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RESEARCH ARTICLE

WILEY SURFACE and INTERFACE ANALYSIS

Theoretical and experimental approach of inhibition effect by sulfamethoxazole on mild steel corrosion in 1-M HCl

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The inhibition effect of sulfamethoxazole on mild steel corrosion in 1-M hydrochloric acid solution is investigated by electrochemical and quantum chemical measurements. Electrochemical polarization studies show that sulfamethoxazole acts as a mixed-type corrosion inhibitor. The adsorption of the inhibitor on mild steel in 1-M hydrochloric acid system is studied at different temperatures (303-333 K). The adsorption of sulfamethoxazole on mild steel surface is an exothermic process and obeys the Temkin adsorption isotherm. Based on the potential of zero charge values and quantum chemical parameters, the mechanism of adsorption is proposed.

KEYWORDS

corrosion, EIS, quantum, SEM

1 | INTRODUCTION

Mild steel is an alloy of iron, which is used in industrial and structural applications because of its superior mechanical properties. When it is in contact with acidic media in various industrial applications, it undergoes metal dissolution. Several corrosion control approaches are used to avoid the metal dissolution in acidic media.[1] The use of corrosion inhibitors is the most efficient and practical method to control the corrosion of metals. The corrosion inhibitors are heterocyclic molecules having heteroatoms such as nitrogen, phosphorous, sulfur, oxygen, and π electrons in their heterocyclic ring system. Through these, inhibitor molecules get adsorbed on the metal surface.[2-4] Therefore, organic compounds get adsorbed on the surface of mild steel and block the active corrosion sites, which retard the corrosion process.

Few heterocyclic compounds such as benzimidazole derivatives,[5,6] triazole derivatives,[7,8] thiosemicarbazide derivatives,[9] bisthiadiazoles,[11] Schiff base,[12] pyridine derivatives,[13] and organic dyes[10,14-18] have been tested as efficient corrosion inhibitors for steel. In recent times, researchers have paid attention to the development of drugs as inhibitors for metallic corrosion. From literature, several drugs such as ketosulfone,[19] ciprofloxacin,[20] lamotrigine,[21] risperidone,[22] Hydralazine,[23] anthranilic acid,[24] and aspirin[25] drugs are reported for their corrosion inhibition activity. The corrosion inhibition behavior of natural extracts like henna, black cumin, chamomile, half a bar, kidney bean, opuntia, and natural honey[26-28] that are also reported was studied by some researchers. Most synthetic organic compounds are expensive and toxic. Therefore, it is necessary to develop cheap, nontoxic, and environment-friendly corrosion inhibitors.

The present study is focused on the inhibition effect of sulfamethoxazole on corrosion of mild steel in 1-M HCl. The investigation is conducted at different concentrations at an elevated temperature range of 303 to 333 K.

Sulfamethoxazole has adsorption centers such as —NH_2 group, —SO_2—NH— group, O, and N heteroatoms, and aromatic rings in its structure might be supportive of its adsorption on the metal surface, which gives importance for the study of corrosion inhibition effect.[29]

The corrosion inhibition effect of sulfamethoxazole is studied by weight loss measurement and electrochemical measurements. Tafel polarization, chronoamperometric, and electrochemical impedance spectroscopy (EIS) measurements for mild steel in 1-M HCl are performed. The surface morphology is examined by scanning electron microscopy (SEM), and theoretically, this study was justified by using quantum chemical analysis by density functional theory (DFT) method.

2 | EXPERIMENTAL

2.1 | Materials

This study was conducted on steel (composition: 0.35% C, 0.032% Mn, 0.028% P, 0.03% S, and remaining Fe) strips, which were available commercially. The steel strip (6 × 1 × 0.5 cm^3) was polished by using SiC emery paper with grade number 80 to 2000. Then, abraded steel strip was degreased with acetone, washed with distilled water, and dried at room temperature. All the corrosion experiments were performed on these pieces.

2.2 | Inhibitor

Sulfamethoxazole is a sulfonamide bacteriostatic antibiotic drug molecule. This is selected for the present study as corrosion inhibitor because of (vice versa) its nontoxicity and presence of electron-rich species such as N, S, and O. The presence of these species facilitates adsorption onto steel surfaces and retards corrosion.

A commercially available analytical standard sulfamethoxazole was purchased from Sigma Aldrich Pvt. Ltd, India, and used for all the experiments. First, it was dissolved in 1 cm^3 of ethanol and then mixed into 1-M HCl solution as an inhibited solution. A wide range of inhibitor concentrations from 10 to 50 ppm was used. The molecular structure of inhibitor is shown in Figure 1.

2.3 | Weight loss measurements

Different mild steel strips were immersed in 1-M HCl solutions having various concentrations of sulfamethoxazole inhibitor for about 6 hours at room temperature. The weight differences of mild steel strip before and after the immersion were recorded and used to calculate the inhibition efficiency.

2.4 | Electrochemical measurements

A conventional 3-electrode system was connected to an electrochemical Compactstat.e10800 (Ivium Technologies, Netherlands) for all electrochemical measurements. The working electrode was polished steel strip with an exposed (to electrolyte) surface area of 1 cm^2 exposed to the electrolyte. The counter electrode was a platinum electrode, and a saturated calomel electrode was used as the reference electrode.

Potentiodynamic Tafel polarization measurements were recorded at a scan rate of 1 mV/s in a given potential range. The impedance measurements were performed by an AC signal with an amplitude value of 1 mV/s at open-circuit potential (OCP) in the frequency range of 100 kHz to 0.1 Hz.

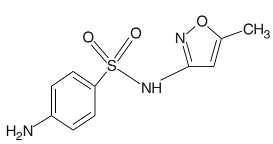

FIGURE 1 Molecular structure of sulfamethoxazole

2.5 | Quantum chemical analysis

Quantum chemical calculations were conducted by complete geometry optimization using standard Hyper Chem, Release 8.0 software (Hypercube, Inc Gm BH Austria, United States). The molecular structure of the sulfamethaxazole molecule was optimized by DFT using 6-31G** basis set. The Polak-Rieberre algorithm is fast and accurate and has been used for computation.

2.6 | SEM measurement

Surface investigation of mild steel was done using SEM (JEOL JSM-840A model). The micrographs of mild steel surface were recorded in the absence and presence of inhibitor in 1-M HCl solution.

3 | RESULTS AND DISCUSSION

3.1 | Weight loss measurement

For weight loss measurements, 100 cm^3 of 1-M HCl was taken in 6 beakers. The first beaker was fixed as a blank solution (uninhibited solution), and 10 to 50 ppm concentrations of the inhibitor (incremented with 10 ppm) were added to the rest of 5 beakers (inhibited solutions). Polished mild steel strips were immersed into each of the 5 inhibited solutions over a period of about 6 hours at 303 K. The weight differences of all the strips before and after immersion in solution were measured. The following equation gives the corrosion rate of each strip:

$$v = \frac{W - W_i}{W_i} \times 100, \quad (1)$$

where W and W_i are the weight difference of steel strip in the absence and the presence of inhibitor from the bulk of the solution, respectively. The following expression computes the inhibition efficiency (ηw) of this method as

$$\eta_w = \frac{\nu - \nu_i}{\nu} \times 100, \quad (2)$$

where ν and ν_i are the corrosion rates in the absence and presence of sulfamethoxazole, respectively. The corrosion parameters are described in Table 1. Figure 2 represents the variation of corrosion rate and inhibition efficiency against the concentration of inhibitor.

Results obtained from Table 1 indicate that increase in the concentration of sulfamethoxazole decreases the corrosion rate (Figure 3A) due to increasing the surface coverage of metal, as it adsorbs inhibitor molecules on it. The surface coverage indicates a

TABLE 1 Corrosion parameters obtained by weight loss measurement

Temperature, K	Corrosive Medium of Sulfamethoxazole, ppm	Corrosion Rate v, g/cm^2 h	Inhibition Efficiency η_w, %
	Blank	0.280	
	10	0.160	42.85
303	20	0.075	73.21
	30	0.068	75.71
	40	0.059	78.92
	50	0.040	85.71

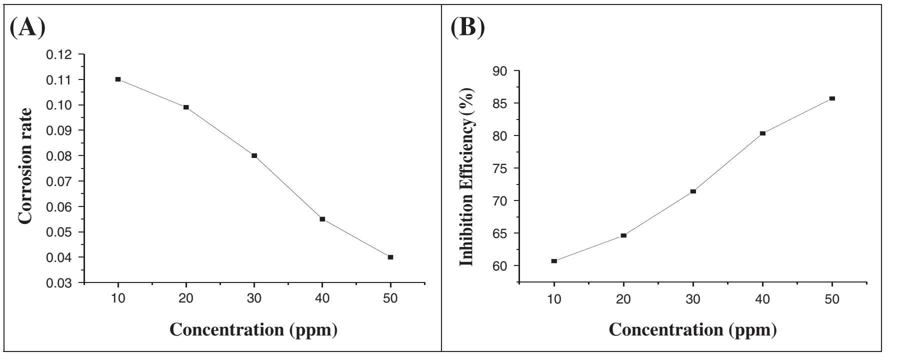

FIGURE 2 Variation of corrosion rate and inhibition efficiency with inhibitor concentration

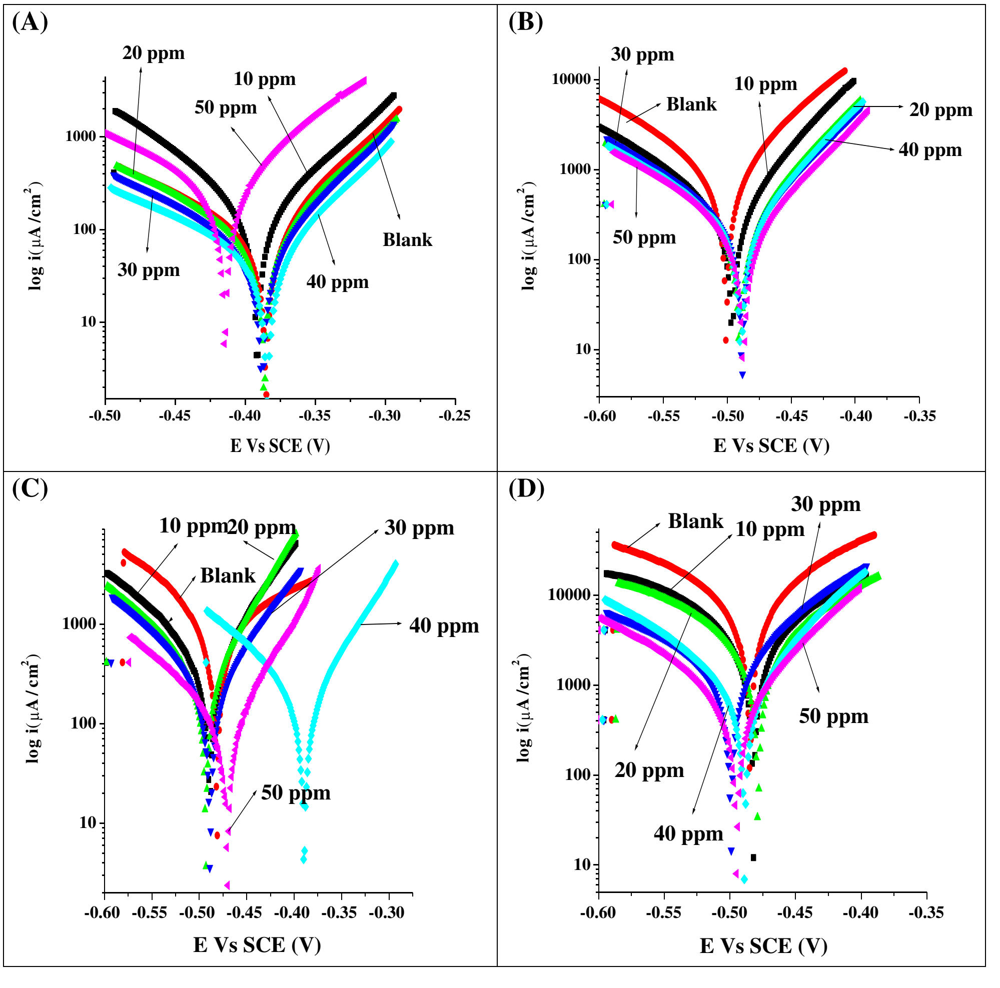

FIGURE 3 Tafel polarization plots for mild steel in the absence and presence of sulfamethoxazole in 1-M hydrochloric acid at A, 303 K; B, 313 K; C, 323 K; and D, 333 K

progressive formation of a passive protective layer on the metal surface. Because of the increased surface coverage by the inhibitor molecule (due to increase in the concentration of inhibitor), the inhibition efficiency is improved (Figure 3B). Maximum inhibition efficiency of 85.71% is observed at 303 K corresponding with 50-ppm concentration.

3.2 | Electrochemical studies

3.2.1 | Electrochemical polarization measurement

Electrochemical polarization method is the best tool to calculate the corrosion kinetic parameters. In this analysis, the relationship of current against the potential for mild steel corrosion in absence and presence of various concentrations of inhibitor in 1-M HCl solution is discussed. The Tafel plots were recorded by varying potential by ±0.1 V from the corrosion potential (E_{corr}) with a scan rate of 1 mV/s by using an electrochemical analyzer. The Tafel plots are given in Figure 3, and the corrosion parameters are recorded in Table 2.

The following expression calculates the inhibition efficiency (η_p) of mild steel in the absence and presence of inhibitor as

$$\eta_P = \frac{i_0 - i}{i_0} \times 100, \quad (3)$$

where i and i_0 are the corrosion current densities in the absence and presence of inhibitor, respectively.

An investigation from Table 2 reveals that an increase in the concentration of inhibitor decreases the corrosion current density (i_{corr}). The results obtained from the Tafel polarization measurement indicate that the inhibition efficiency (η_p) increases with increasing the inhibitor concentrations across the temperature range of 303 to 333 K. This behavior is seen because the inhibitor gets adsorbed onto the surface of mild steel.[30] From Tafel plots (Figure 3), we find that there is a reduction of both anodic and cathodic currents in the presence of sulfamethoxazole with different concentrations with respect to the blank solution. This effect is an indication that with the addition of the inhibitor, the anodic reaction (metal dissolution), and a cathodic reaction (hydrogen evolution) is slowed down. The cathodic Tafel slope (β_c) value of sulfamethoxazole influences the kinetics of the hydrogen evolution reaction.[31] Hence, it is an indication of an increase in the energy barrier for proton discharge that leads to lesser hydrogen evolution. A similar value for anodic Tafel slope (β_a) indicates that sulfamethoxazole is first adsorbed onto the metal surface and blocks the reaction sites of the metal surface without affecting the anodic reaction.[32] In a recent study, a small change in corrosion potential (E_{corr}) value of 30 mV concerning the blank solution is observed, which shows that the sulfamethoxazole acts as a mixed-type inhibitor.

3.2.2 | EIS measurement

Electrochemical impedance spectroscopy has been efficiently used to analyze the corrosion mechanism. Electrochemical impedance spectroscopy measurement of corrosion for mild steel in 1-M HCl solution was investigated in presence and absence of various sulfamethoxazole concentrations over the frequency range from 100 kHz to 0.1 Hz at OCP was recorded. This method provides information about the kinetics of the electrode processes and simultaneously about the surface properties of the investigated systems. Figure 4 shows Nyquist plots for corrosion of steel in 1-M HCl. Nyquist plots consist of high-frequency depressed semicircles. The values of polarization resistance (R_p), double-layer capacitance (C_{dl}), inhibition efficiency

TABLE 2 Corrosion parameters by electrochemical polarization method

Temperature, K	Inhibitor Concentration, ppm	Corrosion Potential E_{corr}, V	Corrosion Current Density i_{corr}, μA/cm^2	Corrosion Rate ν_{corr}, mpy	Cathodic Slope βc, mV/dec	Anodic Slope βa, mV/dec	Inhibition Efficiency η_p, %
303	Blank	−0.415	0.228	0.369	−0.121	0.075	
	10	−0.389	0.130	0.211	−0.084	0.074	42.77
	20	−0.388	0.050	0.121	−0.121	0.068	77.75
	30	−0.387	0.040	0.105	−0.111	0.070	80.77
	40	−0.386	0.034	0.082	−0.117	0.064	84.98
	50	−0.383	0.029	0.070	−0.135	0.067	87.12
313	Blank	−0.500	0.730	1.81	−0.102	0.070	
	10	−0.495	0.297	0.481	−0.099	0.059	59.25
	20	−0.486	0.220	0.356	−0.109	0.062	69.81
	30	−0.486	0.211	0.341	−0.102	0.065	71.09
	40	−0.486	0.200	0.324	−0.106	0.061	72.50
	50	−0.484	0.172	0.278	−0.103	0.065	76.38
323	Blank	−0.481	0.733	8.514	−0.104	0.156	
	10	−0.486	0.297	0.547	−0.066	0.105	53.81
	20	−0.489	0.220	0.415	−0.060	0.106	64.93
	30	−0.485	0.211	0.312	−0.071	0.102	73.64
	40	−0.386	0.200	0.248	−0.067	0.105	79.05
	50	−0.468	0.172	0.146	−0.065	0.109	91.67
333	Blank	−0.481	6.606	10.68	−0.129	0.096	
	10	−0.472	2.957	4.776	−0.090	0.136	55.28
	20	−0.472	2.271	3.672	−0.128	0.092	65.62
	30	−0.502	1.283	2.074	−0.120	0.081	80.57
	40	−0.487	0.785	1.270	−0.096	0.061	88.10
	50	−0.491	0.561	0.908	−0.101	0.064	91.49

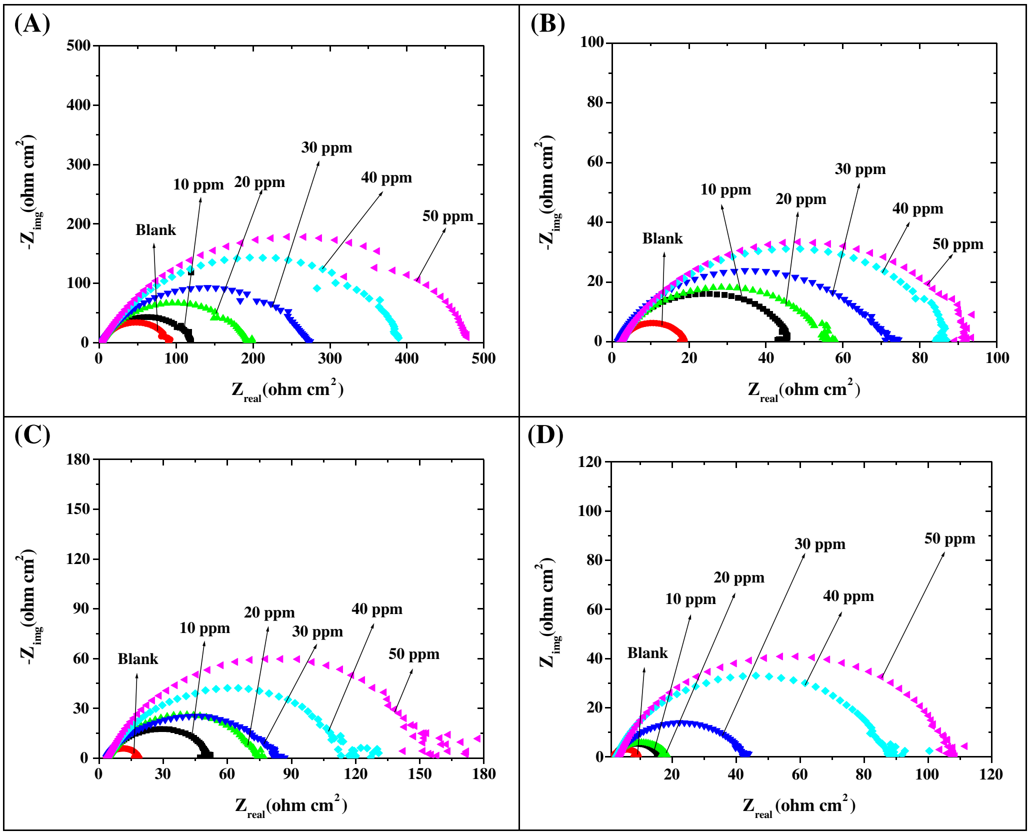

FIGURE 4 Nyquist plots for mild steel in the absence and presence of sulfamethoxazole in 1-M hydrochloric acid at A, 303 K; B, 313 K; C, 323 K; and D, 333 K temperature

(η_z), and surface coverage (θ) are obtained from the Nyquist plots and reported in Table 3. Surface coverage is calculated by the following equation.

$$\theta = \frac{\eta_Z}{100}, \quad (4)$$

where η_Z is the inhibition efficiency obtained from EIS; the measured impedance data are analyzed by fitting into an equivalent circuit as shown in Figure 6.

η_z was calculated using the following equation.[33,34]

$$\eta_z = \frac{R_p - R_p^{o}}{R_p} \text{ x } 100, \quad (5)$$

where R_p and R_p^{o} are polarization resistance values in the presence and absence of inhibitor from the bulk of the solution.

The EIS of mild steel consists of semicircles (Figure 4). The equivalent circuit used to fit the experimental data of mild steel in 1-M HCl solution in the absence and presence of sulfamethoxazole is shown in Figure 5. The model includes the inductance (L) solution resistance (Rs), a series combination of polar resistances (R_{p1} and R_{p2}), in parallel with a capacitance (C), and constant phase angle (Q).

In the given frequency limit, the inductive contribution to the overall impedance is insignificant. Therefore, the Nyquist plot of the impedance is a semicircle characteristic of the parallel arrangement of the double-layer capacitance and charge-transfer resistance corresponding to the mild steel dissolution reaction. Contribution to the total impedance at intermediate frequencies comes mainly from the charge-transfer resistance and inductive component in parallel.

TABLE 3 Corrosion parameters by electrochemical impedance spectroscopy method

Temperature, K	Inhibitor con^n, ppm	R_p Ωcm^2	C_{dl}, μF cm^{-2}	η_z, %	Surface Coverage θ
303	Blank	88.30	1057		
	10	119.01	859	25.80	0.25
	20	193.21	509	54.29	0.54
	30	270.61	462	67.37	0.67
	40	394.89	162	77.63	0.77
	50	484.68	141	81.78	0.81
313	Blank	16.32	1164		
	10	43.69	515	62.64	0.62
	20	54.29	474	69.93	0.69
	30	70.33	381	76.79	0.76
	40	84.03	328	80.57	0.80
	50	89.69	232	81.80	0.81
323	Blank	14.91	934		
	10	46.72	535	68.08	0.68
	20	71089	511	79.25	0.79
	30	80.17	394	81.40	0.81
	40	117.94	346	87.35	0.87
	50	159.09	141	90.67	0.90
333	Blank	7.82	1082		
	10	13.82	874	48.02	0.43
	20	15.87	744	51.72	0.51
	30	40.11	598	80.50	0.80
	40	87.39	427	91.05	0.91
	50	104.68	169	92.52	0.92

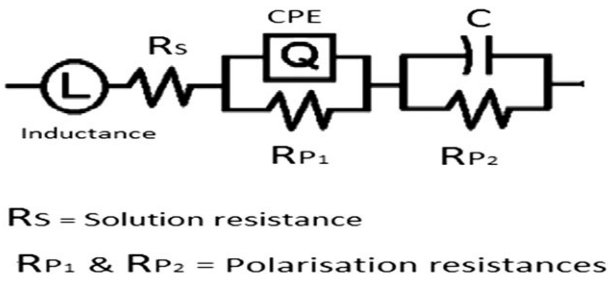

FIGURE 5 Electrical equivalent circuit. CPE, constant phase element

This circuit includes constant phase element (CPE), which is placed in parallel to charge transfer resistances (R_{p1} and R_{p2}). The sum of R_{p1} and R_{p2} values is a measure of charge-transfer resistance that corresponds to the metal dissolution reaction. The CPE is used in this model to compensate for nonhomogeneity in the system and is defined by 2 values, Q and n. The impedance of CPE is represented by

$$Z_{CPE} = Q^{-1}\,(j\omega)^{-n}, \tag{6}$$

where $j = (-1)^{1/2}$, ω is frequency in rad $s{-}1$, $\omega = 2\pi f$, and f is the frequency in Hz. If n equals 1, the impedance of CPE is identical to that of a capacitor, $Z_C\ (i\omega C)^{-1}$, and in this case, Q gives a pure capacitance (C). For the nonhomogeneous system, n values range from 0.9 to 1.

In general, the diameter of the arches represents polarization resistance (R_p) value, which increases with increasing concentration of sulfamethoxazole and temperature. This behavior is attributed to the charge transfer process from the inhibitor molecule present in bulk of the solution onto the charged mild steel surface. Along with this, we observe a deviation from perfect semicircles in Nyquist plots because of the roughness of the metal surface. Hence, increasing R_p values increases the inhibition efficiency of the mild steel by the inhibitor, and a maximum inhibition efficiency of 92% at 333 K is observed in this case.

From Table 3, it is observed that C_{dl} values decrease with an increase in inhibitor concentration, which is because of the decrease in dielectric constant or gains in the thickness of electric double layer due to the adsorption of sulfamethoxazole at the metal/solution interface.

The experimental curve of 10 ppm of inhibitor for mild steel in 1-M HCl precisely fitted with the curve obtained by the electrical equivalent circuit and is shown in Figure 6.

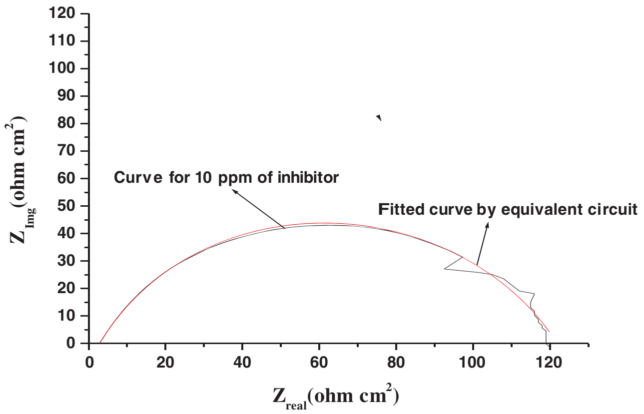

FIGURE 6 The fitted curve for the experimental curve by the electrical equivalent circuit

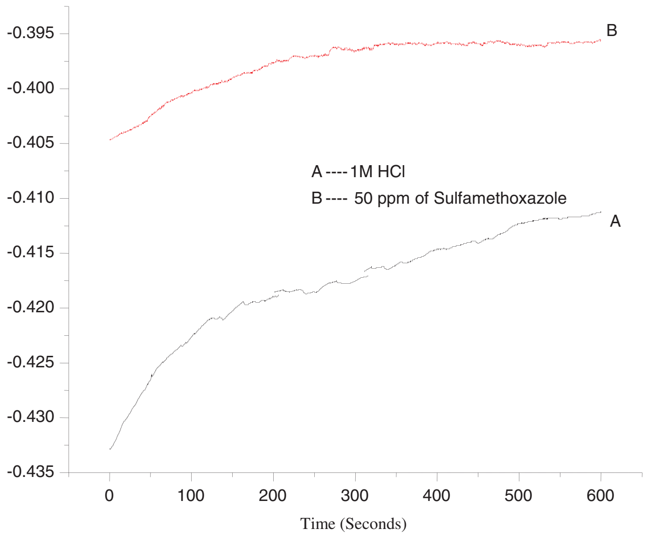

FIGURE 7 Open-circuit potential graph for mild steel in 1-M hydrochloric acid (HCl) with time

3.2.3 | OCP measurements

The change in the OCP with immersion time for mild steel in the absence and presence of 50-ppm sulfamethoxazole in 1-M HCl is given in Figure 7. In HCl solution, the potential stands at a virtually stable value of −0.425 V, whereas solution containing an inhibitor produces a nobler potential of −0.400 V, which tends to shift towards a positive direction with the passage of time.[35,36]

3.3 | Adsorption isotherm and thermodynamic parameters

The corrosion inhibition mechanism of the inhibitor on the corrosion of mild steel surface in acid media can be explained by adsorption mechanism of the inhibitor on the metal surface. Because of this adsorption process, an increase of inhibitor concentration reduces the corrosion rate of mild steel in 1-M HCl solution. Usually, various adsorption isotherms such as Langmuir, Freundlich, Frumkin, and Temkin were tested for the adsorption process.

The degree of surface coverage (θ) for inhibitor is obtained from the EIS data, and θ values are reported in Table 4. To find out the suitable adsorption isotherm, graphs for various adsorption isotherms such as Temkin, Freundlich, and Langmuir models are plotted. By close examination of these adsorption isotherms, we find that Temkin adsorption isotherm is the best fit for this adsorption process because

TABLE 4 Thermodynamic parameters

Temperature, K	R^2	a	K_{ads}, kJ/mol	ΔG^0_{ads}, kJ/mol	ΔH^0_{ads}, kJ/mol	ΔS^0_{ads}, J/mol/K
303	0.994	−0.4	714	−26.67	−82.60	−0.184
313	0.992	−0.14	734	−27.60	−82.60	−0.175
323	0.988	−0.15	707	−28.40	−82.60	−0.167
333	0.947	−0.39	675	−29.15	−82.60	−0.160

regression coefficient (R^2) values are more close to unity ($0.994 \geq R^2 \geq 0.947$). Therefore, the adsorption of sulfamethoxazole obey's the Temkin adsorption isotherm and is explained by the following expression:

$$-2a\theta = \ln K_{ads} + \ln C, \tag{7}$$

where C is the inhibitor concentration in ppm, K_{ads} is the equilibrium constant of the adsorption process, and a is the molecule interaction parameter, which indicates the molecular interaction of the inhibitor in adsorption layer at the metal surface.

The equilibrium constant of adsorption K_{ads} is related to standard free energy change of adsorption (ΔG^0_{ads}) by the following expression.[37]

$$K_{ads} = 1/55.5 \exp\left(\Delta G^0_{ads}/RT\right), \tag{8}$$

where R is the universal gas constant, 55.5 is the concentration of water in solution in mol/L, and T is the absolute temperature. The plot of θ against log C is shown in Figure 8. K_{ads} is calculated from the intercept of the straight lines, and the following expression is used to calculate $\Delta G°_{ads}$.

$$Kads = \frac{1}{55.5} \exp\left(-\Delta G \frac{0ads}{RT}\right), \tag{9}$$

where K_{ads}, a, and ΔG^0_{ads} values are reported in Table 4.

Adsorption takes place through the replacement of water molecule on the surface of mild steel by inhibitor molecule, which is represented as K_{ads}, and the replacement reaction is as follows.

$$\text{Inhibitor}_{(sol)} + xH_2O_{(ads)} \longrightarrow \text{Inhibitor}_{(ads)} + xH_2O_{(sol)}$$

K_{ads} values represent a strong interaction in between the adsorbed inhibitor molecule and the metal surface. In the present work (Table 4), higher value indicates better adsorption and higher inhibition efficiency. The calculated values of molecule interaction parameter (a) are negative, which indicates that repulsion exists in the adsorption layer.[38]

There are 2 modes of adsorption. In one method, protonated inhibitor molecules get adsorbed on the mild steel surface through electrostatic interactions between the inhibitor and metal surface (physisorption). In the second mode, the sulfamethoxazole molecules are chemically adsorbed (chemisorption) on the metal surface due to the following considerations:

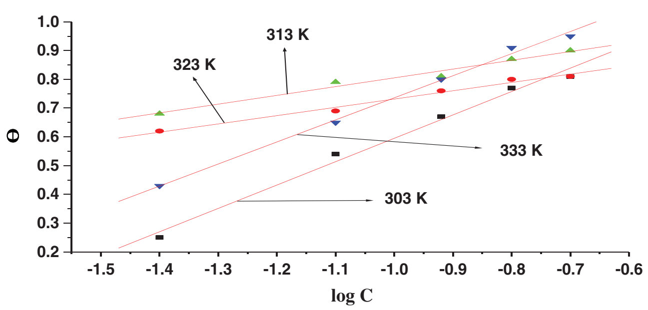

FIGURE 8 Temkin adsorption isotherm

- replacement of water molecules from the mild steel surface by sulfamethoxazole,
- the electronic interaction between π-electrons of the inhibitor molecule and vacant d-orbital of the metal surface.

If the ΔG^0_{ads} value is greater than −40 KJ/mol, the adsorption occurs through chemisorption process. The negative ΔG^0_{ads} value indicates that the adsorption process takes place spontaneously. Hence, the adsorption process involves both electrostatic interaction (π electrons of aromatic ring) and the charge transfer type bond formation from the nonbonding electrons of electroactive groups with the charged metal surface.

A plot of $\Delta G^0_{ads}/T$ v/s $1000/T$ is provided in Figure 9 with the slope equal to the standard enthalpy of adsorption (ΔH^0_{ads}). The magnitude of ΔH^0_{ads} value is lesser than −40 kJ/mol for physisorption process, whereas, for chemisorption, this value approaches −100 kJ/mol.[39,40] In our work, ΔH^0_{ads} is −82.6 kJ/mol, and it suggests that sulfamethoxazole is adsorbed on the steel surface predominately by the chemisorption method.

In this work, ΔS^0_{ads} is found to be −107 J/mol/K, and the negative sign of the value indicates a decrease in entropy during adsorption. It is reasoned that before the adsorption of inhibitor onto the steel surface, the chaotic degree of the steel surface is high. The orderly adsorption of the inhibitor molecules onto the steel surface decreases the entropy.[41]

3.4 | Activation parameters

Activation parameters of the corrosion process are used to investigate the mechanism of inhibition. Data that are obtained from the Tafel polarization measurement at 303 to 333 K temperature are used to study the activation parameters. The activation parameters are calculated from the Arrhenius equation (9) and Transition equation (10) as follows.

$$\ln vcorr = \ln A - \frac{E_a^*}{RT}, \tag{10}$$

$$\frac{\ln ucorr}{T} = \left[\ln\frac{R}{Nh} + \frac{\Delta S^*}{R}\right] - \frac{\Delta H^*}{R}], \tag{11}$$

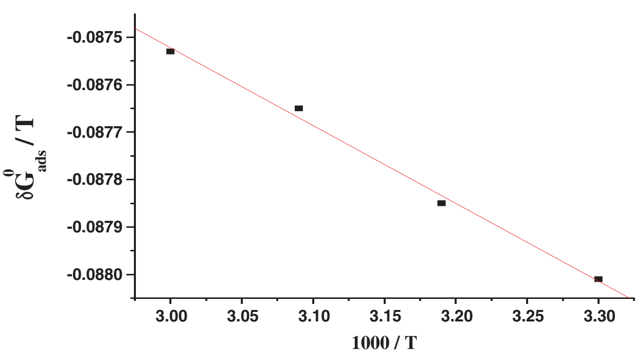

FIGURE 9 Relationship between $\Delta G^0_{ads}/T$ and $1000/T$

where A is the Arrhenius pre-exponential constant, v_{corr} is the corrosion rate, E_a^* is the apparent activation energy, R is the gas constant (8.314 KJ/Kg/K), T is absolute temperature, h is the plank's constant, and N is the Avogadro number. The ΔH^* and ΔS^* are the enthalpy and entropy change of the transition state, respectively. Figure 10 designates that the Arrhenius plot of v_{corr} against 1/T. The apparent activation energy (E_a^*) is calculated from the slope (E_a = slope × 8314 KJ/Kg/K) value, which is obtained from the straight lines of Arrhenius plot. The intercept value is used to calculate the Arrhenius pre-exponential factor (A). Both E_a^* and A values are reported in Table 5.

The enthalpy (ΔH^*) and entropy (ΔS^*) can be calculated by plotting transition plot of 1000/T against ln (v_{corr}/T) as shown in Figure 11. ΔH^* is calculated by slope values of straight lines in transition plots {$\Delta H^* = -m \times R$}, and ΔS^* are calculated by the intercept values of following sequences obtained in the transition plot {$\Delta S^* = C - \ln (R/Nh)$}. Computed ΔH^* and ΔS^* values are reported in Table 5.

While considering the activation parameters, the following discussions are explained (Table 5).

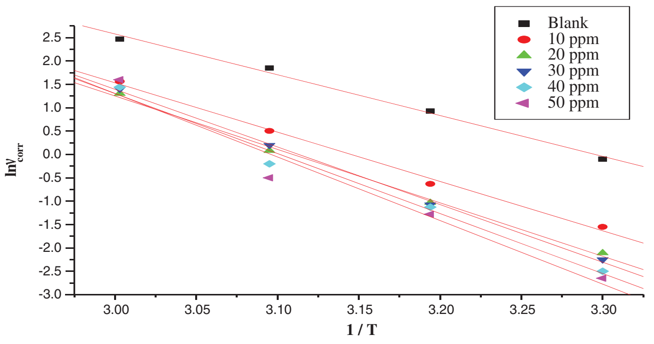

FIGURE 10 Arrhenius plot for mild steel in 1-M hydrochloric acid solution in the absence and presence of different concentrations of the sulfamethoxazole

TABLE 5 Activation parameters for mild steel in 1-M hydrochloric acid in the absence and presence of different the concentration of sulfamethoxazole

Concentration of inhibitor, ppm	E_a*, kJ/mol	A, kJ/mol	ΔH*, kJ/mol	ΔS*, J/mol/K
Blank	72.58	3.12×10^{12}	41.57	−10.1
10	87.71	2.62×10^{14}	32.95	−13.97
20	95.02	2.74×10^{15}	36.33	−12.83
30	102.5	4.70×10^{16}	31.09	−14.94
40	106.75	19.85×10^{16}	27.76	−16.3
50	113.07	1.92×10^{18}	24.36	−17.73

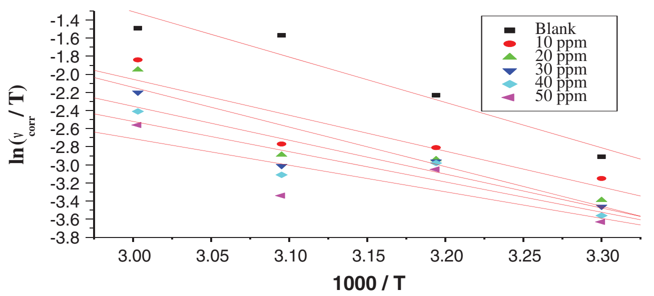

FIGURE 11 Transition plot for mild steel in 1-M hydrochloric acid solution in the absence and presence of different concentrations of the sulfamethoxazole

- According to the Arrhenius equation (9), corrosion rate affects both E_a and A values. E_a and A values increase with increases in the inhibitor concentration.
- In our study, the apparent activation energy (E_a^*) is found ranging from 72.58 kJ/mol to 113.07 kJ/mol, which indicates that sulfamethoxazole is adsorbed physically on the mild steel surface.
- The Arrhenius pre-exponential factor (A) for the corrosion process drastically changes in the presence of inhibitor than that in the absence of inhibitor. These factors are directly related to some active sites covered by the inhibitor molecule.
- A positive value of enthalpy of activation (ΔH^*) is an indication that of adsorption of sulfamethoxazole is endothermic. The obtained ΔH* value indicates the physisorption.
- The negative value of entropy of activation (ΔS^*) indicates that the activated complex in the rate determining step represents an association step. This means that a decrease in disordering takes place ongoing from the reactants to activated complex.

3.5 | SEM studies

The surface study of mild steel strip immersed in 1-M HCl solutions for 4 hours at 303 K in the absence and presence of 50 ppm of sulfamethoxazole was studied by SEM. Figure 12 shows the surface morphology of mild steel strips. The mild steel strip in the absence of sulfamethoxazole is corroded, and the surface becomes porous and rough (Figure 12A). But in the presence of sulfamethoxazole, the

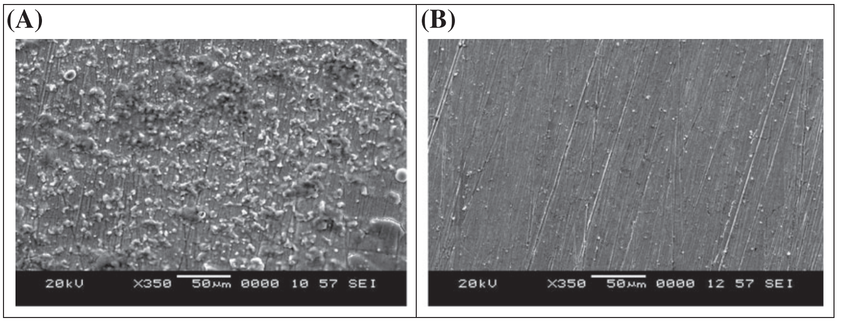

FIGURE 12 Scanning electron microscopy micrographs of A, in absence and B, in the lack of sulfamethoxazole for corrosion of mild steel in 1-M hydrochloric acid solution

surface of the mild steel strip (Figure 12B) is well protected from the attack of corrosion. These results indicate that the corrosion of mild steel in 1-M HCl solution is inhibited by sulfamethoxazole.

3.6 | Quantum chemical studies

The quantum chemical parameters of sulfamethoxazole were obtained using the DFT by a B3LYP method with 6–31G** basis set of HyperChem software. The calculated quantum chemical parameters are tabulated in Table 6, and the optimized structure and distribution of HOMO and LUMO are shown in Figure 13.

The frontier molecular orbital energies (ie, E_{HOMO}, and E_{LUMO}) plays a significant role in predicting the reactivity of a chemical species. E_{HOMO} is always associated with the electron-donating ability of a molecule. Hence, increasing values of E_{HOMO} indicate a higher tendency for the donation of electrons to an appropriate acceptor molecule with low-energy and empty molecular orbital.

TABLE 6 Quantum chemical parameters of sulfamethoxazole

Quantum chemical parameters	Sulfamethaxazole
Molecular formula	$C_{10}H_{11}O_3N_3S$
Molecular weight, amu	253.28
Total energy, a.u	−1175.20
E_{HOMO}, eV	−6.020
E_{LUMO}, eV	−0.929
$\Delta E = E_{LUMO} - E_{HOMO}$, eV	5.091
Dipole moment (μ), *D*	9.71
Ionization potential, *I*	6.020
Electron affinity, *A*	0.929
Electronegativity, χ	3.4745
Global hardness, η	2.5455
Global softness, σ	0.392
Polarizability, log*P*	1.540

The increasing amounts of E_{HOMO} facilitate the adsorption of the inhibitor. Furthermore, the negative sign of the obtained E_{HOMO} value and other thermodynamic parameters indicates physical adsorption mechanism.

Literature study discloses that a soft molecule is more reactive than a hard particle and the energy gap is related to the softness or hardness of a molecule.[42,43] In the present context, sulfamethoxazole possesses smaller energy gap and significant dipole moment. This proves it as a more reactive soft molecule having useful corrosion inhibition behavior.

Furthermore, the high molecular weight, small energy gap, low electronegativity, and high polarizability enhances effective adsorption of sulfamethoxazole on the mild steel surface, and thus, decreasing the corrosion rate of the metal.

The Mulliken charges of some atoms present in sulfamethoxazole molecule are given in Table 7. The more negatively charged particle can be adsorbed on the metal surface through the donor-acceptor type reaction.[44,45] In sulfamethoxazole, some C, N, and O atoms have a negative charge. As a result, O and N atoms and π electrons in sulfamethoxazole act as the most effective active

TABLE 7 The Mulliken charges of some atoms in sulfamethoxazole

Atom	Mulliken charge
(1)C	−0.120388
(4)C	−0.118751
(5)C	−0.205617
(7)N	−0.664800
(9)N	−0.712518
(11)N	−0.229673
(12)C	−0.194496
(14)O	−0.389698
(15)C	−0.383453
(16)O	−0.551093
(17)O	−0.531060

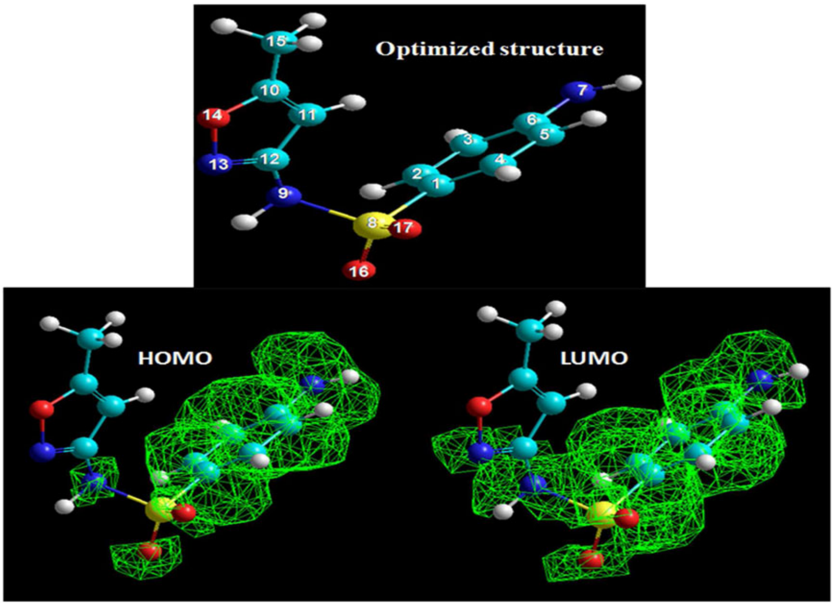

FIGURE 13 Optimized structure, distribution of HOMO and LUMO of sulfamethoxazole

centers of adsorption on the metal surface. By reviewing all these quantum results, it can be deduced that sulfamethoxazole molecule serves as an active corrosion inhibitor. Some hetero atoms and π electrons are responsible for the process of adsorption through electrostatic interaction.

4 | CONCLUSIONS

- Sulfamethoxazole acts as an active corrosion inhibitor for corrosion of mild steel in 1-M HCl solution. Inhibition efficiency increases with increase in the concentration of the inhibitor up to 90% at 50-ppm concentration.
- Tafel polarization measurement concludes that inhibitor acts as a mixed type of inhibitor.
- The EIS measurement concludes that the decrease of the electrical double layer with an increase in the concentration of inhibitor suggests that the sulfamethoxazole shows inhibitory action due to the adsorption process. The increase of R_p and inhibition efficiency indicates that sulfamethoxazole is an active inhibitor.
- Adsorption and activation parameters reveal that sulfamethoxazole shows better inhibition efficiency because of close adsorption of the inhibitor on the mild steel surface.
- Quantum chemical studies suggest that the heteroatoms like O and N atoms and also π electrons in the sulfamethoxazole are the primary active sites of adsorption.

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