $\mathrm{CR_0}$ denotes the corrosion rate without the presence of inhibitors, while $\mathrm{CR_i}$ represents the corrosion rate in the presence of inhibitors. The experiment was conducted multiple times at different temperatures (303 K, 313 K, 323 K, and 333 K) using a circulating water Ultra thermostat. The purpose was to investigate the impact of temperature on the inhibition efficiency and determine the temperature dependence of the inhibitors' effectiveness.

Potentiodynamic polarization (PP) studies

The Princeton Applied Research Versa STAT MC instrument was utilized for the electrochemical measurements. A standard three-compartment glass cell was employed for the measurements. The cell consisted of mild steel samples, which served as the working electrode (WE) and possessed a surface area of 0.785 cm². The counter electrode (CE) was composed of platinum mesh, while the reference electrode consisted of Ag/AgCl (KCl). To ensure stability, the electrode potential was allowed to equilibrate for sixty minutes prior to conducting the measurements. All experiments were conducted at a constant temperature of 303 K. Potentiodynamic polarization (PP) curves were recorded within the range of +250 mV to -250 mV relative to the open circuit potential (OCP) at a scan rate of 1 mV/s.

The percentage inhibition efficiency (η %) was calculated using the given equation[32]:

$$\eta\ \% = 1-\frac{i'_{corr}}{i_{corr}} \times 100 \quad \ldots(4)$$

Here, the variable "i'_{corr}" represents the measured corrosion current when an inhibitor is introduced, while "i_{corr}" refers to the corrosion current measured under conditions where no inhibitor is present.

Electrochemical Impedance Spectroscopy (EIS) studies

Impedance measurements were carried out across a wide frequency range, from 1,000,000 Hz to 0.1 Hz, using an AC signal with peak-to-peak amplitude of 10 mV. To ensure the accuracy and consistency of the results, the experiments were repeated multiple times.

The effectiveness of inhibition, expressed as a percentage (η %) was determined by applying a specific equation to the measured polarization resistance values.

$$\eta\% = \frac{\mathrm{R_{ct(inh)}}-\mathrm{R_{ct}}}{\mathrm{R_{ct(inh)}}} \times 100 \quad \ldots(5)$$

where, the charge transfer resistances in the presence and absence of the inhibitor, $R_{ct(inh)}$ and R_{ct}, respectively. The following relationship with constant phase element (CPE) and double layer capacitance (C_{dl}) was used to calculate C_{dl} value[33]:

$$C_{dl} = \left(\mathrm{Y_0 R_{ct}^{1-n}}\right)^{1/n} \quad \ldots(6)$$

where CPE constant is denoted as "$\mathrm{Y_0}$", while CPE exponent is represented by the symbol "n". The value of "n", ranging between 0 and 1, indicates the departure from ideal behaviour.

Atomic Force Microscopy (AFM) Investigation

After immersing in 15% HCl solution with and without the presence of optimum concentration of inhibitor CPOI (300 ppm) for 6 h at 303 K, the samples were carefully taken out from the solution and rinsed with distilled water and subsequently dried. AFM images of polished, blank and inhibited mild steel samples (dimensions: 1.0 cm × 1.0 cm ×

0.1 cm) were examined using model - Dimension Icon with scanasyst by Bruker. This analysis aimed to investigate the influence of inhibitors on the interface between the metal and the solution[34-37].

Field Emission Scanning Electron Microscopy (FE-SEM) Investigation

The surface properties of the mild steel samples (dimensions: 1.0 cm × 1.0 cm × 0.1 cm) were examined utilizing a FE-SEM. The samples were subjected to a 15% HCl solution for duration of 6 h, at 303 K under two conditions: one group with the optimal inhibitor concentration (300 ppm) and another group without inhibitor. After immersion, the samples were taken out and washed thoroughly with distilled water, dried using a cold air blaster and their FE-SEM images were recorded using the instrument model Zeiss Gemini 300 FE-SEM system.

Results and Discussion

Corrosion behaviour of mild steel by weight loss technique

Effect of inhibitor concentration and temperature

As discussed, the process reference[29] has been used for the synthesis of inhibitor i.e. CPOI, the analytical and spectral data of the synthesized compound are given as Yield: 62%; IR(KBr) in cm^{-1}:3340 (N-H str), 3010 (C-H of aromatic ring), 1714 (C=O of azetidinone ring), 1700 (C=O str); ^1H NMR(DMSO): δ7.60-8.72 (m, 4H, Ar-H in pyridine), 6.73-7.19 (m, 5H, Ar-H), 8.65(s, 1H, -CONH-), 5.34(s, 1H, CH-Cl of azetidinone ring), 3.21(s, 1H, azetidinone proton); MS(m/z):324(M+1). The compound was used to investigate corrosion parameters including corrosion rate (CR), surface coverage (θ), and inhibition efficiency (η) of mild steel in the presence and absence of different concentrations of inhibitor and different temperature range. Table 2 represents the variations in corrosion parameters of mild steel immersed in 15% HCl solution under different temperature conditions (ranging from 303 K to 333 K) and inhibitor concentrations (ranging from 100 ppm to 300 ppm). The experimental data clearly demonstrates that as the concentration of the inhibitor increases, the inhibition efficiency also increases.

To illustrate, the inhibition efficiency of CPOI at 100 ppm was found to be 72.76% at 303 K. The maximum inhibition efficiency reached 93.14% at the same temperature, when the inhibitor concentration of CPOI was 300 ppm. This phenomenon can be attributed to the fact that higher inhibitor concentrations result in greater surface coverage, consequently reducing the solubility of the metal. After 300 ppm concentration, the percentage inhibition efficiency was observed to be almost constant. Therefore, the optimum concentration and concentration range for other studies were taken as 100 ppm to 300 ppm. It was also observed from Table 2 that the inhibition efficiency of the inhibitor decreases with increasing temperature range 303 K to 333 K due to a shift of the equilibrium constant towards desorption of inhibitor molecules on the surface of mild steel[38].

Thermodynamic and activation parameters

Weight loss measurements were conducted to investigate the adsorption process and determine the thermodynamic activation parameters of mild steel in 15% HCl solution. The experiments were performed at temperatures ranging from 303 K to 333 K, with and without the presence of inhibitors. The immersion period lasted for 6 h. The apparent activation energy (E_a) was determined by applying the Arrhenius equation:

$$\log\ (CR) = \frac{-E_a}{2.303RT} + \log\ (A) \quad \ldots(7)$$

Apparent activation energy (E_a) is a measure of the energy required to start the corrosion process. The molar gas constant (R) is a physical constant that is used to convert between energy and temperature. The absolute temperature (T) is the temperature in Kelvin. The Arrhenius pre-exponential

Table 2 — Corrosion characteristics of mild steel in a 15% HCl solution at different temperatures, evaluated through weight loss measurements, and comparison of corrosion rates in the presence and absence of inhibitor

	303 K			313 K			323 K			333 K		
	CR (mmy^{-1})	θ	η%	CR (mmy^{-1})	θ	η%	CR (mmy^{-1})	θ	η%	CR (mmy^{-1})	θ	η%
Blank	22.8	-	-	38.7	-	-	77.4	-	-	126.4	-	-
CPOI												
100	6.21	0.727	72.76	12.62	0.673	67.39	29.51	0.618	61.87	52.63	0.583	58.36
200	3.28	0.856	85.61	7.06	0.817	81.75	15.78	0.796	79.61	28.17	0.777	77.71
300	1.56	0.931	93.14	3.15	0.918	91.86	8.81	0.886	88.61	18.87	0.85	85.07

factor (A) is a measure of the rate at which the corrosion process occurs.

In Fig. 1, a graphical representation illustrates the relationship between the logarithm of corrosion rate [log (CR)] and the reciprocal of temperature (1/T). The graph clearly indicates that as the temperature rises, the corrosion rate also increases. However, an interesting observation from the graph is that the presence of the inhibitor CPOI leads to a notable reduction in the corrosion rate.

The data in Fig. 1 suggests that the inhibitor CPOI works by slowing down the rate at which the corrosion process starts. This is consistent with the idea that the inhibitor CPOI forms a barrier on the surface of the mild steel, which prevents the HCl solution from reacting with the metal.

The information in Table 3 reveals that the addition of inhibitors has an impact on the standard enthalpy of activation (ΔH^*) and the standard entropy of activation (ΔS^*) for the inhibited and uninhibited electrolytes. The data indicates that the presence of inhibitors leads to an increase in the standard enthalpy of activation and a decrease in the standard entropy of activation. These findings imply that inhibitors have a retarding effect on the corrosion process. This occurs because inhibitors raise the energy threshold needed to initiate the reaction and reduce the overall disorder within the system.

The ΔH^* and ΔS^* are calculated using the transition state equation:

$$CR = \frac{RT}{Nh}\exp\left(\frac{\Delta S^*}{R}\right)\exp\left(-\frac{\Delta H^*}{RT}\right) \quad \ldots(8)$$

In the given context, "h" refers to Planck's constant, and "N" represents the Avogadro number.

Fig. 2 shows a plot of log (CR/T) against the reciprocal of temperature (1/T). The resulting linear relationships were used to calculate the activation thermodynamic parameters, ΔH^* and ΔS^*. The slopes of the lines correspond to $-\Delta H^*/2.303R$, while the intercepts represent $[\log(R/Nh) + \Delta S^*/ (2.303R)]$. The calculated values of ΔH^* and ΔS^* are listed in Table 3.

The E_a and the ΔH^* values change in a similar way when the concentration of the inhibitor changes. This is consistent with the transition-state theory, which predicts that these two values should be closely related. The negative value of the activation entropy (ΔS^*) for the inhibitor suggests the rate-determining step involves formation of an activated complex rather than a dissociation step. This observation suggests that the transition from reactants to active complexes is associated with a decrease in disorder[39].

Adsorption isotherm

The interaction between the inhibitor molecules and the mild steel surface can be described by an adsorption isotherm. The graph plotted C_{inh}/θ vs. C_{inh} provides a straight line (Fig. 3) with a correlation coefficient (R^2) and slope values at different temperatures are given in Table 4. The R^2 and

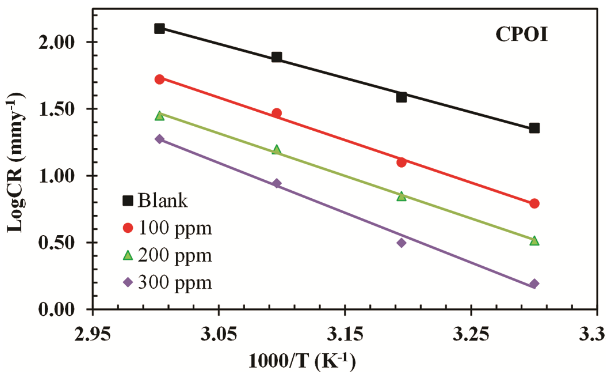


Fig. 1 — Arrhenius plot of log CR versus 1000/T concerning the corrosion of mild steel in 15% HCl solution containing different concentration of CPOI

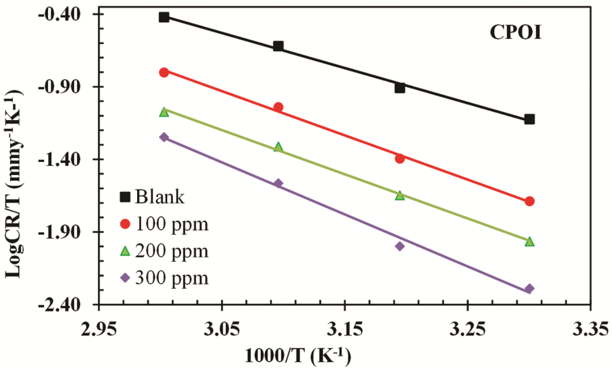


Fig. 2 — Transition state relationship between log (CR/T) and 1000/T for mild steel in 15% HCl solution at different CPOI concentrations

Table 3 — The activation parameters for the corrosion of mild steel in a 15% HCl solution with and without the presence of inhibitor (CPOI) determined using weight loss measurements

Inhibitor	Concentration (ppm)	E_a (kJ mol^{-1})	ΔH^* (kJ mol^{-1})	ΔS^* (JK^{-1} mol^{-1})
Blank-		40.90	46.259	-66.59
	100	60.94	58.303	-37.56
CPOI	200	60.92	58.284	-42.73
	300	71.28	68.64	-15.37

slope values in Table 4 are close to unity. This finding suggests that the Langmuir adsorption isotherm can be applied to the adsorption of CPOI on the MS surface and represented by the following equation[40]:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \qquad \ldots(9)$$

where, C_{inh} is the concentration of inhibitor and K_{ads} is the equilibrium constant for adsorption-desorption process.

To calculate the adsorption equilibrium constant (K_{ads}) of the inhibitor, we utilize the intercept of the C_{inh}/θ vs. C_{inh} plots. The free energy of adsorption (ΔG^0_{ads}) is determined using the following equation:

$$\Delta G^0_{ads} = -RT \ln(55.5K_{ads}) \qquad \ldots(10)$$

The value of gas constant (R) (8.314 $JK^{-1}mol^{-1}$) is used to calculate the energy of a system. The system absolute temperature, T, is used in Kelvin. The water molar concentration is the amount of water in a solution in moles per litre which has a value of 55.5.

At a temperature of 333 K, the values for the adsorption parameters K_{ads} and ΔG^0_{ads} were determined as 3.7 × 10^2 M^{-1} and -8.04 kJ mol^{-1}, respectively. K_{ads} represents the adsorption equilibrium constant, reflecting the strength of the interaction between the inhibitor and the surface. A higher K_{ads} value signifies a more robust interaction. ΔG^0_{ads} denotes the standard free energy of adsorption, indicating the energy change associated with the adsorption of the inhibitor onto the surface. A negative ΔG^0_{ads} value indicates an exothermic adsorption process, meaning heat is released.

The presence of a negative ΔG^0_{ads} value indicates the spontaneous nature of CPOI molecule adsorption on the MS surface. Consequently, this adsorption process releases heat and is therefore favoured. The calculated ΔG^0_{ads} value (-8.04 kJ mol^{-1}) represents a fall below the threshold limit of 20 kJ mol^{-1}, which suggests that the adsorption exhibits primarily physical characteristics[40]. Physical adsorption refers to a type of adsorption driven by weak interactions, such as van der Waals forces. In this particular scenario, the interaction between the CPOI molecules and the MS surface is likely attributed to electrostatic forces. Similar observation was also reported by Bhuvaneswari et al.[41] who studied the corrosion inhibition of mild steel in hydrochloric acid by leaves extract of *Tephrosia purpurea*.

Electrochemical measurements

Potentiodynamic polarization studies

Potentiodynamic polarization (PP) analysis was utilized to investigate the electrochemical performance of an inhibitor substance. The obtained results, depicted in Fig. 4, were obtained by conducting the experiment in 15% HCl solution at a temperature of 303 K. The study was carried out in

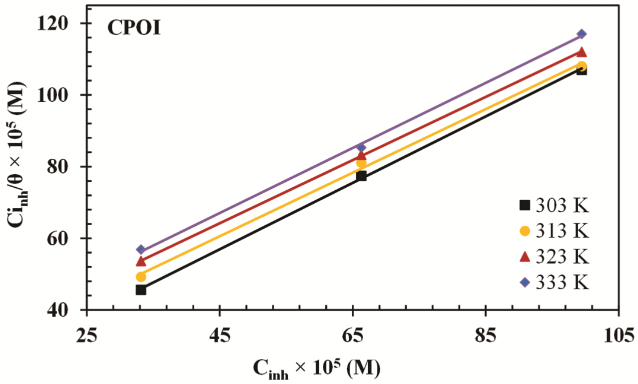


Fig. 3 — Plots illustrating the relationship between (C_{inh}/θ) and C_{inh} for CPOI, following the Langmuir adsorption model

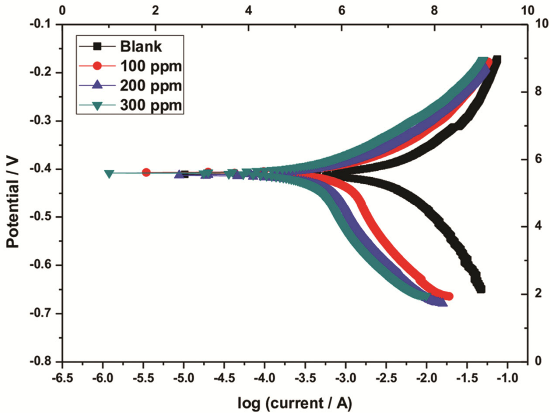


Fig. 4 — Potentiodynamic polarization curves for mild steel in a 15% HCl solution with and without CPOI at 303 K

Table 4 — Adsorption parameters for CPOI for mild steel in 15% HCl solution at a temperature range of 303 K–333 K

Inhibitor	Temperature (K)	K_{ads} (M^{-1})	ΔG^o_{ads} (kJ mol^{-1})	*Slope*	R^2
CPOI	303	6.1 × 10^2	-9.01	0.984	0.992
	313	4.2 × 10^2	-8.32	0.973	0.989
	323	3.9 × 10^2	-8.21	0.993	0.995
	333	3.7 × 10^2	-8.04	0.991	0.994

Table 5 — Investigation of percentage Inhibition efficiency (*η%)* obtained from polarization studies for mild steel in 15% HCl solution in the presence and absence of inhibitor at 303 K

Inhibitor	Concentration (ppm)	E_{corr} (mV)	β_a (mV dec^{-1})	-β_c (mV dec^{-1})	I_{corr} (mA cm^{-2})	η%
Blank	-	-410.7	239.9	348.1	9.56	-
CPOI	100	-406.73	134.8	440	1.744	81.75
	200	-413.9	113.1	307.6	0.840	91.21
	300	-408.1	111.8	353	0.603	93.69

two scenarios: in the absence and presence of varying concentrations of the inhibitor (referred to as CPOI). The presented figure clearly illustrates the impact of the inhibitor on the potential of the metal. In presence of the inhibitor, the metal's potential slightly shifts towards more positive values and reducing the anodic and cathodic current densities suggests a slowdown in the anodic and cathodic process. This indicates that inhibitor acts as mixed type inhibitor[42]. These findings strongly indicate that the introduction of CPOI inhibitors can significantly enhance the effectiveness of corrosion inhibition procedures.

Electrochemical parameters and percentage inhibition efficiency (η%) were determined through polarization studies conducted on mild steel immersed in 15% HCl solution at 303 K, both in the presence and absence of inhibitor. Table 5 shows the current and potential values obtained from potentiodynamic experiments using Tafel polarization. The I_{corr} value of mild steel in blank solution was found to be 9.56 mA cm^{-2} and at the maximum concentration of 300 ppm it decreased upto 0.603 mAcm^{-2}. The maximum inhibition efficiency at the optimum concentration of the inhibitor (300 ppm) was found to be 93.69%. The potentiodynamic results in Table 5 show that increasing the inhibitor concentration led to a decrease in I_{corr} values and an increased the inhibition efficiency due to adsorption of CPOI inhibitor on the metal surface and blocking the available reaction sites.

EIS studies

Figs 5 and 6 show the Nyquist and Bode plots of polished mild steel after being immersed in a 15% HCl solution with and without inhibitors respectively. Additionally, Table 6 provides valuable information on the impedance parameters of this inhibitor at different concentrations. Fig. 5 depicts the Nyquist plots obtained from EIS measurement, which display the behaviour of mild steel in 15% HCl with varying concentrations of CPOI. The Nyquist plot for this experiment shows that the inhibitor is most effective at maximum concentration of 300 ppm and greatest percentage of inhibition efficiency. This is because the charge transfer resistance (R_{ct}) is also at its highest at this concentration. The presence of the inhibitor clearly influences the impedance characteristics of mild steel, as observed in the spectra, indicating changes in the impedance responses[43].

Fig. 6 depicts the Bode phase angle plot obtained from EIS measurement, which exhibits a single maximum (one time constant) at intermediate frequencies, the broadening of this maximum in the presence of inhibitor accounts for the formation of protective layer on metal surface.

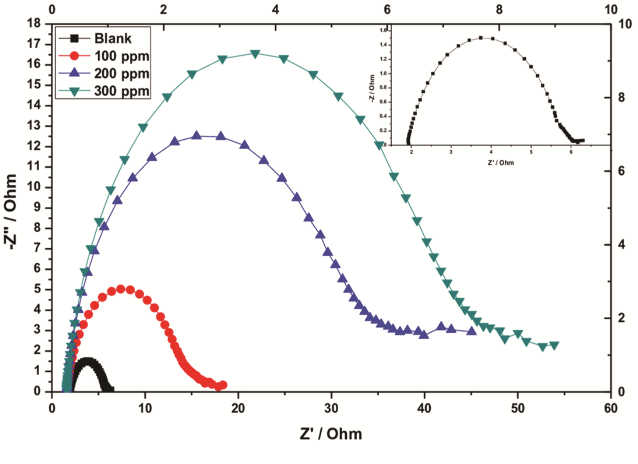


Fig. 5 — Nyquist plot analysis of mild steel corrosion in 15% HCl solution with and without CPOI at 303 K

Table 6 — Investigation of corrosion inhibition of mild steel in 15% HCl by CPOI at various concentrations: EIS measurements at 303 K

Inhibitor	Concentration (ppm)	R_{ct} (Ω cm^2)	Y_0 (μF cm^2)	n	C_{dl} (μF cm^{-2})	η %
Blank	-	4.2	476	0.848	185.89	-
CPOI	100	16.1	262	0.859	103.12	73.91
	200	38.3	167	0.877	57.08	89.03
	300	46.8	89	0.913	19.69	91.02

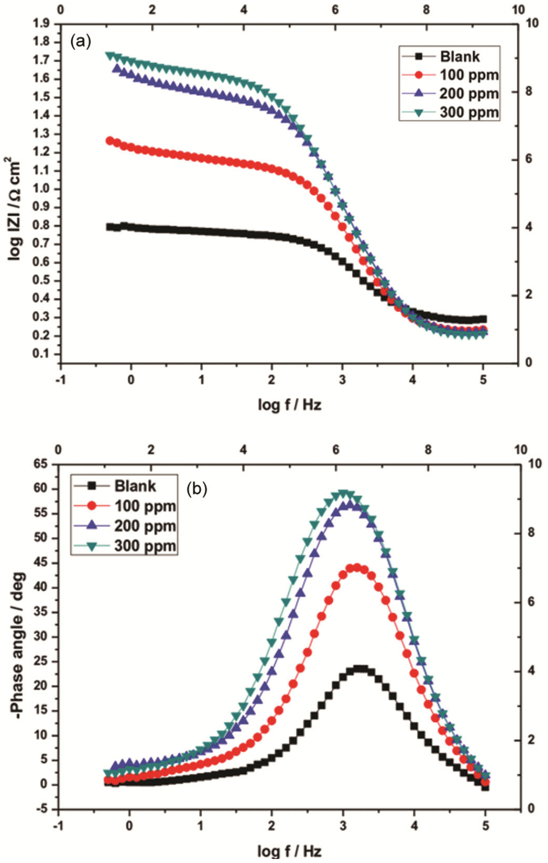


Fig. 6 — Bode plot analysis of mild steel corrosion in 15% HCl solution with and without CPOI at 303 K

There is only one maximum phase in Bode plot for the inhibitor. This indicates only one relaxation process, which would be a charge transfer process occurring at metal-electrolyte interface. This figure shows larger impedance value in the presence of inhibitor and the impedance value increases as the inhibitor concentration increases. This indicates that the corrosion rate decreases as the inhibitor concentration increases[45].

Surface studies by AFM analyses

The two dimensional (2D) and three dimensional (3D) images of polished mild steel sample, immersed in 15% hydrochloric acid for 6 h, both with and without the presence of inhibitor was examined using atomic force microscope (AFM) are shown in Fig. 7. This facilitates inspection of surface appearance at the nano-to-micro level[44-45].

The 2D and 3D AFM images showed that the surface of the polished mild steel was smooth with few scratches and the image mean roughness (Rq) and average roughness (Ra) were 16.0 nm and 23.4 nm, respectively, as shown in Fig. 7(a, b). When polished mild steel was exposed to corrosive solution, the aggressive attack causes the surface of the mild steel to become rough and irregular with large pits and deep cracks, as shown in Fig. 7(c, d) and the Rq and Ra values were 213.0 nm and 155.0 nm, respectively.

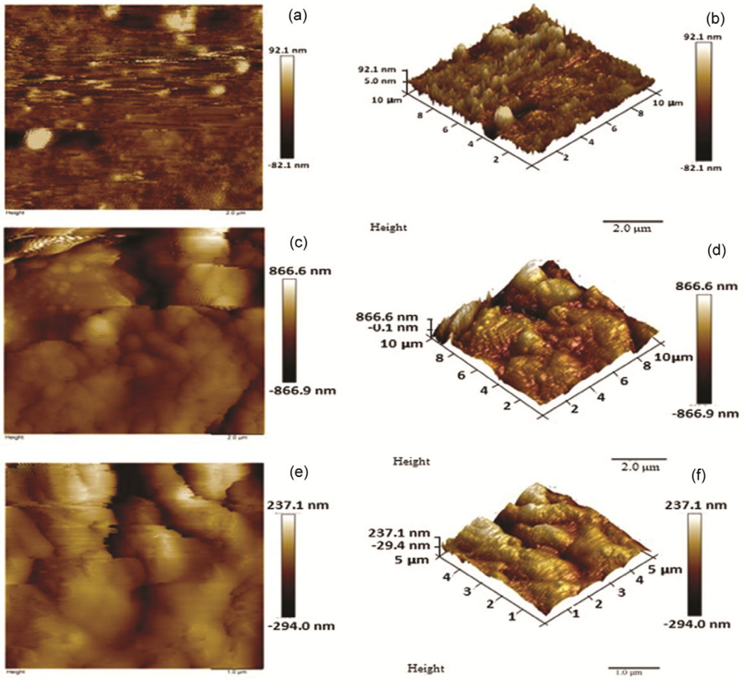


Fig. 7 — Comparison of 2-D and 3-D AFM images of mild steel surfaces: (a,b) polished, (c,d) exposed in 15% HCl solution, and (e,f) treated with inhibitor CPOI

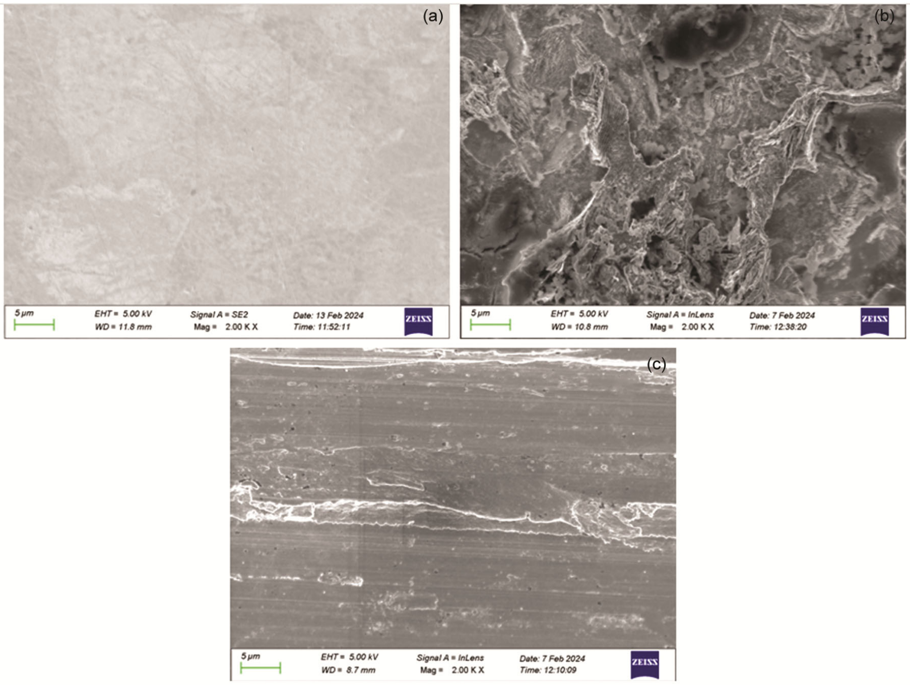


Fig. 8 — Comparison of FE-SEM images of mild steel surface in three different conditions: (a) polished, (b) exposed to 15% HCl solution, and (c) treated with inhibitor CPOI

The surface roughness of mild steel in the presence of optimum concentration (300 ppm) of inhibitor (CPOI) in corrosive solution was reduced compared to that exposed in 15% HCl solution and the Rq and Ra values were 71.0 nm and 52.8 nm, respectively, as shown in Fig. 7(e, f). This is because the inhibitor molecules bond to the surface of the metal, forming a protective layer that prevents the corrosive solution from dissolving the metal.

Surface studies by FESEM analyses

The surface of mild steel was examined using a FE-SEM following its exposure to a 15% HCl solution for 6 h with and without the addition of a corrosion inhibitor (CPOI). Fig. 8(a-c) illustrates the FE-SEM images, revealing distinct observations. The morphology of polished mild steel was very smooth which is shown in Fig. 8a while polished mild steel specimen immersed in 15% HCl solution in the absence of CPOI, the surface exhibited significant corrosion and it is characterized by noticeable cracks and cavities (Fig. 8b). However, in the presence of 300 ppm of the concentration of CPOI, the surface of mild steel displayed a much more uniform appearance (Fig. 8c) as compared to blank solution, suggesting that the inhibitor molecules formed a protective layer on the metal's surface, effectively preventing corrosion.

Conclusion

The synthesized corrosion inhibitor CPOI demonstrated significant effectiveness and inhibition efficiencies when used for the corrosion of mild steel in 15% HCl solution. The inhibition efficiency of the inhibitor increased at each concentration by increasing the temperature of the inhibitor solution from 303 K to 333 K. According to potentiodynamic polarization studies, changes in anodic and cathodic Tafel slopes with inhibitor concentrations indicated that both anodic and cathodic reactions were controlled and showed a mixed type of inhibition. In electrochemical impedance spectroscopy study, in the presence of inhibitor, the charge transfer resistance increases while the double layer capacitance decreases suggesting the adsorption of the inhibitor molecules on the surface of mild steel. Through the utilization of AFM, FE-SEM and Langmuir adsorption isotherm it was observed that the inhibitor molecules exhibit an affinity towards the surface of steel, leading to the formation of a protective, thin layer. This layer effectively protects mild steel from corrosion.

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