Comparative Study of Amoxicillin and Sulphadoxine as Corrosion Inhibition Behaviour on Mild Steel in 1M Sulfuric Acid Medium

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Abstract: The corrosion study of mild steel in 1 M sulfuric acid solution has been done in absence and in presence of inhibitors- Amoxicillin and Sulphadoxine in 1M sulfuric acid solution. The comparative study of corrosion inhibition tendencies of these inhibitors reveals, Amoxicillin is better inhibitor than Sulphadoxine. The corrosion study of mild steel in 1M sulfuric acid solution in absence and in presence of these inhibitors have been done by Weight loss, Potentiodynamic polarization and Open Circuit potential techniques. The result hold mutually in good agreement with these techniques. The surface analysis has been done by Scanning Electron Microscopic Analysis is in accordance to the result obtained by above mentioned techniques. It also obeys the Langmuir adsorption isotherm.

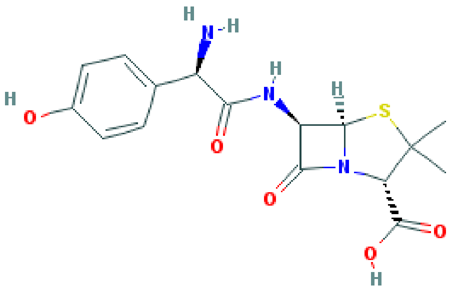
Keywords: Corrosion, Inhibitor, Mild steel, Potential, Polarization, Adsorption.

Introduction

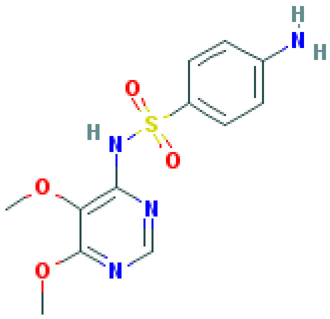
Corrosion of mild steel may cause physical damage, destruction, loss of life or drastic change in environment; therefore, it is today's need to study corrosion and its inhibition mechanism. The metal dissolution may occur by the use of sulfuric acid solution during acid pickling, acid descaling and industrial cleaning etc. consequently, unwanted loss of metal takes place. The nascent hydrogen is formed during the process of acidic corrosion which gets dissolved in metal in atomic state, consequently the ductility of metal decreases[1, 2]. Aside from acid corrosion, other factors like temperature variation, tidal action of seawater, man-made pollutants, sufficient oxygen and ultraviolet rays causes severe corrosion damage[3]. Corrosion of metal cannot be totally eliminated, but its intensity can be reduced by the selection of appropriate inhibitor material. There are various techniques like ceramic oxide film formation, metal coating, sol-gel method and addition of inhibitor in aggressive corrosive medium for control of corrosion[4]. Addition of inhibitor in corrosive medium is a most reliable method since it is cost effective and least consumption of inhibitor which avoids the wastage. Many inorganic and organic compounds show good corrosion inhibition effect, but most of them are toxic, expensive and non-biodegradable. The cost, health issues and environmental regulation restrictions have made researchers more focus on the development of heterocyclic aromatic organic compounds used as good corrosion inhibitors[5]. Most of the organic inhibitors are adsorbed on the metal surface and forming a compact barrier film[6]. Organic compounds containing heteroatom such as nitrogen, sulfur, oxygen, phosphorous etc. and aromatic ring, double bond and triple bond serves as good corrosion inhibitors especially more effective in sulfuric acid medium[7-10]. The efficiency of inhibitor depends on the number of heteroatoms, lone pair of electrons and p-electrons present in alkenes, alkynes and aromatic rings of compounds[11-15]. Nitrogen containing compounds are more effective in hydrochloric acid, whereas sulphur containing compounds are sometimes preferred for sulfuric acid[24]. Organic inhibitors containing both N and S atoms have been investigated more effective[16-18].

In present research on pharmaceutically active inhibitors such as Amoxicillin and Sulphadoxine attention is paid to the relationship between them and their adsorption behaviour on mild steel surface in acid medium. It has been observed that the adsorption is depends mainly on the electronic and structural properties such as functional group, steric factor, aromaticity, electron density on the donor atoms and also energy gap between Highest Occupied Molecular Orbitals (HOMO) and Lowest Unoccupied Molecular Orbitals (LUMO) of donor atom in inhibitor molecule[25,26]. It is found that the conclusions drawn by conventional weight loss method also agree with the open circuit potential and Potentiodynamic polarization methods.

Inhibitors: The organic compounds used as inhibitors in the present investigation are of AR grade. All the compounds procured from different chemical companies and used as received. Chemical structures of these compounds are shown in Figure 1A & B as follows:



(A) Amoxicillin



(B) Sulphadoxine

Figure 1: Molecular structure of: (A) Amoxicillin (B) Sulphadoxine

Methods

1) **Weight loss measurement:** An average value of triplet readings of weight loss measurements of mild steel in 1M sulfuric acid after immersion time of 24 hrs. at 28^0C ±1 ^{0}C were taken with and without different concentrations of inhibitor.

2) **Open Circuit Potential (OCP) Measurement:** Corrosion behavior of mild steel in 1M sulfuric acid and with different concentration of inhibitors in 1M sulfuric acid solution was studied by monitoring the changes in corrosion potential (E_{corr}) with time, 2 hrs of each experiment to obtained steady curve.

3) **Potentiodynamic Polarization Measurement:** Potentiodynamic polarization curves of mild steel in different concentrations of inhibitors are depicted in figure 4.

Result and discussion

Weight loss measurement: The data obtained is shown in Table-1. It is revealed that corrosion inhibition increases as the concentration of Amoxicillin increases. 500 ppm solution exhibits the best performance of about 91 %. It may form a uniform protective film on the surface of mild steel[27,28]. However, inhibition efficiency of amoxicillin at 400ppm decreases and observed less than 300 ppm solution. Sulphadoxine its best performance at 400 ppm solution. Corrosion inhibition efficiencies (IE) were calculated according to previous report.

$$IE\ \% = [W_o - W] / W_o \times 100$$

Where, W and W_o are the weight loss of mild steel in presence and absence of inhibitor respectively.

Table 1: Weight loss data for inhibition of corrosion of mild steel exposed to 1M sulfuric acid with different concentration of Amoxicillin & Sulphadoxine.

Inhibitor	Conc. (ppm)	Weight Loss (mg)	Surface coverage (θ)	Inhibition Efficiency (IE %)
Control	-	283	-	-
(A) Amoxicillin	10	94	0.6678	66.78
	100	91	0.6784	67.84
	200	54	0.8091	80.91
	300	34	0.8798	87.98
	400	40	0.8586	85.86
	500	23	0.9187	**91.87**

(B) Sulphadoxine	10	114	0.5971	59.71
	100	111	0.6077	60.77
	200	91	0.6784	67.84
	300	105	0.6289	62.89
	400	83	0.7067	**70.67**
	500	97	0.6572	65.72

Adsorption isotherm: Adsorption isotherms are often used to demonstrate the adsorbent performance on the substrate which describes the relation between surface coverage, θ and bulk concentration[29]. It is observed that the surface coverage values, θ (defined as θ = IE%/100) increases with increasing inhibitor concentrations as a result of more adsorption of inhibitor molecules on the surface of mild steel takes placed (Table 1). It is noticed that Amoxicillin shows maximum inhibition at 500 ppm solution; where as Sulphadoxine shows maximum inhibition at 400 ppm solution. Adsorption behavior of all these inhibitors obeys the Langmuir's adsorption isotherm as it gives a straight line when graph of log θ/(1-θ) is plotted against log C as shown in Figure 2. The protective layer of inhibitor on the mild steel is the combination of both, physisorption and chemisorption.

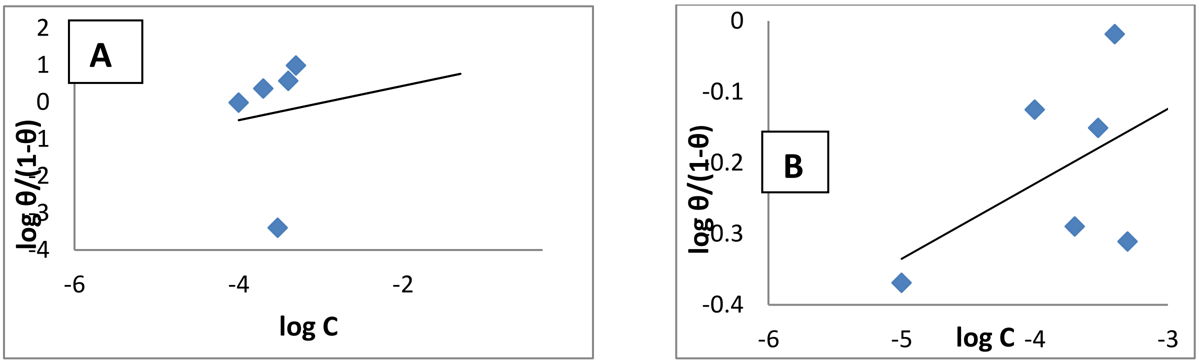


Figure 2: Adsorption isotherm of inhibitors: (A) Amoxicillin, (B) Sulphadoxine

OCP Measurement: It is observed that as the working electrode (mild steel) immersed in to the studied solution, the potential immediately increases for few seconds and then decreases and again increases. Then gradually attain steady state up to the end of the experiment as shown in Figure 3. This sudden increase in potential may be due to the oxygen present on the surface of mild steel which in few seconds comes out in the form of baubles and then the exposed surface of the substrate starts corroding consequently the potential decreases which shows corrosion of mild steel. After few seconds as the molecules of inhibitor start adsorption on the surface of mild steel, potential again start increasing and within 30 min. it achieved equilibrium and obtained a steady curve of corrosion potential throughout the experiment. Figure 3 show that OCP in absence of inhibitor has more negative (lower potential) value than in presence of inhibitor. It is seen that curves go towards the positive direction as the concentration of inhibitors increases. This indicated the decrease in the rate of corrosion of mild steel in presence of inhibitor due to the formation of protective film on the surface of mild steel.

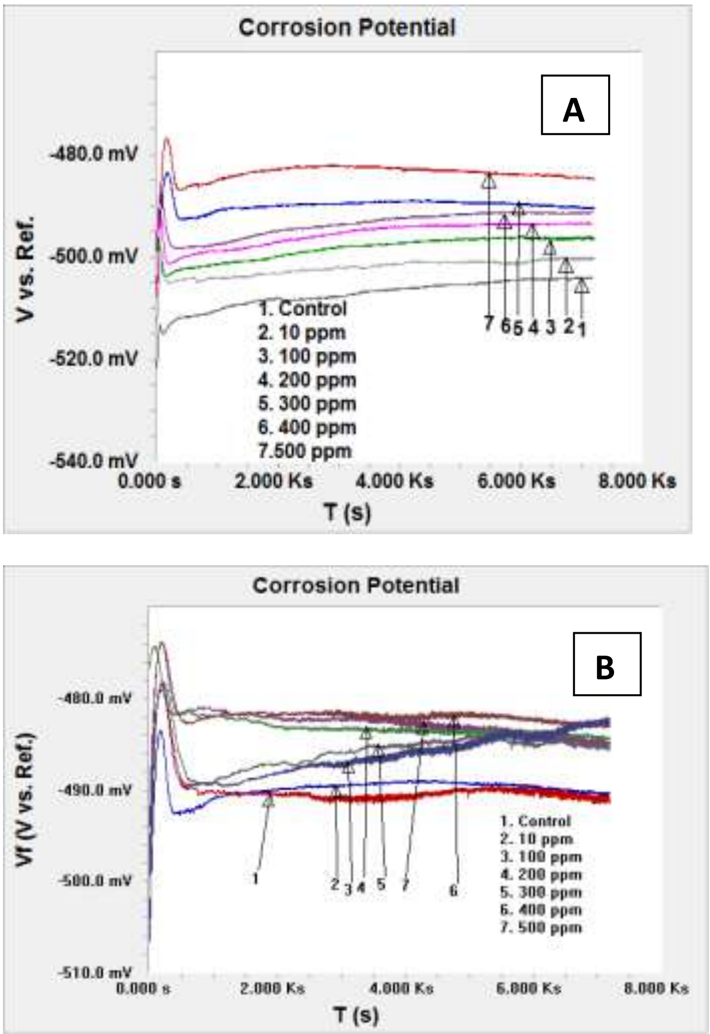
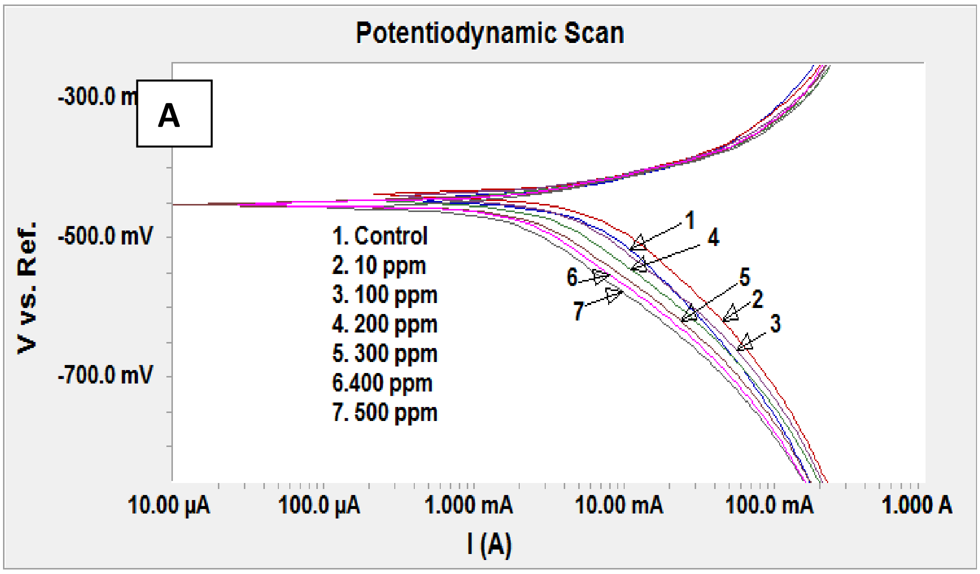


Figure 3: Open circuit potential of mild steel with different concentration of (A) Amoxicillin, (B) Sulphadoxine

Potentiodynamic Polarization Measurement: Potentiodynamic polarization curves of mild steel in different concentrations of inhibitors are depicted in figure 4. It is seen that cathodic curves are comparatively more polarized than anodic curves. The classification of compounds evidenced that when the change in E_{corr} value is more than 85 mV, the compound is an anodic or a cathodic type of inhibitor[30,31]. But, the displacement of potential observed of these inhibitors is less than 85 mV. Therefore, these inhibitors should be mixed type of inhibitors but are predominantly cathodic. The cathodic portion indicating that the hydrogen evolution reaction is activation controlled. The results demonstrate that the hydrogen reduction inhibited and thus the inhibition efficiencies increase. The inhibition action is pronounced with increase in inhibitor concentration. Thus, Amoxicillin show inhibition efficiency 93 % at 500 ppm solution. Nevertheless, Sulphadoxine shows its best performance of about 71% at 400 ppm solution. Corrosion efficiency was calculated by using the following equation:

$$\text{Inhibition Efficiency, (IE \%)} = 100(i_0 - i) / i_0$$

Where, i_0 and I are the corrosion current densities in the absence and presence of inhibitor respectively.



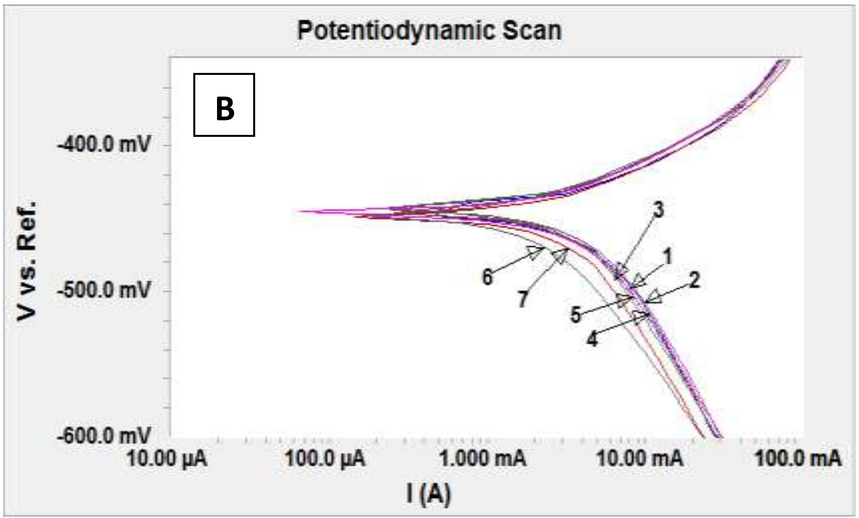


Figure 4: Potentiodynamic polarization parameters of mild steel with different concentration of (A) Amoxicillin, (B) Sulphadoxine

Table 3: Electrochemical parameters of mild steel in 1M sulfuric acid with and without different concentration of inhibitors: (A) Amoxicillin, (B) Sulphadoxine, (C) Glucosamine.

Inhibitor	Conc.(ppm)	βa (V/dec.) e-3	βc (V/dec.) e-3	I_{corr} (µA.cm^{-2})	E_{corr} (mV)	Corro.Rate (mpy)	IE %
Control	-	163.4	316.5	13200	-435	6.043e^3	-
(A) Amoxicillin	10	66.80	131.3	4190	-438	1.913e^3	68.25
	100	71.10	193.3	4140	-441	1.892e^3	68.63
	200	59.00	170.4	2590	-447	1.185e^3	80.37
	300	75.80	161.8	1500	-452	687.2	88.63
	400	54.30	161.4	1710	-456	783.2	87.04
	500	44.70	124.3	933	-451	380.5	92.93
(B) Sulphadoxine	10	94.80	238.3	5360	-448	2.450e^3	59.39
	100	78.60	197.2	5020	-444	2.295e^3	61.96
	200	69.30	187.4	4110	-443	1.879e^3	68.86
	300	79.00	203.9	4910	-445	2.242e^3	62.80

	400	90.10	195.2	3710	-449	$1.694e^{3}$	71.89
	500	76.40	174.2	4400	-446	$2.009e^{3}$	66.66

Scanning Electron Microscopy (SEM) Analysis: SEM micrographs of mild steel in 1M sulfuric acid for 24 hrs. in absence and presence of 500 ppm solution of Amoxicillin. And 400 ppm solution of Sulphadoxine shown in Figure 5(A-D).

It is seen that the polished substrate is smooth Figure 5(A). In 1M sulfuric acid solution in absence of inhibitor is rough and strongly damaged Figure 5(B); whereas the substrate in 500 ppm of Amoxicillin comparatively is smooth (shown in Figure 5(C). It is revealed that inhibitor adsorbed with formation of protective film on the surface of mild steel which is responsible for the inhibition of corrosion of mild steel.

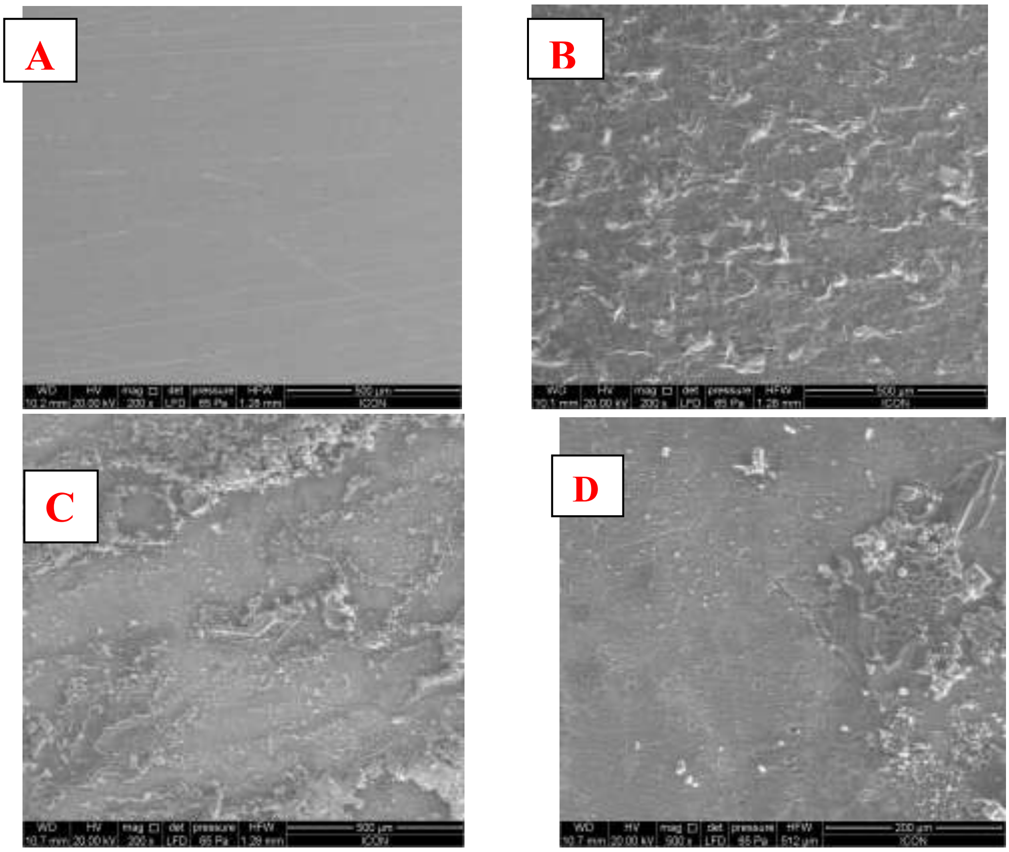


Figure 5: SEM of mild steel: (A) Polished and without inhibitor, (B) After immersion in 1M sulfuric acid without inhibitor, (C) After immersion with 500 ppm solution Amoxicillin (D) After immersion with 400 ppm solution of Sulphadoxine.

Mechanism

Mild steel in 1M sulfuric acid is highly corrosive but in presence of inhibitors, Amoxicillin and Sulphadoxine containing N, S and O heteroatoms, the rate of corrosion drastically decreases. Presence of heteroatoms in Amoxicillin and Sulphadoxine, make them more efficient inhibitors[32-35]

Amoxicillin is amphoteric, because of -NH2 and -COOH groups, allowing it to react with both acids and bases[36]. It gives protons in aqueous solution which are reduced at the cathodic region of the mild steel and negative charged acetate group thus electrostatically weakly adsorbed on the positive charged iron surface[37] (physisorption). Sulphadoxine being weak acidic because of sulphonamide group, (-SO2NH-) adsorb on positive charged iron surface of mild steel and undergoes physisorption.

Donor atoms such as N and S donate lone pair of electrons to the empty d-orbitals of iron forming strong coordinate-covalent bonds. The delocalized π-electrons of aromatic rings also covalently bonded with the partially filled d-orbitals of iron[38-41]. Corrosion inhibition efficiency depends on the number of aromatic rings in the compound[42]. Amoxicillin and Sulphadoxine are plays the same role during corrosion inhibition mechanism but their inhibition efficiency is in decreasing order. The presence of amine group favours the coordinate bonding. The molecule in protonated form is very similar to the neutral form, in the sense that "charge neutrality" process facilitates adsorption.

The result obtained by the weight loss and polarization study reveal that Amoxicillin shows a better inhibition efficiency in sulfuric acid media probably due to the possibility for these molecules to adsorb through sulphur. This adsorption behaviour of sulphur on the iron surface is also supported by F. Bentiss et al.[43, 44]. Amoxicillin molecules, the LUMO of sulphur is well distinct, whereas on oxygen atom of Sulphadoxine LUMO is absent. In addition, the strong LUMO density is also observed on nitrogen atoms of Amoxicillin, whereas in Sulphadoxine it is more distributed on phenyl rings. The small energy difference between HOMO and LUMO Amoxicillin molecules indicating the low excitation energy to move an electron from HOMO to LUMO causes higher inhibition efficiency. The similar mechanism is supported by I. Lukovits et al[45]. Thus, the possibility for Amoxicillin molecules to adsorb through sulphur is easier than Sulphadoxine molecules. Sulphadoxine is a Sulphanilamide. Its sulpha-group is blocked by oxy-groups. Its two methoxy-groups on pyrimidine decrease the mesomeric effect of methyl group towards the pyrimidine and smaller molecular size rendering less efficient than Amoxicillin.

Conclusion

The result obtained by gravimetric and electrochemical studies are mutually in good agreement with each other. This revealed that Amoxicillin is acting as a very good corrosion inhibitor with about 93% inhibition efficiency. The inhibition efficiency of Amoxicillin increases with concentration. Thus, they exhibit their maximum inhibition efficiency at 500 ppm solution; whereas Sulphadoxine shows its best performance of about 72% at 400 ppm solution. All these inhibitors exhibit polarization of both the electrodes, hence these are mixed type of inhibitors; but they are more cathodic, since their cathodic polarization is more. The SEM examination of mild steel with inhibitors shows smooth and uniform surface as compared to absence of inhibitors in 1M sulfuric acid solution. The smooth mild steel surface indicates the formation of uniform and protective surface film of inhibitor molecules on the mild steel. The best correlation among the experimental results obtained by weight loss and polarization measurements on the mild steel surface fit the Langmuir adsorption isotherm.

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