

Pharmaceutically Active Compound as Corrosion Inhibitor for Mild Steel in Acidic Medium

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Pharmaceutically active compounds have become important and environmentally acceptable, readily available source as corrosion inhibitors. Most of the drugs having the hetero atoms N, S and O give higher inhibition efficiency and are potentially good corrosion inhibitors. The large molecular size and the presence of unsaturation also provide the adsorption centers for the inhibition process in many drug systems. This study investigates the corrosion inhibition of mild steel in aggressive media using (6*R*,7*R*,*Z*)-7-(2-(2-aminothiazol-4-yl)-2(methoxyimino)acetamido)-3-((1-methylpyrrolidinium-1-yl)methyl)-8-oxo-5-thia-1-aza-bicyclo[4.2.0]oct-2-ene-2-carboxylate (AMC) by using the various corrosion monitoring techniques such as weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy. All the techniques used for the studies shows the increase in inhibition efficiency and decrease in the corrosion rate by increasing the inhibitor concentration. The mechanism of inhibition is also proposed

Keywords: Mild Steel; Corrosion inhibition; Electrochemical impedance spectroscopy, Polarization, Adsorption

1. INTRODUCTION

Steel is most important engineering and construction material for various industries due to its excellent mechanical properties [1]. Acids are widely used for the pickling, cleaning, descaling and acidization of oil well. The addition of the inhibitors secures the metal from an acid attack effectively. The applicability of the organic compounds as corrosion inhibitors for the metals has been in practice. Most commonly used organic inhibitors contain nitrogen, sulphur and oxygen atoms [2,3]. It is well known that generally organic compounds inhibit corrosion by the adsorption on the metal surface. Adsorption of these inhibitors depends on the electronic structure of the inhibiting molecules, aromaticity, and electron density at donor sites, presence of functional groups, molecular size and

weight [4-6]. Most of the organic compounds are toxic in nature for the environment as well as human being [7]. Due to increasing awareness towards environment and the negative effects of the chemicals, researchers are attracted to the less toxic pharmaceutically active compounds or commonly used drugs [4, 8-12] and the plant extracts [7].

In view of the use of the drugs and pharmaceutically active compounds, the present study deals with the investigation of inhibitive properties of (6*R*,7*R*,*Z*)-7-(2-(2-aminothiazol-4-yl)-2(methoxyimino)acetamido)-3-((1-methylpyrrolidinium-1-yl)methyl)-8-oxo-5-thia-1-azabicyclo[4.2.0]oct-2-ene-2-carboxylate (AMC) against mild steel in hydrochloric acid environment using the electrochemical impedance spectroscopy (EIS), potentiodynamic polarization and weight loss techniques. This compound AMC is commonly known as Cefepime having molecular formula $C_{19}H_{24}N_6O_5S_2$ and molecular mass $480.56 \text{ g mol}^{-1}$. It is generally used to treat moderate-severe nosocomial pneumonia infection caused by multi resistant microorganisms. Chemical structure of the AMC is shown in Figure 1.

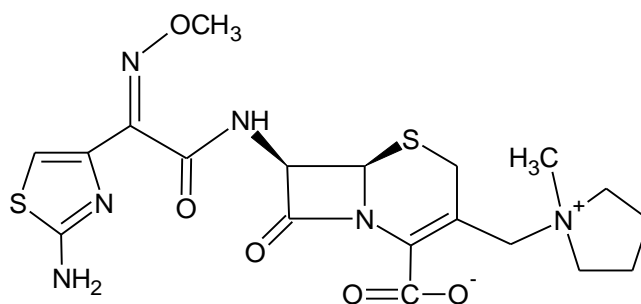


Figure 1. Chemical structure of AMC

2. EXPERIMENTAL

2.1. Inhibitor

Stock solution of AMC was made in 10:1 ratio of water: ethanol mixture by volume to ensure the solubility. All the experiments were carried out using this stock solution.

2.2. Corrosion measurements

Prior to all measurements, the mild steel specimens having composition (wt %): C 0.14, Mn 0.035, Si 0.17, S 0.025, P 0.03 and balance Fe were abraded successively with emery papers from 600 to 1200 mesh in grade. The specimen were washed with double distilled water, degreased with acetone and dried in hot air blower. After drying, the specimen were placed in desiccators and then used for the various experiments. The aggressive solution of 1M HCl was prepared by the dilution of analytical grade hydrochloric acid (37%) with double distilled water and all the experiments were carried out in the unstirred solutions.

The weight loss study was carried out on mild steel strips of 5.0cm x 2.0cm x 0.025cm dimension. The electrochemical measurements were carried out on mild steel strips with the dimension 1.0cm x 1.0cm exposed with a 7.5 cm long stem (coated by the commercially available lacquer).

2.3. Electrochemical impedance spectroscopy

The EIS tests were performed at 308±1K in a three electrode assembly. A saturated calomel electrode was used as a reference and a 1 cm² platinum foil was used as counter electrode. All the potentials were measured versus SCE. The electrochemical impedance spectroscopy measurements were performed using a Gamry instrument potentiostat / galvanostat with a Gamry framework system based on ESA 400 in a frequency range 10⁻²Hz – 10⁵ Hz under potentiodynamic conditions with amplitude of 10 mV peak to peak, using AC signal at E_{corr}. Gamry applications include software DC105 for corrosion and EIS300 for EIS measurements and Echem analyst version 5.50 software packages for data fitting. The experiments were carried out after 30 minutes of immersion in the test solution without deaeration and stirring.

The inhibition efficiency of the inhibitor was calculated from the charge transfer resistance values using following equation:

$$\mu_{R_t} = \frac{(1/R_t^o) - (1/R_t^i)}{(1/R_t^o)} \times 100 \quad (1)$$

where R_t^o and R_t^i are the charge transfer resistances in the absence and in presence of inhibitor respectively.

2.4. Potentiodynamic polarization

The electrochemical behavior of mild steel sample in inhibited and non-inhibited solution was studied by recording anodic and cathodic potentiodynamic polarization curves. Measurements were performed in the 1M HCl solution containing different concentrations of the tested inhibitor by changing the electrode potential automatically from -250 to +250mV versus corrosion potential at a scan rate of 1mVs⁻¹. The linear Tafel segments of anodic and cathodic curves were extrapolated to corrosion potential to obtain corrosion current densities (I_{corr}).

The inhibition efficiency was evaluated from the measured I_{corr} values using the following relationship:

$$\eta_p = \frac{I_{corr}^o - I_{corr}^i}{I_{corr}^o} \times 100 \quad (2)$$

where I_{corr}^o and I_{corr}^i are the corrosion current densities in the absence and presence of inhibitor, respectively.

2.5. Weight loss measurements

Weight loss or gravimetric measurements were performed on mild steel sample by immersing it in the absence and presence of different concentrations of AMC at 35°C for 3h duration in 1M HCl solution. The inhibition efficiency (%) was determined using the following equation:

$$\eta_{WL} = \frac{W_o - W_i}{W_o} \times 100 \quad (3)$$

where W_o and W_i are the weight loss values in the absence and presence of inhibitor. The weight loss measurements were also carried out at different time intervals, different concentrations of the acid solution and at different temperatures.

3. RESULTS AND DISCUSSIONS

3.1. Electrochemical impedance spectroscopy (EIS)

EIS measurements were carried out to study the kinetics of the electrode process and the surface properties of the system. Nyquist and Bode plots are presented in the Figure 2 a-c for mild steel corrosion in 1M HCl in the absence and presence of the different concentrations of AMC. It is clear from Figure 2a that the impedance spectra is not perfect semicircle and depressed capacitive loop is the result of the surface heterogeneity [6, 13-14]. Figure 2b and c suggest one time constant Bode plot. The phase angle at higher frequencies is attributed to anticorrosion performance. The more negative the phase angle, the more capacitive the electrochemical behavior [10, 15, and 16].

The data originated from the EIS study were analyzed using the equivalent circuit for iron / acid interface model described elsewhere [17]. The values of the solution resistance (R_s), charge transfer resistance (R_t), magnitude of the constant phase angle (Y_o) and deviation parameters (n) obtained from the fitting of the recorded data with the equivalent circuit are reported in Table1. Increase in the R_t values is attributed to the formation of the protective film of the inhibitor on metal / solution interface resulting in the increase in the inhibition efficiency by increasing the AMC concentration. Deviation in the values of n from unity suggest that the iron / steel system does not show the ideal capacitor behavior due to the roughness and /or uneven current distributions on the electrode surface resulting in frequency depression [18,19].

Double layer capacitance (C_{dl}) values were derived from the CPE parameters by using following equation [20] and listed in table1.

$$C_{dl} = (Y_o \cdot R_t^{1-n})^{1/n} \quad (4)$$

The values of the double layer capacitance decreased with increase in the AMC concentration. C_{dl} is inversely proportional to the thickness of the protective layer. So the decrease in the double layer

capacitance by increasing the inhibitor concentration shows increase in the thickness of protecting layer resulting in the increase in the inhibition efficiency.

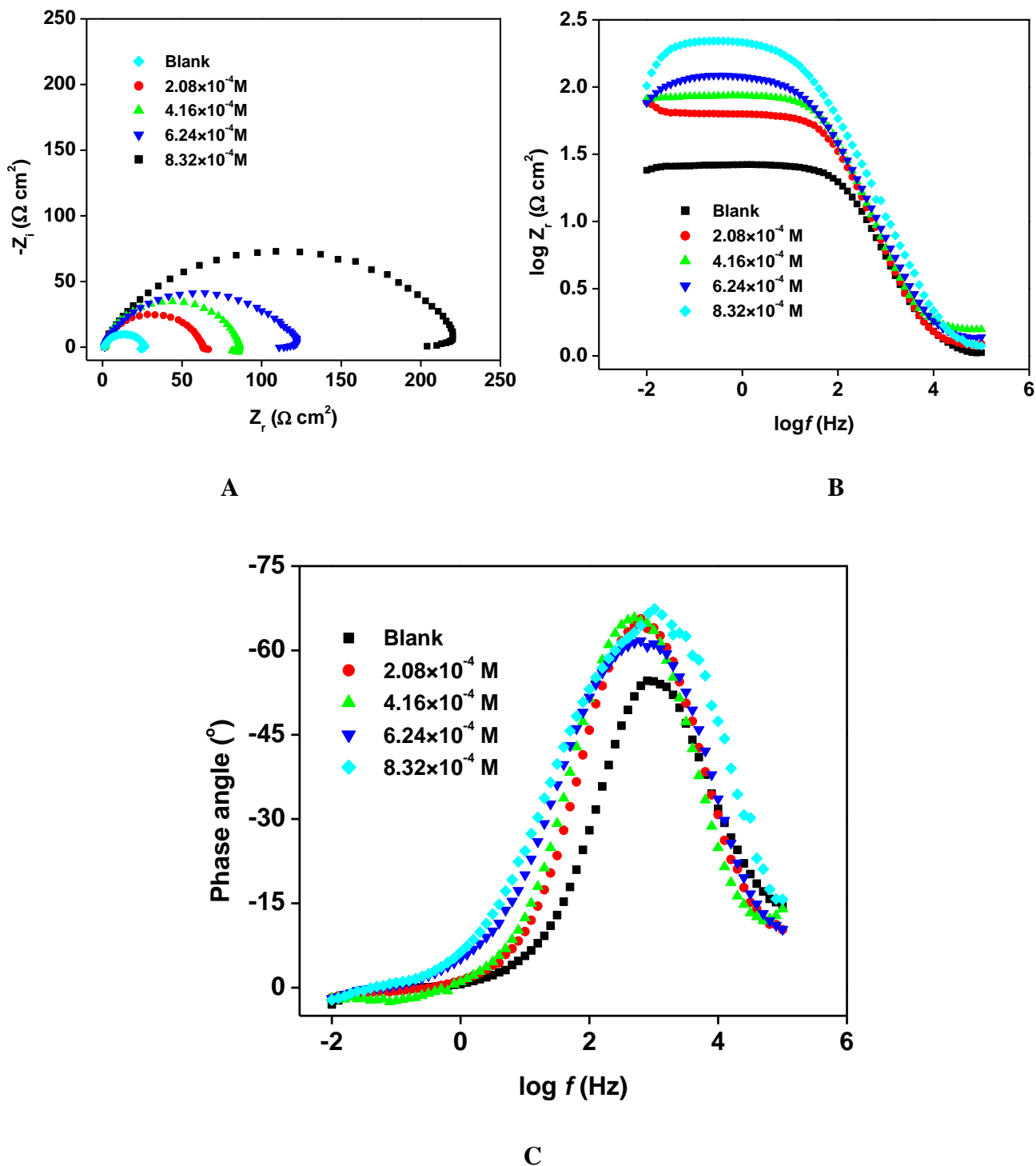


Figure 2. Electrochemical impedance plots (a) Nyquist plot (b) Bode magnitude plot (c) Phase angle plot: for mild steel in absence and presence of different concentrations of AMC.

Table 1. Electrochemical impedance spectroscopy parameters for mild steel in 1M HCl in the absence and presence of different concentrations of AMC.

Inh. Conc. ($\times 10^{-4}$ M)	R_s (Ω cm ²)	R_t (Ω cm ²)	n	Y_o ($\times 10^{-6}$ Ω^{-1} Cm ⁻²)	C_{dl} (μ F cm ⁻²)	η_{Rt} (%)
Blank	0.966	26.43	0.883	162.1	78.70	-
2.08	1.140	62.90	0.869	134.3	65.39	57.98
4.16	1.503	84.70	0.803	97.6	30.09	68.80
6.24	1.215	119.00	0.785	86.2	24.50	77.79
8.32	0.970	216.00	0.790	72.9	24.18	87.76

3.2. Potentiodynamic polarization measurements

The potentiodynamic polarization measurements were carried out to study the kinetics of cathodic and anodic reactions. Figure 3 shows the cathodic and anodic polarization curves of mild steel corrosion in 1M HCl without and with different concentrations of AMC. Electrochemical parameters namely corrosion potential (E_{corr}), corrosion current (I_{corr}), anodic and cathodic tafel slopes (b_a and b_c) obtained from the extrapolation of the polarization curves are listed in Table 2.

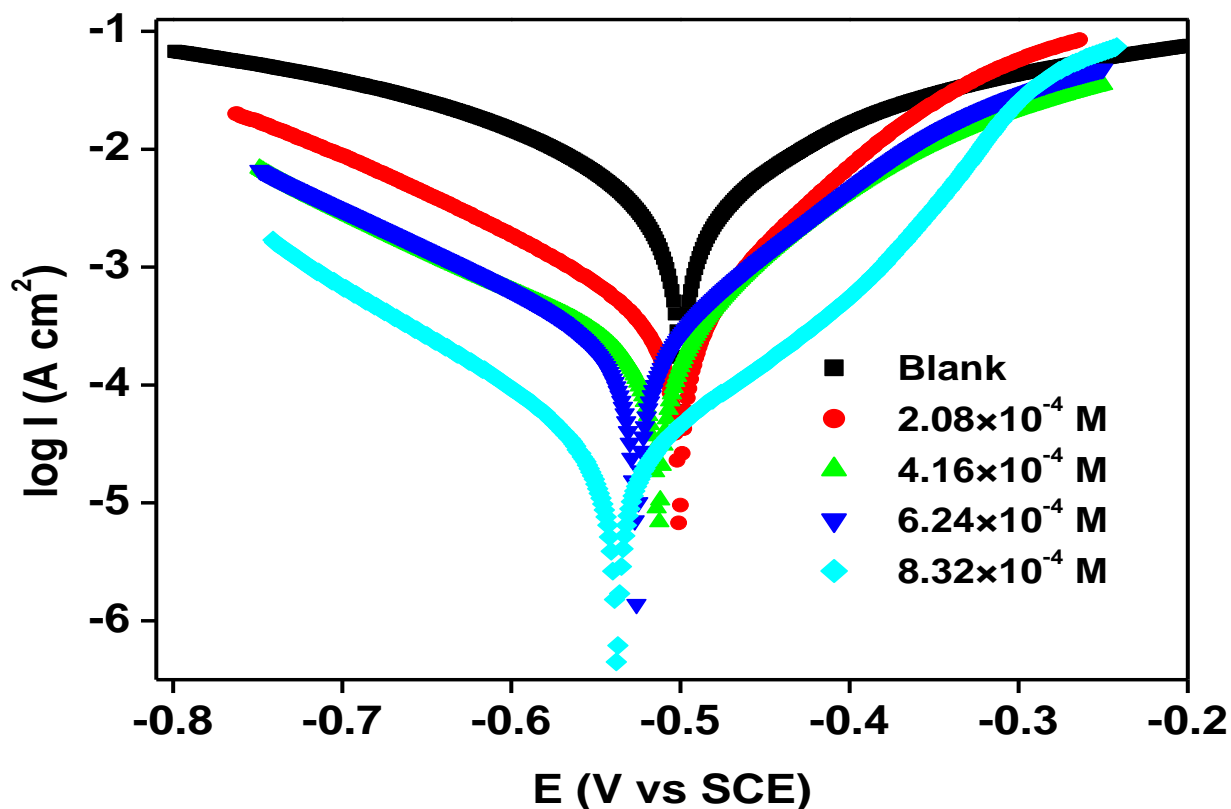


Figure 3. Tafel polarization curves for corrosion of mild steel in 1M HCl in the absence and presence of different concentrations of AMC.

Table 2. Potentiodynamic polarization parameters for the mild steel corrosion in 1M HCl in the absence and presence of different concentrations of AMC.

Inh. Conc. ($\times 10^{-4}$ M)	$-E_{\text{corr}}$ (mV vs SCE)	b_a (mV/dec)	b_c (mV/dec)	I_{corr} ($\mu\text{A cm}^2$)	η_p (%)
Blank	503	63.2	115.0	1275	-
2.08	509	76.7	135.5	435	65.88
4.16	510	84.5	155.2	295	76.86
6.24	520	81.9	140.4	201	84.24
8.32	540	73.0	129.1	156	87.77

It is evident from Table 2 that the value of the b_c changed with increase in AMC concentration which indicates the influence of the inhibitor on the hydrogen evolution reaction. Whereas the shift in the b_a values suggests that the chloride ion and/or inhibitor molecules adsorbed on the metal surface and alter the anodic dissolution. The I_{corr} values decreases with increase in the inhibitor concentration resulting the increase in the adsorption of the inhibitor molecule on to the metal surface. Inhibition efficiency calculated from I_{corr} values listed in Table 2 suggests the effectiveness of the inhibitor with increase in concentration.

It is reported by different workers [21,22] that, if the displacement in corrosion potential is more than 85 mV with respect to blank solution, the inhibitor can be considered as a cathodic or anodic type. In the present study, maximum displacement was 37 mV with respect to the corrosion potential of the uninhibited sample which indicates that the AMC is a mixed-type inhibitor. The results obtained from the polarization studies shows good agreement with the results obtained from the EIS studies.

3.3. Weight loss study

The values of weight loss, inhibition efficiency (η_{WL}), corrosion rate and surface coverage (θ) obtained from the weight loss measurements at different concentrations of AMC in 1M HCl at 308 K are listed in Table3.

The variations in the inhibition efficiency and corrosion rate with AMC concentration shown in Figure 4 suggest that AMC inhibits mild steel at all the concentration range used in the study. Maximum inhibition efficiency was reported at 8.32×10^{-4} M concentration of AMC. It is evident from the table that the corrosion rate decreases and inhibition efficiency increases with increase in AMC concentration.

Table 3. Corrosion parameters for mild steel in aqueous solution of 1M HCl in the absence and presence of different concentrations of inhibitor from weight loss measurements at 308K.

Inh. Conc. ($\times 10^{-4}$ M)	Weight loss (mg cm^{-2})	η_{WL} (%)	Corrosion Rate (mmy^{-1})	Surface coverage (θ)
Blank	16.75	-	62.23	-
2.08	6.10	63.58	22.66	0.64
4.16	4.18	75.04	15.53	0.75
6.24	2.51	85.01	7.99	0.85
8.32	1.53	90.86	5.68	0.91

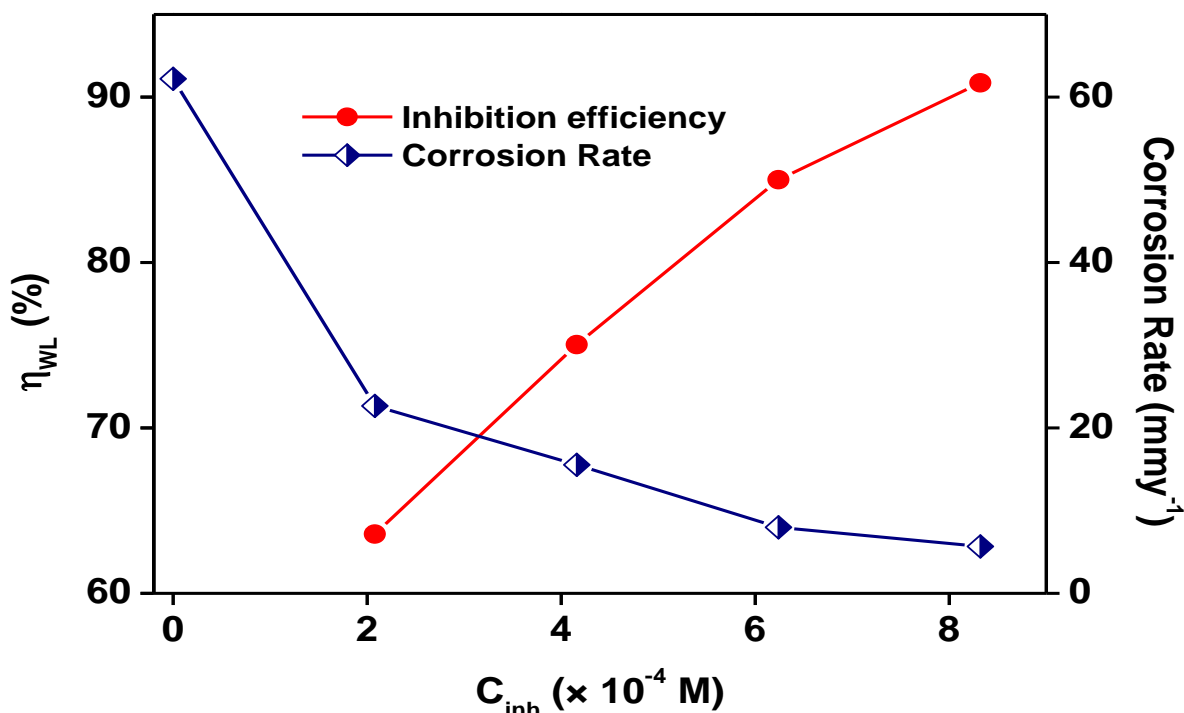


Figure 4. Variation of inhibition efficiency and corrosion rate in 1M HCl on mild steel surface without and with different concentrations of AMC.

3.4. Adsorption isotherm

Adsorption of the inhibitor molecule depends mainly on the charge and the nature of metal surface, electronic characteristics of metal surface, adsorption of solvent and other ionic species, on the electrochemical potential at solution interface. The adsorption isotherm study describes the adsorptive behavior of inhibitor in order to know the adsorption mechanism of inhibitor to the metal surface. The most frequently used adsorption isotherms are Langmuir, Temkin, Frumkin, Freundlich isotherms. The Langmuir adsorption isotherm was found to provide the best description of the adsorption behavior (Figure 5) with the regression coefficient almost unity (0.99805). This suggests that the Langmuir adsorption isotherm provides the best description for the adsorption of AMC on mild steel surface.

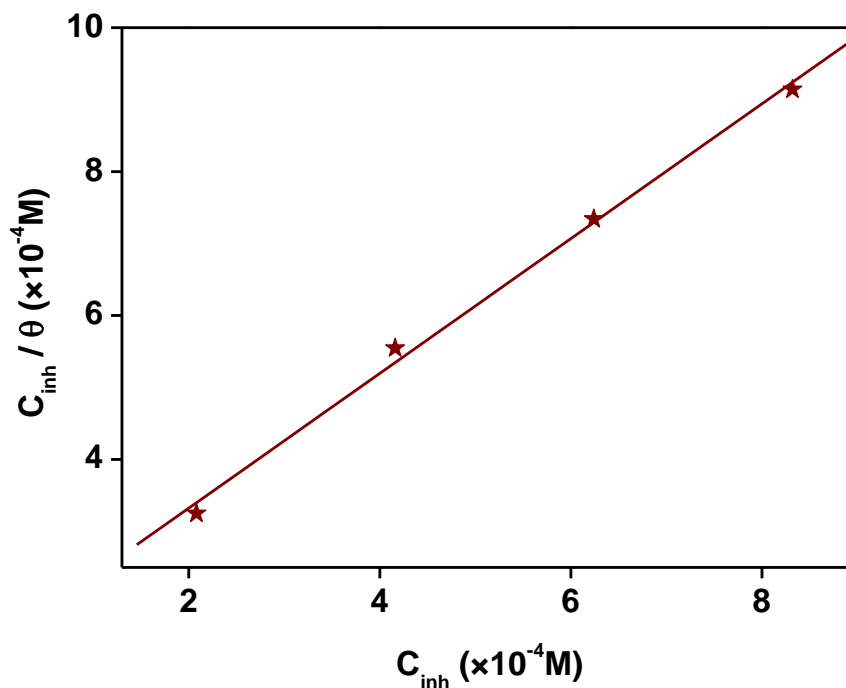


Figure 5. Langmuir's adsorption isotherm plot for the adsorption of AMC in 1M HCl on the surface of mild steel

3.5. Mechanism of Inhibition

Corrosion inhibition of mild steel in 1M HCl by AMC may be explained on the basis of molecular adsorption on the mild steel surface. Organic compounds adsorbed on the metal surface by electrostatic interaction between the charged molecule and charged metal, interaction of π electron with the metal and interaction of unshared pair of electrons in the molecule with metal [23, 24]. The inhibition efficiency of the inhibitor depends on many factors such as the adsorption centers, mode of interaction, charge density, molecular size and the formation of metallic complexes. Inhibitor molecule is protonated in the acid medium. Thus they become cation and exist in the equilibrium with the corresponding molecular form. It is well known that steel bears positive charge in acid solution [25]. The protonated inhibitor molecule could be attached to the mild steel surface by electrostatic interaction between Cl^- and protonated AMC molecule [26].

4. CONCLUSIONS

All the measurements show that the AMC shows excellent inhibition properties against mild steel in hydrochloric acid solution. EIS measurements indicate that the inhibitor performance increases with increase in concentration due to the adsorption of molecule on the metal surface. Potentiodynamic polarization measurements showed that the inhibitor acts as mixed-type inhibitor. The inhibition efficiencies determined by electrochemical impedance spectroscopy, polarization measurements and

weight loss study are in good agreement. The inhibitor follows the Langmuir adsorption isotherm on the metallic surface.

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