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Effect of pharmaceutically active compound Omeprazole, on the corrosion of mild steel in hydrochloric acid solution

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ABSTRACT

A pharmaceutically active compound Omeprazole is used as corrosion inhibitor for mild steel corrosion in 1.0 M HCl medium were analysed by electrochemical impedance spectroscopy (EIS), potentiodynamic polarization and weight loss techniques. The inhibitor showed □ 97% inhibition efficiency at optimum concentration. Electrochemical impedance spectroscopy techniques were also used to investigate the mechanism of corrosion inhibition. Adsorption of inhibitor molecules on the mild steel surface in hydrochloric acid obeyed the Langmuir adsorption isotherm.

Keywords: Mild steel; Weight loss; EIS; Corrosion inhibition; Omeprazole.

INTRODUCTION

Some organic compounds are effective inhibitors of acid corrosion of a number of metals and alloys. The corrosion of steel is a fundamental academic and industrial concern that has received a considerable amount of attention. Acid solutions are widely used in industry, e.g., chemical cleaning, descaling and pickling, which leads to corrosive attack. The majority of the well-known inhibitors are organic compounds containing heteroatoms, such as oxygen, nitrogen or sulphur, and multiple bonds, which allow an adsorption on the metal surface [1-5]. Most of the commercial inhibitors are toxic in nature therefore development of non-toxic compounds is necessary. In the recent years, the researchers are paying more emphasis on development of green corrosion inhibitors. For this purpose there are many pharmaceutically active compounds and many plants extract have been evaluated as effective corrosion inhibitors for different metals [6-12].

Omeprazole is the commercial name of 6-methoxy-2-((4-methoxy-3,5-dimethylpyridin-2-yl) methylsulfinyl)-1*H*-benzo[*d*]imidazole. It is a proton pump inhibitor and used for short term treatment for erosion and ulceration of the esophagus caused by gastroesophagael reflux diseases and laryngopharyngeal reflux. It can be used as a maintenance therapy for long term use after initial response is obtained. The inhibition effect of Omeprazole on mild steel corrosion in hydrochloric acid solutions was studied by using the weight loss, electrochemical impedance and potentiodyanamic polarization methods.

EXPERIMENTAL SECTION

Materials

Specimens

The mild steel strips which used for the weight loss as well as electrochemical studies having the composition (wt %): C 0.076%; Mn 0.192%; Si 0.026%; Cr 0.050%; P 0.012%; Cu 0.135%; Al 0.023%; Ni 0.05%; and balance Fe. For the weight loss study the size of rectangular strips was 2.5 × 2.0 × 0.025cm. These were abraded with emery paper of 600, 800, 1000, and 1200 grades, washed thoroughly with doubled distill water, degreased with acetone and finally dried.

Inhibitor and Solutions

The compound Omeprazole used as inhibitor is available Lomac which is manufactured by Cipla LTD. Sikkim (India) shown in Figure 1. The selection of drug as corrosion inhibitor is based on following considerations. The molecule is made of planer aromatic rings of benzoimidazole, and pyridine ring and also contains S, N, O atoms and π electrons. It is easily protonated in 1.0 M HCl.

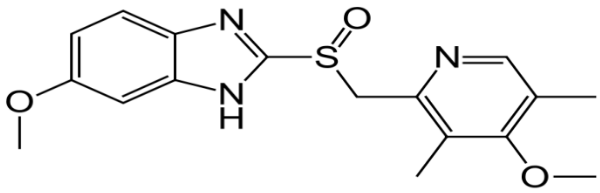


Figure 1: Molecular structure of Omeprazole.

The test solution 1.0 M HCl, was prepared by dilution of AR grade 37% HCl in distill water. The stock solution of Omeprazole was made in 1.0 M HCl by dissolving Omeprazole in ethyl alcohol. The inhibitor concentration on the weight loss and electrochemical study was taken in ppm by weight.

Weight Loss Measurements

Weight-loss measurements were carried out on the mild steel specimen size 2.5 × 2.0 × 0.025cm sizes were abraded with a series of emery paper (grade 600-800-1000-1200) and then washed with distilled water and acetone. After weighing accurately, the specimens were immersed in 100 ml of 1.0 M HCl with and without different concentrations of Omeprazole. After 3 h, the strips were taken out washed, dried and weighed accurately [13]. The mean value of the weight loss was reported.The inhibition efficiency $(I.E._{\%})$ was determined by following equation:

$$I.E._{\%} = \frac{W_0 - W_i}{W_0} \times 100 \qquad (1)$$

Where W_0 and W_i is the weight loss value in the absence and presence of inhibitor, respectively.

Electrochemical measurements
All electrochemical measurements were carried out using a Gamry Potentiostat/Galvanostat (Model G-300) with EIS software Gamry Instruments Inc., USA. The electrochemical studies were carried out using three electrodes cell assembly at room temperature with a platinum counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The mild steel strip (8 cm long stem) with the exposed surface of 1 cm^2 was used as working electrode. The EIS measurements were carried out using ac signal of 10 mV amplitude for the frequency spectrum from 100 kHz to 0.01 Hz. For the linear polarization resistance measurement, the potential of the electrode was scanned from -0.02 to +0.02V vs. corrosion potential at a scan rate of 0.125 mV s^{-1}. The Tafel polarization was carried out from anodic and cathodic potential at a scan rate of 1 mV s^{-1} to study the effect of inhibitor of mild steel corrosion. Measurements were performed by changing the electrode potential automatically from -250 to +250mV vs. corrosion potential [14].

RESULTS AND DISCUSSION

Weight loss measurements
Effect of inhibitor concentration
The inhibition efficiency values of mild steel with the addition of Omeprazole in 1.0 M HCl various are listed in Table 1and shown in Figure 2a. It can be seen from Table 1, that inhibition efficiency corrosion rate values in 1.0 M HCl solution containing Omeprazole, increased as the concentration of inhibitor increased. This result is due to fact that the adsorption amount and coverage of inhibitor on mild steel surface increases with inhibitor concentration.

Table 1: **Corrosion parameters from weight loss measurements for 3 h of immersion time for mild steel in 1.0 M HCl solution with or without different concentrations of Omeprazole.**

Concentration of Inhibitor (ppm)	Weight loss (mg cm^{-2})	Corrosion rate (mm y^{-1})	Inhibition efficiency $(I.E._{\%})$
1.0 M HCl	135	50.08	-
10	17	6.30	87.40
20	10	3.71	92.59
30	8	2.96	94.07
40	6	2.22	95.56
50	5	1.85	96.29
60	4	1.48	97.03

Effect of Temperature
The values of inhibition efficiency $(I.E._{\%})$ obtained from weight loss measurement for the optimum inhibitor concentrations in 1.0 M HCl are shown in Figure 2b. It can be seen from Figure 2b, that inhibition efficiency decreased with increasing temperature, which indicates desorption of inhibitor molecule.

Effect of immersion time
Figure 2c shows the effect of immersion time (3-12 h) at 303 K on the inhibition efficiency of Omeprazole at optimum concentration. The inhibition efficiency $(I.E._{\%})$ slightly decreased with different immersion of time at optimum concentration of inhibitor.

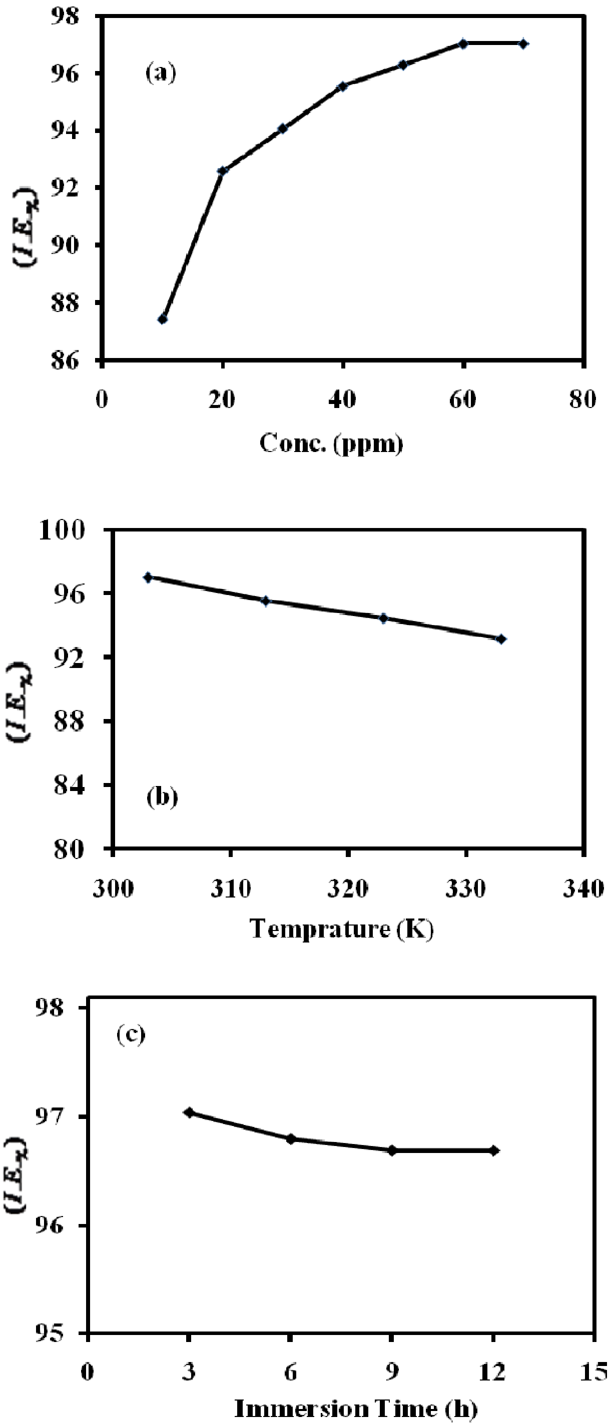


Figure 2: Variation of inhibition efficiency in 1.0 M HCl on mild steel with (a) different conc. of Omeprazole inhibitor (b) different temperatures at optimum inhibitor conc., (c) immersion time at optimum inhibitor conc.

Electrochemical studies

Electrochemical impedance spectroscopy (EIS) measurements

All of the impedance spectra obtained in the absence and in the presence of inhibitor at different concentrations in the form of Nyquist plots shown in Figure 3. The diameter of the semicircle was increased with increasing inhibitor concentration. The inhibition efficiency $(I.E._{\%})$ of the inhibitor was calculated by the charge transfer resistance values using the following equation:

$$I.E._{\%} = \frac{R_t^i - R_t^0}{R_t^i} \times 100 \quad (2)$$

Where, R_t^0 and R_t^i are the charge transfer resistance in absence and in the presence of inhibitor, respectively. The Nyquist plots are deviation from perfect circular shape; such behavior is the characteristic of solid electrodes and often referred to as frequency dispersion. This frequency dispersion can be attributed to roughness and heterogeneities of the solid surfaces. Therefore, a constant phase element (CPE) instead of capacitive element is used to get a more accurate fit of EIS data [15, 16]. The simple equivalent CPE circuit for studies has shown in Figure 4.The impedance of the CPE is given by:

$$Z_{CPE} = Y_0^{-1}(i\omega)^{-n} \quad (3)$$

where Y_0 is the CPE constant, ω is the angular frequency (in rad s-1), i^2 =-1 is the imaginary number and n is a CPE exponent which can be used as a gauge of the heterogeneity or roughness of the surface [17]. When n =1, than $Y_0 = C$ the double layer capacitance values C_{dl} derived from the CPE parameters according to:

$$C_{dl} = \frac{Y^0 \omega^{n-1}}{\sin(n\pi/2)} \quad (4)$$

where $\omega = 2\pi f$max ($f$max is the frequency at which imaginary component of complex plane plot is maximum). Table 2 reveals that R_t value increase with increasing Omeprazole concentration and however, C_{dl} value decreases much in the presence of Omeprazole. This situation was a result of the adsorption of inhibitor molecules at the metal/solution interface.

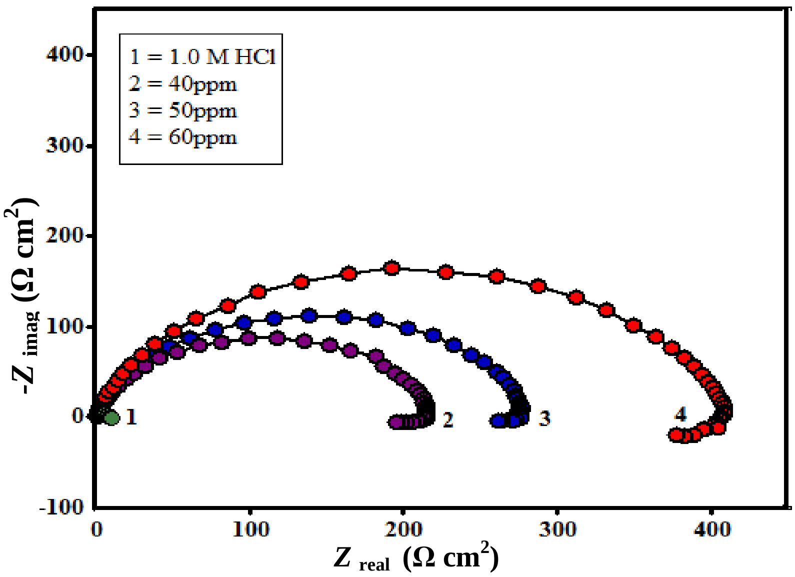


Figure 3: Nyquist plots of mild steel in 1.0 M HCl with different concentration of Omeprazole.

Table 2: Electrochemical impedance parameters for mild steel in 1.0 M HCl containing different concentration of Omeprazole.

Concentration of Inhibitor (ppm)	R_t (Ω cm^2)	Y (10^{-6} Ω^{-1} cm^{-2})	n	C_{dl} (μF cm^{-2})	Inhibition efficiency ($I.E._{\%}$)
1.0 M HCl	17.25	153.00	0.852	79.35	–
40	203.96	35.01	0.892	20.28	91.54
50	267.73	30.91	0.889	19.89	93.56
60	390.86	33.75	0.885	19.32	95.59

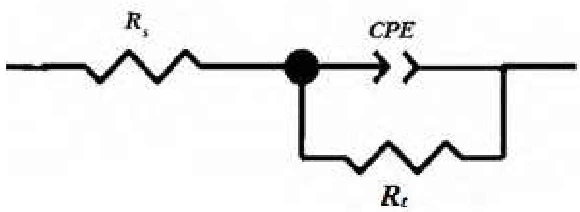


Figure 4: Electrical equivalent circuit.

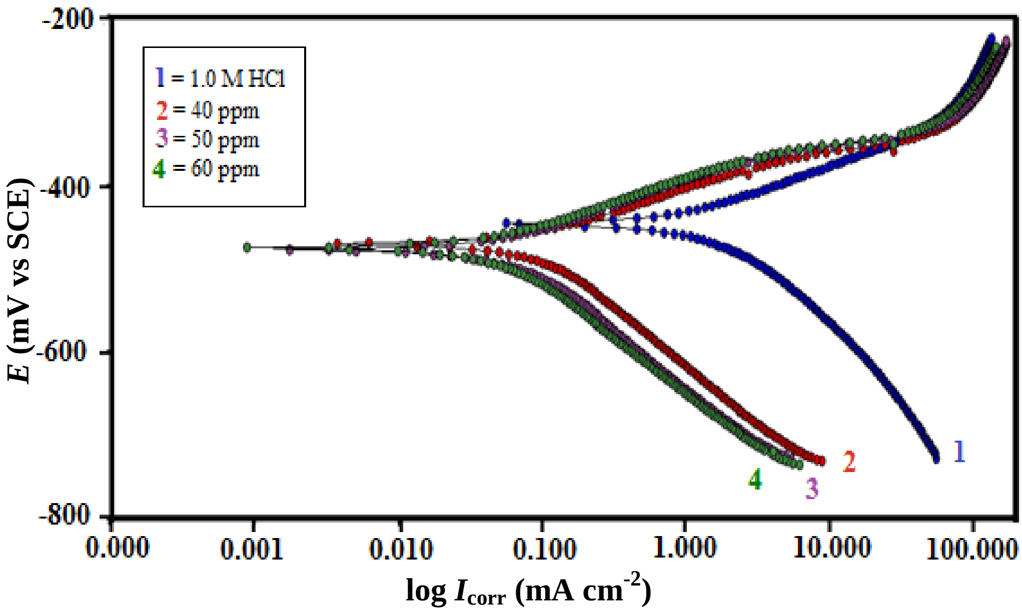


Figure 5: Tafel curves for mild steel in 1.0 M HCl in absence and presence of different concentrations of Omeprazole.

Tafel polarization

Polarization curves of mild steel in 1.0 M HCl in the absence and presence of various concentrations of Omeprazole are shown in Figure 5. The inhibition efficiency $(I.E._{\%})$ was evaluated from the calculated I_{corr} values using the relationship:

$$I.E._{\%} = \frac{I^0_{corr} - I^i_{corr}}{I^0_{corr}} \times 100 \qquad (5)$$

Where, I^{0}_{corr} and $I^{\text{i}}_{\text{corr}}$ are the corrosion current density in absence and in the presence of inhibitor, respectively [18].

The important corrosion parameters derived from these curves are listed in Table 3. It reveals that the corrosion current (I_{corr}) decreased prominently and inhibition efficiency increased with increased inhibitor concentration.

Table 3: Tafel polarization for the corrosion of mild steel in 1.0 M HCl in the absence and presence of different concentration of inhibitor.

Concentration of Inhibitor (ppm)	E_{corr} (mV vs.SCE)	β_a (mV dec^{-1})	β_c (mV dec^{-1})	I_{corr} (μA cm^{-2})	Inhibition **e**fficiency $(I.E._{\%})$
1.0 M HCl	- 458	72.50	168.10	892.00	_
40	- 470	67.50	152.50	105.00	88.23
50	- 475	72.55	137.02	67.20	92.47
60	- 478	70.00	144.10	56.40	93.68

Table 4: Linear polarization resistance for corrosion of mild steel in 1.0 M HCl containing different concentration of Omeprazole.

Concentration of Inhibitor (ppm)	R_p (Ω cm^2)	Inhibition **e**fficiency $(I.E._{\%})$
1.0 M HCl	18.20	_
40	200.01	90.90
50	260.05	93.00
60	390.00	95.33

Linear polarization resistance

The inhibition efficiencies and polarization resistance parameters are presented in Table 4. The inhibition efficiency $(I.E._{\%})$ was calculated using the relationship:

$$I.E._{\%} = \frac{R^{\text{i}}_{\text{p}} - R^{0}_{\text{p}}}{R^{\text{i}}_{\text{p}}} \times 100 \qquad (6)$$

Where, R^{0}_{p} and R^{i}_{p} are the polarization resistance in absence and in the presence of inhibitor, respectively. The results obtained from Tafel polarization and EIS showed good agreement with the results obtained from linear polarization resistance. From the Table 4, it is shown increasing in the R_{p} value and inhibition efficiency with increases in the inhibitor concentration.

Adsorption isotherm and thermodynamic parameters

Adsorption isotherm

The degree of surface coverage (θ) for different inhibitor concentrations was evaluated from weight loss measurements. The best correlation between the experimental results and isotherm functions was obtained using Langmuir adsorption isotherm. The plots of log (*C*) vs log (θ/1-θ) yield straight line with nearly unit slope showing that the adsorption of Omeprazole can be fitted to Langmuir adsorption as shown in Figure 6.

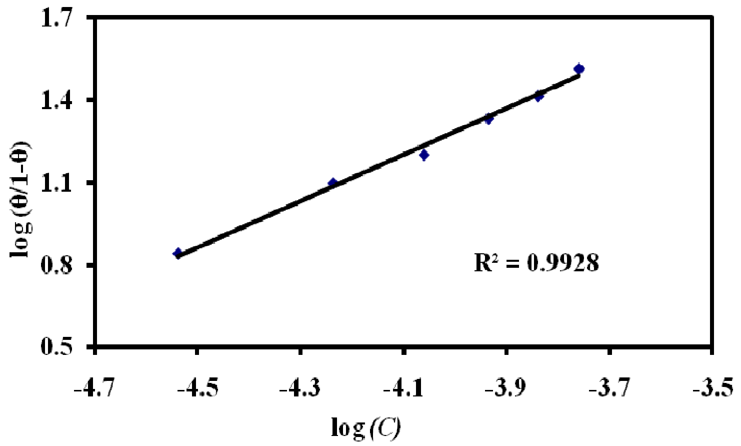


Figure 6: Langmuir adsorption isotherm plot for the adsorption.

Adsorption equilibrium constant (K_{ads}) and free energy of adsorption (ΔG^0_{ads}) were calculated using the relationships:

$$\ln K_{ads} = \frac{-\Delta G^0_{ads}}{RT} + \ln \frac{1}{55.5} \quad (7)$$

Where 55.5 is the concentration of water in solution in mol L^{-1} and R is the universal gas constant. The negative values of ΔG^0_{ads} ensure the spontaneity of the adsorption process. Generally, values of ΔG^0_{ads}, around -20 kJ mol^{-1} or lower are consistent with the electrostatic interaction and when it is around -40 kJ mol^{-1} or higher values then this is chemisorptions interaction [19,20]. The calculated ΔG^0_{ads} values are shown in Table 5, indicated that the adsorption of Omeprazole on the mild steel surface is a typical chemisorption.

Table 5: Thermodynamic adsorption parameters for mild steel in 1.0 M HCl in the presence of optimum concentration of Omeprazole at different temperatures.

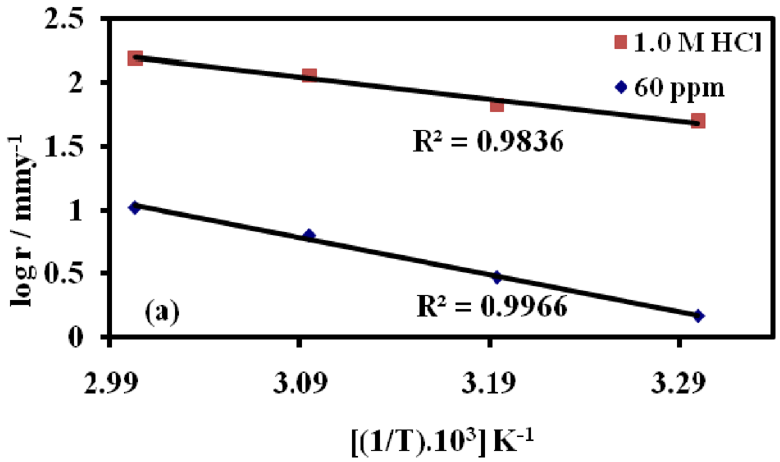
Temperature (K)	K_{ads} (10^4 M^{-1})	ΔG^0_{ads} (kJ mol^{-1})
303	28.13	- 40.72
313	22.34	- 40.98
323	21.23	- 41.67
333	21.16	- 42.33

Thermodynamic parameters

Thermodynamic parameters are important to study the inhibition mechanism. These parameters are calculated from logarithm of corrosion rate (*r*) of steel in acidic solution by using Arrhenius equation:

$$\log r = -\frac{E_a}{2.303RT} + A \quad (8)$$

Where r is the corrosion rate, E_a is the apparent activation energy, A is the pre exponential factor. Arrhenius plots of log r vs. $1/T$ for the blank and different concentrations of Omeprazole gives a straight line and slope equal to $-\frac{E_a}{2.303R}$ show in Figure 7a, from which, E_a was calculated and listed in Table 6.



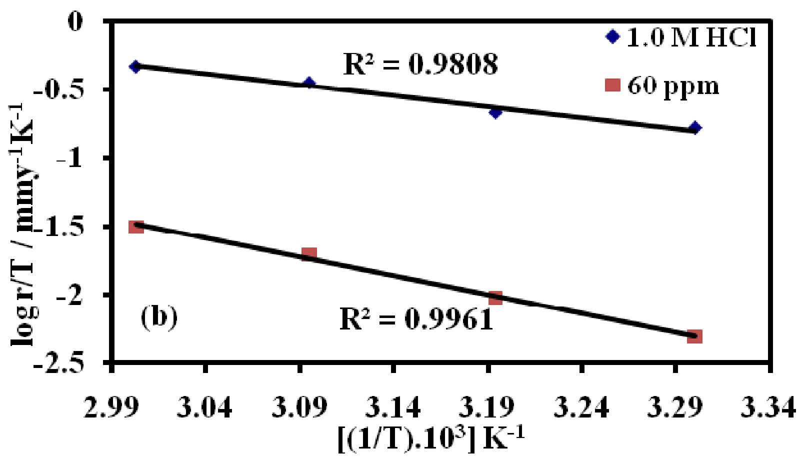


Fig. 7 (a) Adsorption isotherm plot for log *r* vs. 1/*T*. (b) adsorption isotherm plot for log *r/T* vs. 1/*T*.

From the transition state equation:

$$r = \frac{RT}{Nh}\exp(-\frac{\Delta H^*}{RT})\exp(\frac{\Delta S^*}{R}) \quad (9)$$

Where ΔH^* is the enthalpy of activation, ΔS^* is the entropy of activation, h is the Planck's constant, N is the Avogadro number, and R is the universal gas constant. The plot of log (r/T)

vs.1/*T* gives straight lines with slope equal to $-\frac{\Delta H^*}{2.303R}$ and intercept $\left(\log\frac{R}{Nh}+\frac{\Delta S^*}{2.303R}\right)$ from which, ΔH^* and ΔS^* values were calculated, and listed in Table 6. The positive sign of enthalpy reflects

Table 6: Thermodynamic activation parameters for mild steel in 1.0 M HCl in the absence and presence of different concentrations of Pantoprazole.

Concentration of Inhibitor (ppm)	E_a (kJ mol^{-1})	ΔH^* (kJ mol^{-1})	ΔS^* (J mol^{-1}K^{-1})
1.0 M HCl	32.99	30.37	- 112.69
60	55.43	52.78	- 67.56

the endothermic nature that is dissolution of steel is difficult in the presence of inhibitor. The increases of entropy, revels that an increase in disordering takes place from reactant to the activated complex [21,22]. This is the driving force for the adsorption of inhibitors onto the mild steel surface.

Mechanism of corrosion inhibition

Corrosion inhibition of mild steel in 1.0 M HCl by Omeprazole can be explained on the basis of molecular adsorption. The compound inhibits corrosion by controlling both the anodic and cathodic reactions. In acidic solutions the Omeprazole exists as protonated species. These protonated species adsorb on the cathodic sites of the mild steel and decrease the evolution of hydrogen. The adsorption on anodic sites occurs through π-electron of aromatic ring and lone pair of electrons of hetero atom, which decreases anodic dissolution of mild steel [23].

CONCLUSION

Results obtained from different methods weight loss, EIS, and polarization curves measurements were consistent and inhibition of mild steel corrosion in 1.0 M HCl solution increases with increase in the concentration of Omeprazole. The Omeprazole showed the maximum inhibition efficiency 97.03 %. Langmuir adsorption isotherm and impedance studies showed that Omeprazole inhibits through adsorption mechanism. Potentiodynamic polarization showed that Omeprazole is a mixed-type of inhibitor. All measurements showed that the Omeprazole has good inhibition properties for the corrosion inhibition of mild steel in 1.0 M HCl solution.

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