Int. J. Electrochem. Sci., 10 **(2015)** 4666 - 4681

International Journal of
ELECTROCHEMICAL
SCIENCE
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Corrosion Inhibition and Adsorption Behavior of 4–Amino Acetophenone Pyridine 2-Aldehyde in 1 M Hydrochloric Acid

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Received: 27 January 2015 / *Accepted:* 28 March 2015 / *Published:* 28 April 2015

The corrosion inhibition and adsorption behavior of 4 –Amino Acetophenone Pyridine 2-Aldehyde (4AAPA) towards mild steel has been studied in 1 M HCl using mass loss, potentiodynamic polarization measurements and electrochemical impedance spectroscopy. The 4AAPA efficiently inhibits the corrosion process and the inhibition efficiency increases with increasing concentration of 4AAPA. The maximum inhibition efficiency (91%) can be achieved at the concentration and temperature of 60 ppm and 308 K, respectively. The inhibition efficiency of 4AAPA decreases with increasing the temperature over 308 K. The potentiodynamic polarization experiment indicates that 4AAPA acts as mixed type corrosion inhibitor and the adsorption process follows the Langmuir adsorption isotherm. The surface morphology of mild steel specimen was investigated by atomic force microscopy and scanning electron microscopy. The obtained results clearly reveal that 4AAPA performs well as corrosion inhibitor for mild steel in hydrochloric acid solution.

Keywords: Mild steel, Corrosion inhibition, 4 –Amino Acetophenone Pyridine 2-Aldehyde Polarization

1. INTRODUCTION

Mild steel is a household material and has been widely used in different industries. The main problem of using mild steel is its dissolution in acidic solutions. The acid solutions are commonly used for removal of rust and scale in industries [1-5]. Hence, the inhibitors are commonly used to prevent the metal dissolution [6-9]. The organic compounds containing nitrogen, sulfur, oxygen, heterocyclic compounds with a polar functional group and conjugated double bonded compounds have been widely used as acid inhibitors [13-16]. Heterocyclic compounds, such as pyridine, pyridine derivatives, pyrazole, triazole, tetrazole, benzotriazole, benzimidazole, and benzothiazole derivatives, have also been reported and they show good inhibition efficiency for mild steel in different media [17-24]. These compounds adsorb on the metal surface and protect metals from attack in aggressive solutions [25]. The synthetic organic compounds are non- toxic to the environment, particularly, the pyridine containing compounds. Previously, many synthetic organic compounds such as 2,2'-Dithiobis (3-cyano-4,6-dimethylpyridine) [26], N-decylpyridinium bromide [27], carboxypyridinium bromide [28], 3-(4-amino-2-methyl-5-pyrimidyl methyl)-4-methyl thiazolium chloride [29], 1-dodecyl-4-methoxy pyridinium bromide [30], bipyrazolic compounds [31], 1-{[benzyl-(2-cyano-ethyl)-amino]-methyl}-5-methyl-1H-pyrazole-3-carboxylic acid methyl ester, 1-{[benzyl-(2-cyano-ethyl)-amino]-methyl}-5-methyl-1H-pyrazole-3-carboxylic acid ethyl ester [32], 4-Methyl-6-phenyl-tetrahydro pyrimidine-2-thione, 4,6-Diphenyl-tetrahydro pyrimidine-2-thione, 4-Phenyl- 4a, 5, 6, 7, 8, 8a-hexahydro quinazoline-2-thiol [33], 3,4-dihydropyrimidin-2(1H)-ones [34], 2-amino-5-mercapto-1,3,4-thiadiazole , 2-mercaptothiazoline [35], 4- [5- ((4-chlorophenyl) diazenyl)-2- hydroxybenzylideneamino)- 1,5-di methyl-2-phenyl-1H pyrazole-3-(2H)-one [36] have been investigated as corrosion inhibitor in acidic environment. Besides these, they are important and useful intermediates in preparing variety of heterocyclic compounds [37-40]. Inhibition by these organic compounds is usually attributed to their interaction with the mild steel surface via adsorption. Adsorption of an inhibitor by a metal surface depends on the nature and surface charge on the metal, the mode of adsorption, the chemical structure of the inhibitor, and the type of electrolyte solution.

In the present work, we have studied the inhibitive effect of 4AAPA on corrosion of mild steel in 1 M HCl solution. The inhibition of corrosion by 4AAPA was studied by different measurements with sufficient detail. Thermodynamic and kinetic studies have also been evaluated and discussed in detail.

2. EXPERIMENTAL

2.1 Materials preparation

Mild steel specimens containing C-0.05%, Mn-0.6%, P-0.36%, Si-0.03% and Fe=98.96% were used for the study. The specimens were mechanically pressed and cut into different coupons, each of dimensions 2.5 × 2.5 × 0.4 cm. Then, they were ground with silicon carbide abrasive papers, polished, washed thoroughly with acetone, dried and stored in moisture-free desiccators for further weight loss measurements.

2.2. Test Solutions

The solution of 1M hydrochloric acid (Test solution) was prepared for each experiment using analytical grade of hydrochloric acid (98%) and diluted with distilled water. The concentration range of inhibitor was 20 to 60 ppm.

2.3 Synthesis of 4AAPA

The mixture of 1-(4 aminophenyl) methadone and picolinaldehyde was dissolved in 30 mL ethanol. About 10 mL of 50 % sodium hydroxide solution was added and stirred at 5 – 10◦C for 3 h. The resulting precipitate was collected by filtration and recrystallized in ethanol to get yellow crystals of 4AAPA [41].

2.4 Methods

2.4.1 Mass loss measurements

Polished mild steel specimens were initially weighted in an electronic balance. Weighed specimens were immersed in 100 mL 1M HCl solutions with out and with different concentrations of 4AAPA (0-60 mg L^{-1}) at 308–343 K for 2 h. After 2 h of immersion, the specimens were taken out from solution, washed in double distilled water, dried and then weighed. The mass loss (ΔM) was used to calculate the corrosion rate (CR) and the inhibition efficiency (% IE):

$$\mathrm{CR\ (mpy)} = 534 \times \Delta M / D \times S \times T \quad (1)$$

$$\mathrm{IE\ \%} = (ML_0 - ML_i) / ML_0 \times 100 \quad (2)$$

Here $\Delta M = (ML_0 - ML_i)$, where ML_0 and ML_i are the mass loss of mild steel without and with inhibitor solutions, mpy is mils per year, D is the density of the iron (g cm^{-3}), S is the area of the specimen in $inch^2$, and T is the period of immersion in hours.

2.4.2 Electrochemical measurements

Tafel polarization curve and Electrochemical impedance spectroscopy (EIS) measurements were performed using CH electrochemical analyzer Model 604D. All electrochemical measurements were carried out at 308 K using 100 ml of electrolyte (1 M HCl) in stationary condition. The working polished mild steel electrode with exposed area 0.5 cm^2 was immersed in 1M HCl solution. A platinum electrode and saturated calomel electrode were used as counter and reference electrodes, respectively. Before each Tafel and EIS measurements, the electrode was allowed to corrode freely in 1M HCl solutions and its open circuit potential (OCP) was recorded. Tafel polarization curves were recorded from -300 to +300 m Vs. SCE, (versus OCP) with a scan rate of 1 mV s^{-1}. Electrochemical impedance spectroscopy measurements were carried out at OCP in the frequency range of 0.1 Hz to 100 KHz with a 5 mV peak- to- peak amplitude using ac voltage. The cell set up was the same as that used for polarization measurements. The real part and imaginary part of the cell impedance were measured in ohms for various frequencies. The charge-transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) values were calculated using the equation.

$$R_{ct} = (R_s + R_{ct}) - R_s \quad (3)$$

$$C_{dl} = ½ .\pi R_{ct}\, f_{max} \quad (4)$$

Where R_s is the solution resistance and f_{max} is the maximum frequency. Each experiment was run in triplicate to check the reproducibility of the data.

2.4.3. Surface analysis and spectroscopic studies

The mild steel specimens were immersed for 2h in 1M HCl solution containing 60 mg L^{-1} of inhibitor for 2 h at 308K. Then, the specimens were properly washed with double distilled water and dried in warm air. The surface morphology of the mild steel was examined by using the JEOL (JSM 6390) Scanning Electronic Microscope and scanning probe microscope (Akilan Technology UK 5500 series). The phytochemical constituents of 4AAPA treated with 1 M HCL after 2 h mild steel immersion was analyzed using JASCOW 32 spectrophotometer. The absorption spectra of these solutions were determined with test solution as a reference.

3. RESULTS AND DISCUSSION

3.1 Mass loss measurements

Table 1 Corrosion rate and inhibition efficiency data obtained from mass loss measurements in 1M HCl in absence and presence of 4AAPA.

Acid solution	Temperature K	Concentration ppm	CR mpy	θ	IE%
1M HCL	308	0	0.169	-	-
		20	0.028	0.8343	83.43
		40	0.023	0.8639	86.39
		60	0.015	0.9112	91.12
	313	0	0.427	-	-
		20	0.064	0.8501	85.01
		40	0.052	0.8782	87.82
		60	0.032	0.925	92.5
	323	0	0.58	-	-
		20	0.077	0.8673	86.73
		40	0.066	0.8862	88.62
		60	0.038	0.9344	93.44
	333	0	1.023	-	-
		20	0.19	0.8142	81.42
		40	0.163	0.8406	84.06
		60	0.111	0.8914	89.14
	343	0	1.528	-	0
		20	0.386	0.746	74.6
		40	0.266	0.8269	82.69
		60	0.193	0.8736	87.36

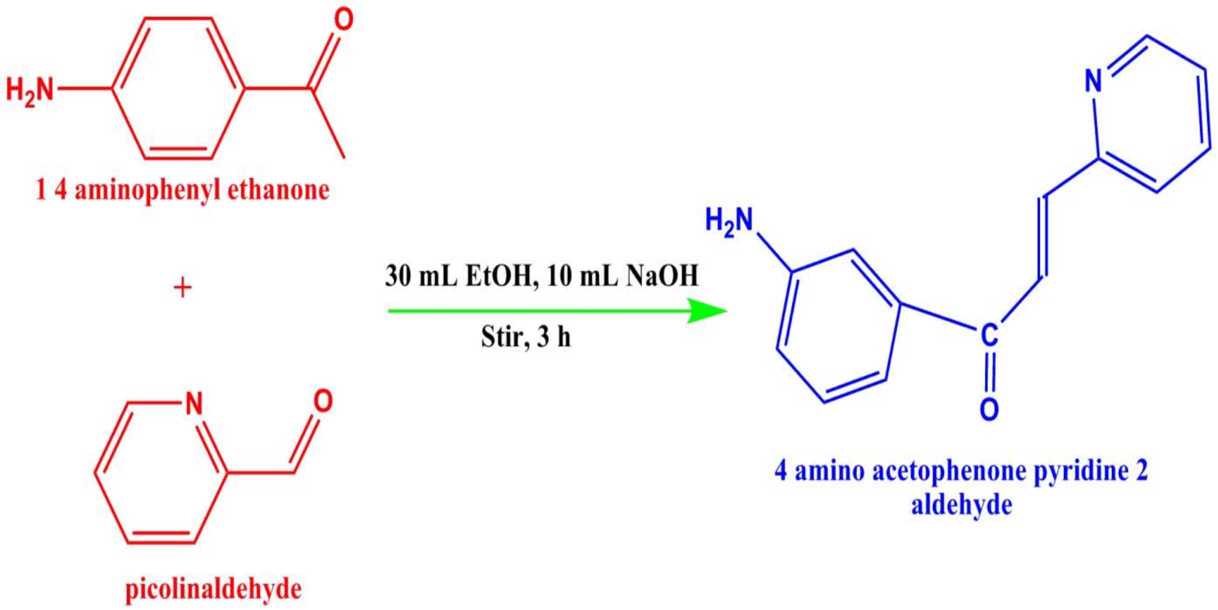


Figure 1. Scheme for the synthesis of 4AAPA

The data in the Table 1 reveal that the corrosion rate of mild steel decreases with increasing 4AAPA concentration. This indicates a superior coordination of the inhibitor on the surface of the mild steel. The inhibition efficiency increases with temperature upto 323 K, which indicates the considerable surface coverage by the inhibitor and strong bonding to the mild steel surface. The inhibition efficiency decreases from 89.14 to 87.36 % upon increasing the temperature (323 to 333 K), indicating that the inhibitor molecules desorb at higher temperatures from the metal surface.

3.2 Potentiodynamic polarization measurements

The polarization behavior of mild steel in 1 M HCl solution in the presence and absence of 4AAPA was studied and is shown in Fig. 2. In the presence of 4AAPA , the corrosion potential of mild steel shifts 28-35mV anodically compared to the blank. An inhibitor can be classified as cathodic or anodic type if the displacement in corrosion potential is more than 85mV with respect to corrosion potential of the blank [42]. In the present study, 4AAPA acts as a mixed-type inhibitor with predominant anodic effectiveness [43–45]. As it would be expected, both anodic and cathodic reactions of mild steel corrosion in 1M HCl solution are effectively suppressed and this inhibition effect becomes more pronounced with increasing 4AAPA concentration. This result suggests that the addition of the inhibitor reduces the anodic oxidation of mild steel and also retards the hydrogen evolution reaction. This suppression of the corrosion process can be attributed to the covering of adsorbed inhibitor molecules on the mild steel surface. The corrosion reaction is more diminished in the presence of high concentration of inhibitor [46].

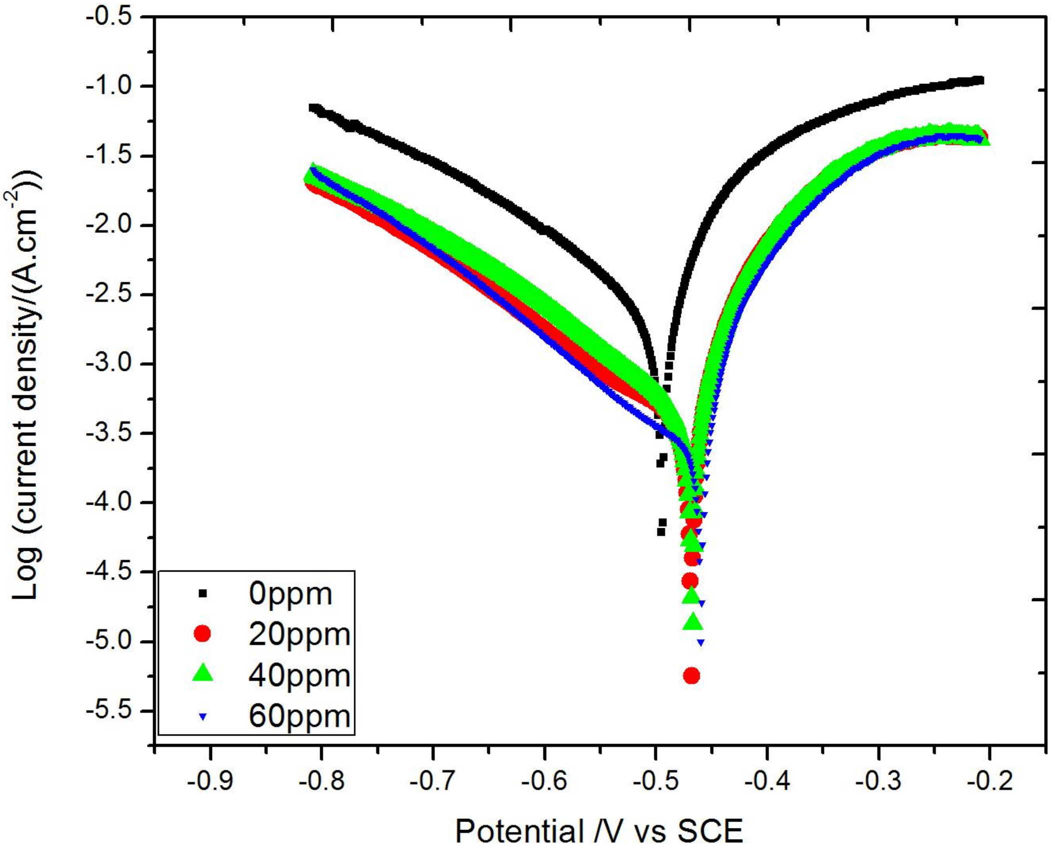


Figure 2. Tafel plots of mild steel immersed in 1M HCl with and without 4AAPA

The inhibition efficiency is defined as

$$IE\ \% = (i^0_{corr} - i_{corr}/i^0_{corr}) \times 100 \qquad (5)$$

Where, i^0_{corr} and i_{corr} are the corrosion current density values in the absence and presence of inhibitor, respectively. The anodic and cathodic current potential curves were extrapolated up to their intersection at the point where corrosion current density (I_{corr}), cathodic and anodic Tafel slopes (b_c and b_a), corrosion potential (E_{corr}) and inhibition efficiency are obtained from polarization measurements and are given in Table 2. It is evident from Table 2 that corrosion current density value decreases from 4408 to 937 μA cm^{-2} in the presence of 4AAPA which is due to the increase in the blocked fraction of the electrode surface by adsorption.

Table 2. Potentiodynamic polarizations parameters for the corrosion of mild steel in 1 M HCl containing different concentration of 4AAPA

C_{inh} (mg l^{-1})	E_{corr} mV	I_{corr} (μA cm^{-2})	bc (mv decade^{-1})	b_a (mv decade^{-1})	IE%
0	-495	4408	173.01	154.65	-
20	-467	1604	187.52	126.11	63.61
40	-468	1095	173.11	104.18	75.15
60	-460	937	146.36	99.46	78.74

3.3 Electrochemical impedance spectroscopy (EIS)

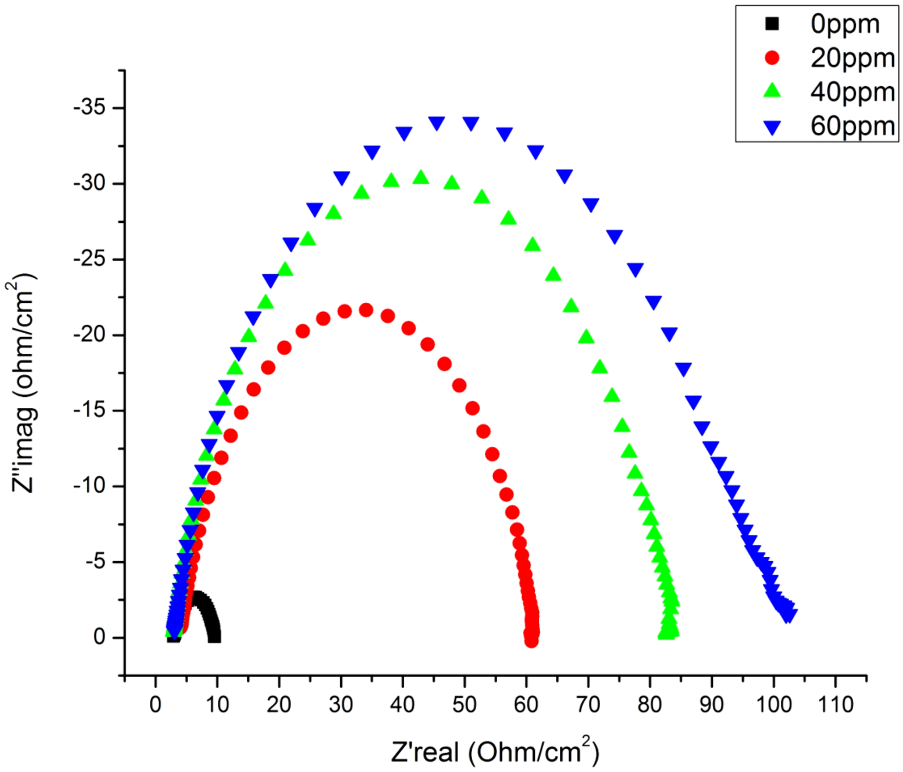


Figure 3. Nyquist plots for mild steel immersed in 1 M HCl and with different concentrations of 4AAPA at 308 K

Nyquist diagrams of mild steel in 1 M HCl solutions containing different concentrations of 4AAPA are given in Fig. 3 The impedance spectra exhibit one single depressed semicircle. The diameter of semicircle increases with the increase of 4AAPA concentration which indicates that the corrosion of mild steel is controlled by the charge transfer and the presence of 4AAPA does not change the mechanism of mild steel dissolution [47]. The difference in real impedance at lower and higher frequencies is commonly considered as a charge-transfer resistance. In this study, the difference in real impedance at lower and higher frequencies is accepted as charge-transfer resistance (R_{ct}) which is shown in Table 3.

Table 3 Electrochemical impedance parameters for mild steel in 1M HCl in the absence and presence of 4AAPA

$C_{inh\ (mg\ l^{-1})}$	$R_{s\ (\Omega\ cm^{2})}$	$R_{ct\ (\Omega\ cm2)}$	$C_{di(F\ cm^{2})}$	IE%
0	2.19	2.73	4.90×10^{-2}	-
20	2.08	61.28	1.19×10^{-4}	95.54
30	0.22	85.73	6.10×10^{-5}	96.81
40	4.50	99.35	4.73×10^{-5}	97.25

It can be observed from Table 3 that the R_{ct} value of mild steel in uninhibited 1M HCl solutions increases after the addition of 4AAPA. This increase in R_{ct} value is caused by insulation of inhibitor molecules onto mild steel surface by blocking the active sites. The inhibition efficiencies were calculated using charge transfer resistance obtained from Nyquist plots, according to the equation [48]

$$IE\ \% = (R_{ct} - R^0_{ct}/R_{ct}) \times 100 \qquad (6)$$

Where, R^0_{ct} and R_{ct} are the charge transfer resistances in the absence and presence of the inhibitor, respectively. It is clear from Table 3 that the C_{dl} values decrease and R_{ct} increase after addition of inhibitor concentrations. The decrease in the C_{dl} is due to the decrease in local dielectric constant and/or an increase in the thickness of electrical double layer is attributed to the gradual replacement of water molecules and other ions originally adsorbed on the surface by the adsorption of inhibitor molecules on the mild steel surface, thereby causing the increase in R_{ct} values [49]. Inhibition efficiency of the studied inhibitor increases due to the formation of a protective film of 4AAPA on the mild steel surface. This film creates a barrier between mild steel and aggressive solution [50].

3.4 Effect of temperature

The apparent activation energy (E_a), the enthalpy of activation (ΔH^*) and entropy of activation (ΔS^*) for the corrosion of mild steel in 1M HCl solutions in the absence and presence of various concentrations of 4AAPA were calculated from Arrhenius equation:

$$CR = A \exp(E_a/RT) \qquad (7)$$

and from Transition state equation:

$$CR = RT/hN \exp(\Delta S^*/R) \exp(-\Delta H^*/RT) \qquad (10)$$

Where, A is the frequency factor, R is the gas constant (R = 8.314 J mol^{-1} K^{-1}), T is the absolute temperature, N is the Avogadro's number and h is the Planck's constant.

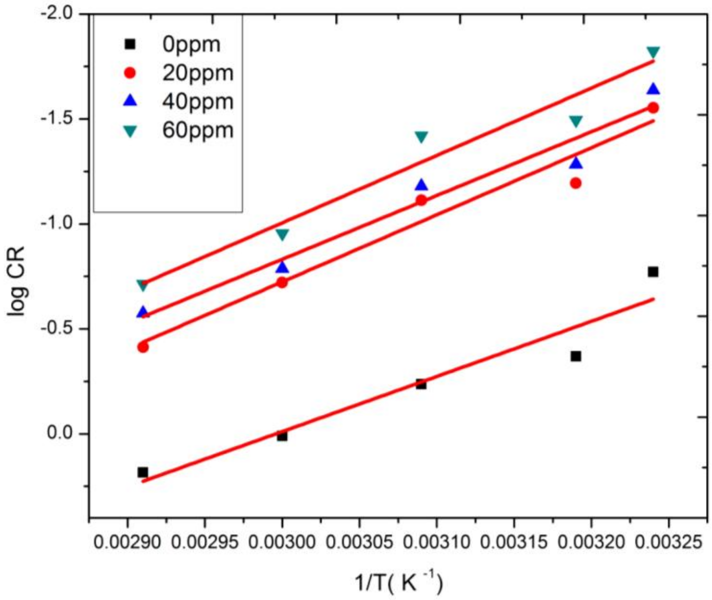


Figure 4. Arrhenius plots in the absence and presence different concentrations of 4AAPA

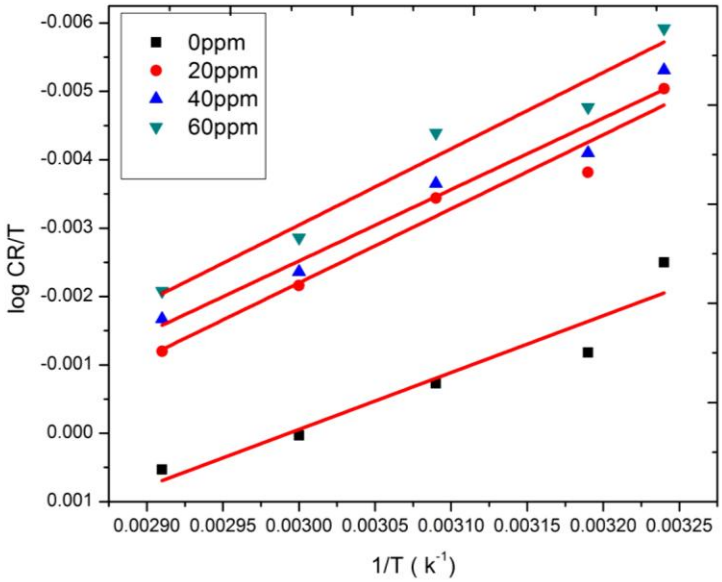


Figure 5. Transitions state plots of mild steel immersed 1M HCl in the absence and presence of different concentrations of 4AAPA

Table 4 Corrosion kinetic parameters for mild steel in 1M HCl in the absence and presence of different concentrations of 4AAPA

C_{inh} (mg l^{-1})	E_a(kJmol^{-1})	ΔH* (kJ mol^{-1})	-ΔS* (J mol k^{-1})
0	50.28	159.22	195.1
20	58.16	199.89	194.5
40	61.15	207.17	194.7
60	61.48	213.49	194.5

Fig.4 represents plot of log CR against 1/T for mild steel in 1M HCl in the presence and absence of different concentrations of 4AAPA. Straight lines were obtained with slope equal to -E_a/2.303R. On the other hand, Fig.5 represents log CR/T vs. 1/T for mild steel in 1M HCl in the presence and absence of different concentrations of 4AAPA. This relation gave straight lines with slope equal to -ΔH*/2.303R. The obtained values of Ea, ΔS* and ΔH* are given in Table 4.

Table 4 shows that the values of E_a for inhibited solution are higher than uninhibited solution. The higher values of E_a indicate that the dissolution of mild steel is slow in presence of 4AAPA. The increase in the activation energy suggests physical adsorption [51, 52]. The positive values of enthalpies (ΔH*) reflects the endothermic nature of the steel dissolution process meaning that the dissolution of mild steel is difficult [53]. On comparing the values of entropy of activation (ΔS*) given in Table 4, it is clear that the entropy of activation increased positively in the presence of studied inhibitor compared to the free acid solution. In 1M HCl solution, the transition state of the rate determining recombination step represents a more orderly arrangement relative to the initial state, so a high value of ΔS* is obtained. In the presence of 4AAPA, the rate determining step is the discharge of hydrogen ions to form adsorbed hydrogen atoms. Since the surface is covered with inhibitor molecules, this will retard the discharge of hydrogen ions at the mild steel surface causing the system to pass from a random arrangement and hence entropy of activation is increased. The increase in the entropy of activation in the presence of 4AAPA increases the disordering on going from reactants to the activated complex [54, 55].

3.5 Adsorption consideration

The inhibition process is commonly related to adsorption of inhibitor molecules onto the metallic surface. In this study, the experimental data were tested with various isotherms including Langmuir, Temkin and Freundlich adsorption isotherms. The data best fit Langmuir adsorption isotherm. Langmuir theory allows the most basic presentation of adsorption on an ideal surface. The Langmuir adsorption isotherm may be written in the form:

$$C/\theta = 1/K + C \qquad (9)$$

Where, C is the concentration of inhibitor (mg l^{-1}), K is the adsorption equilibrium constant and θ is the surface coverage which is given as

$$\theta = \%\ IE\ /100 \qquad (10)$$

The relationship between C/θ against C (g L^{-1}) gave straight lines at all studied temperatures for 4AAPA as shown in Fig. 6. From the intercept of the straight lines, the values of K were calculated and are summarized in Table 5.

Table 5. Langmuir absorption parameters and free energy of absorption of 4AAPA as an inhibitor on the surface of mild steel

Temp (K)	$-\Delta G^\circ$ (kJ mol^{-1})	K	R^2 (langumuir isotherm)	R^2 (Temkin isotherm)	R^2 (Freundlich isotherm)
308	18.86	28.58	0.998	0.922	0.928
313	19.31	30.23	0.998	0.916	0.922
323	20.21	33.51	0.998	0.894	0.857
333	20.21	26.74	0.998	0.850	0.900
343	19.42	16.38	0.999	1	0.999

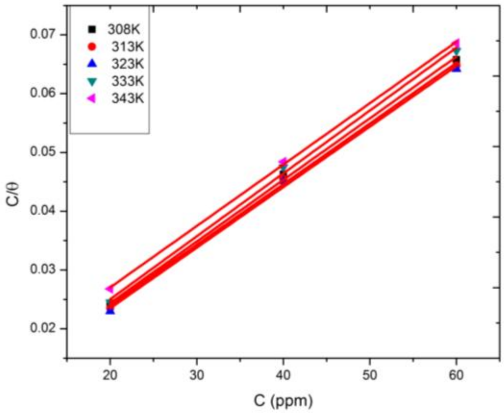


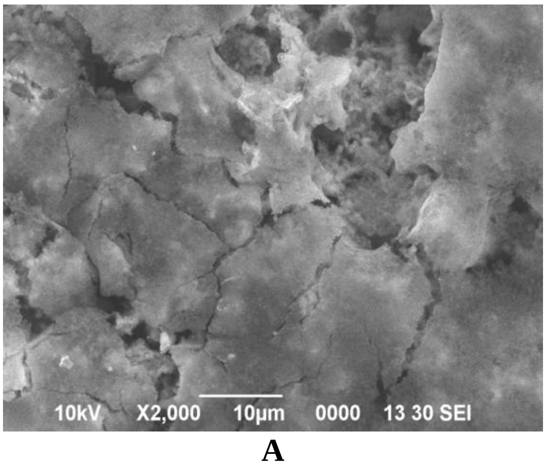
Figure 6. Langmuir adsorption plots of mild steel immersed in 1M HCl with and without 4AAPA at 308 K.

The standard free energy of adsorption (ΔG_{ads}) and the equilibrium constant (K) are related by the following equation

$$\Delta G_{ads} = RT \ln (55.5K) \qquad (11)$$

Where, R is the universal gas constant, T is the temperature and 55.5 is the molar concentration of water in solution. The values of K were found to decrease with increasing temperature showing that the molecules of inhibitor was physically adsorbed on the mild steel surface. Results presented in the table indicate that the values of ΔG_{ads} are negative in all cases and lies between -18.86 and 21.21 kJ/mol. The negative values of ΔG_{ads} clearly indicates the spontaneous adsorption of 4AAPA on mild steel surface through physical adsorption mechanism. Such data explain the decrease in the protection efficiency with increasing temperature. Usually, values of ΔG_{ads} up to -20 kJ mol^{-1} (as obtained in this study) signify physical adsorption and values more negative than -40 kJ mol^{-1} signify chemical adsorption. Physical adsorption is consistent with electrostatic interaction between charged molecules and a charged metal while chemical adsorption is consistent with charge sharing or charge transfer from inhibitor to the metallic surface to form co-ordinate type of bond [56, 57].

3.6. Surface morphology and spectroscopic studies



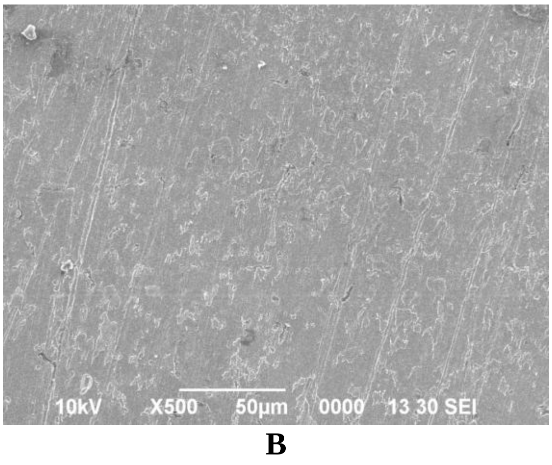
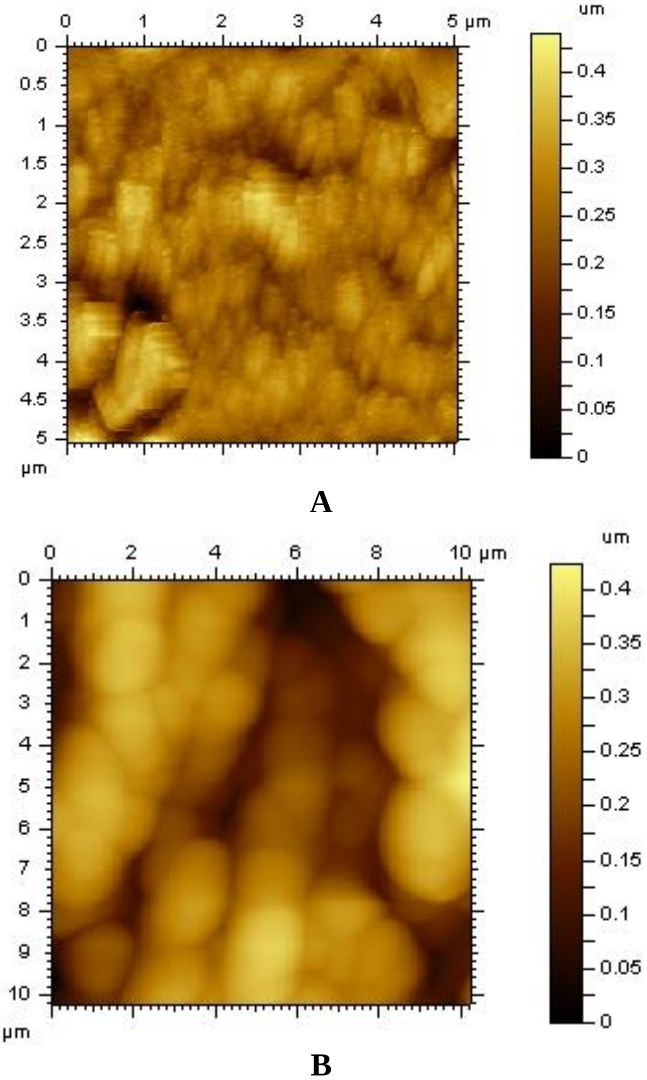


Figure 7. SEM images of mild steel in 1M HCl a) without inhibitor and b) with 60 mg l^{-1} of inhibitor.

Polished mild steel specimens immersed in 1 M HCl solution in the absence and presence of 60 mg L^{-1} 4AAPA for 2 h was investigated by SEM and given in Fig. 7a, b. Inspection of Fig.7a reveals that the mild steel surfaces after 2h immersion in 1M HCl shows an aggressive attack of the corroding medium on the mild steel surface. Furthermore, the surface layer is highly porous and deep holes appeared. In contrast, in the presence of 60 mg L^{-1} 4AAPA after 2 h immersion (Figure 7b), the specimen surface smoother and no pits are observed on the mild steel surface. The rate of corrosion reduced and the smooth surface is observed in Fig. 7b, which is due to the formation of a protective film on the metal surface and responsible for the inhibition of corrosion. AFM is a powerful technique to investigate the surface morphology studies which have been useful to study the influence of inhibitors on the metal/solution interface [58, 59]. The topography AFM images of mild steel surface in 1m HCl in the absence and presence of 60 ppm 4AAPA and shown in Fig. 8a and b. As shown in the Fig. 8a, the surface of mild steel electrode exposed to 1M HCl solution had a considerable porous structure with large and deep pores. On the other hand, in the presence of on 4AAPA inhibitor, the mild steel surface appears more flat, homogeneous and uniform, indicating that 4AAPA shows an appreciable resistance to corrosion.



A

B

Figure 8. AFM images of mild steel in 1M HCl a) without inhibitor and b) with 60 mg l^{-1} of inhibitor.

In order to confirm the possibility of the formation of inhibitor-Fe complex, UV– visible absorption spectra were performed in 1 M HCl solution containing 60 mg L^{-1} 4AAPA before and after the mild steel immersion and the results are shown in Fig. 9 a and b. The absorption spectra of a 4AAPA before immersion have absorption maximum 210, 242 and 315 nm, which can be attributed to $\pi - \pi^*$ transitions. After 2 h immersion of mild steel, the change in the position of absorption maximum or the change in the absorbance values indicates that the complex formation between two species in solution. However, there is no change in the shape of absorption spectra. These experimental findings provide the formation of complex between Fe^{2+} and 4AAPA and confirm the inhibition of steel from corrosion.

3.7. Mechanism of inhibition

It is well known that the organic molecules can be adsorbed on the metal surface. The adsorption process is affected by the chemical structure of the inhibitors, the nature and charged surface of the metal, and the distribution of charge over the whole inhibitor molecule. In general, owing to the complex nature of adsorption and the inhibitive action of the inhibitor, single mode of adsorption of the inhibitor on the metal surface is not possible. Organic inhibitor molecules may be absorbed on the metal surface by one or more of the following mechanisms [60, 61],

1. Electrostatic interaction between the charged molecules and the charged metal;
2. Interaction of unshared electron pairs in the molecule with the metal;
3. Interaction of π- electrons with the metal; and / or a combination of all

The efficiency of inhibition depends on many factors, including molecular size, heat of hydrogenation, mode of interaction, with the metal surface, formation of metallic complexes, and the charge density on the adsorption sites [62]. The efficiency of inhibition by 4AAPA may be attributed to the presence of electron rich N and O atoms and the aromatic ring. A phenyl ring, a hydroxyl group, an amide linkage, and two electron-donating methyl groups are present in the structure of 4AAPA. Therefore, possible reaction centers are the unshared electron pair of heteroatoms and π- electrons of the aromatic ring. From the experimental and theoretical results obtained, the adsorption and inhibition effect of 4AAPA in 1 M HCL solution can be explained as follows:

Schiff bases may be protonated in the acid solution as

$$[4\,AAPA] + x\,H^+ \rightarrow [4AAPA\,H_x]^{x+}$$

In aqueous acidic solutions, 4AAPA is present either as the neutral molecule or as protonated 4AAPA (cation). Two modes of adsorption by the surface of the metal can be considered. In one mode, neutral 4AAPA is adsorbed on the surface of the mild steel by physisorption involving displacement of water molecules from the metal surface and sharing of electrons between heteroatoms such as nitrogen and oxygen and the metal surface.

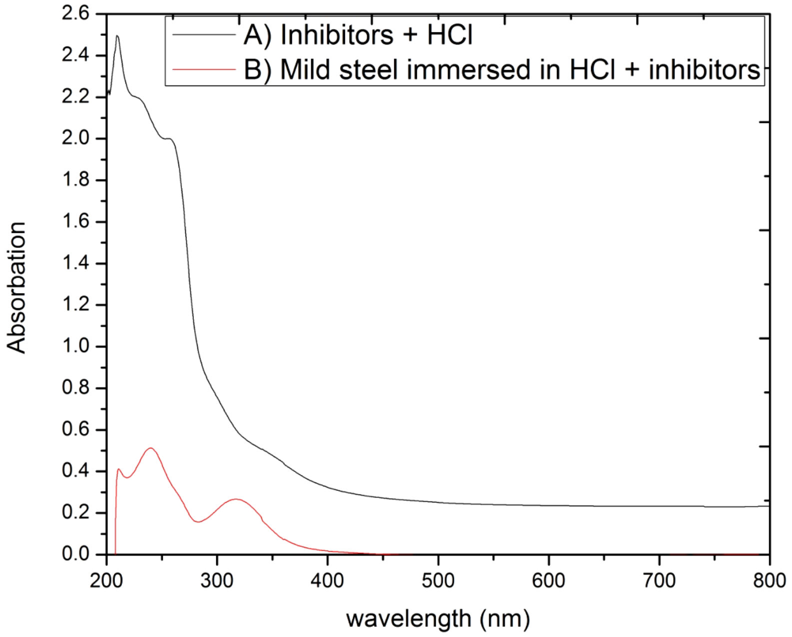


Figure 9. UV-visible spectra of the solution containing 1M HCl before (a) and after the mild steel immersion in inhibitor (b)

The inhibitor molecules can also be adsorbed by the mild steel surface on the basis of donor-acceptor interactions between p - orbitals of the heterocyclic ring and vacant d- orbitals on the iron surface. In another mode, because it is well known that the steel surface is positively charged in acid solution [63], it is difficult for the protonated 4AAPA to approach the positively charged mild steel surface (H_30^+- metal interface) because of electrostatic repulsion. The protonated 4AAPA is adsorbed as a result of electrostatic interactions between the positively charged molecules and the negatively charged metal surface. It should be noted that the molecular structure of protonated 4AAPA is uncharged relative to the neutral form and the N-atoms on the ring remaining strongly blocked. So when protonated 4AAPA adsorbs by the metal surface, coordinate bonds may be formed by partial transfer of electrons from the hetero atoms to the metal surface.

4. CONCLUSION

In conclusion, the corrosion inhibition and adsorption behavior of 4 4AAPA towards mild steel has been studied in 1 M HCl. The inhibition efficiency increases with increasing the concentration of 4AAPA and decreases with increasing the temperature over 323 K. Polarization study reveals that the 4AAPA acts as a mixed type inhibitor controlling both anodic and cathodic processes. Electrochemical impedance spectra confirm the formation of protective layer on the mild steel surface. The surface morphology studies confirme that the 4AAPA shows an appreciable resistance to corrosion of mild steel surface. In addition, the 4AAPA can be used as corrosion inhibitor for mild steel in the industries.

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