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Synthesis, Characterization and Corrosive Inhibition Study of Phenylamino Cyclohexenone: Mild Steel Corrosion Studies in Acidic Medium

Ezhilarasi M.R.[1]* and Prabha B.[2]
1. Department of Chemistry, Dr. N.G.P. Arts and Science College, Coimbatore-48, Tamil Nadu, INDIA
2. Department of Chemistry, Karpagam Academy of Higher Education, Coimbatore-21, Tamil Nadu, INDIA
*mrezhilarasi@gmail.com

Abstract

The present study reveals the greener synthesis and corrosion inhibition study of phenylamino cyclohex-2-enone (PAC) derivatives. Microwave assisted synthesis is one of the safe and environmental friendly method to synthesize cyclohex-2-enone compounds in presence of sodium bisulphate used as a catalyst and it is a highly economical one. The cyclohex-2-enone compounds corrosion inhibitive effect proved with the help of its weight loss. Synergetic process, electro chemical impedence and potentiodynamic polarization studies was carried out for the target compounds.

The structures of synthesized cycloexenone compounds were elucidated with the help of IR, ^{1}H and ^{13}C NMR. The type of adsorption isotherm was confirmed by using synergetic process. The synergetic process was done by observing the correlation between halides and inhibitor. The final results show that the compounds follow the Langmuir adsorption isotherm.

Keywords: 5,5-dimethyl -3-(phenylamino)-cyclohex-2-enone, Microwave irradiation, Adsorption isotherm, Kinetics, Synergetic effect.

Introduction

The movement of electron between ionic current of the solution and electronic current in the metal causes the corrosion in the metal surface. Corrosion is an electrochemical process in nature. It occurred at oil pickling process pipes and other industrial pipe lines which are used to carry the acidic, basic solutions to internal processes. The acidification of a well increases its permeability but corrosion risks should also be considered[16,18].

Inhibitors are chemical compounds which are used to control the corrosion effect on the pipe lines, metallic machines and other iron components. The use of inhibitor is one of the economic and common techniques to reduce the corrosion process in the pipes[13,21].

The organic compounds have ability to control this corrosion process[14]. Mostly, active inhibitors contain hetero atoms like N, S, O in their skeleton structures[3,4]. The ability of the inhibitors has been observed by considering physic-chemical properties such as inhibitors functional group, electron density of donor atom, molecular size, pi-orbital character and electronic structure[1,9]. The combination of chemical and electrochemical technique studies along with surface analytical techniques is very effective method to find out the active inhibitors[1]. Current studies proved that if the number of heteroatom increases in the inhibitor its corrosion inhibition property increases[11]. Good inhibition result was found from the inhibition study of Schiff bases at mild steel on acidic medium[2,5,12]. The skeleton structure of Schiff bases contains both hetero atom and pi-electron system which are most preferred one for adsorption property of a molecule. Inhibition efficiency always depends on active adsorption centres present in inhibitor molecule[6]. Present study reveals that the most of the organic compounds have effective inhibition property, the molecules pyridazine[17], mercaptans, oximes, thioethers[19], methionine methyl ester hydrochloride[15], pyrazole[7,8] and alkyl esters[6,10]. The piperidone have an effective inhibitor property due to presence of C=O and NH- group[2]. Our newly synthesized PAC derivatives also have the same groups in its electronic structure. They stimulate present corrosion inhibition effect of PAC compounds on mild steel in the HCl and H_2SO_4 environment. The compound inhibition efficiency have been evaluated with the help of electrochemical impedance and polarization values.

Material and Methods

The metal strips which are used for corrosion studies contain 3.15 % of carbon, 0.61% of manganese, 0.155 % of chromium, 0.07% of phosphorus, 0.049 % of sulphur, 0.035 % of tin and remaining percentage is of iron[11].

Materials: The triple distilled analytical grade water was used to prepare the acid solutions. 1M H_2SO_4 and 1M HCl were used as corrosion medium. 10, 20, 30, 40 and 50 ml concentration inhibitors were employed for the studies. The experiments were performed as triplicate and the average value of the weight loss and electrochemical test were reported. The clean set of electrodes and freshly prepared solutions were used. The metallic rod for the weight loss tests have the dimension of 1cm x 5 cm x 0.33 cm and working electrodes have surface area about 0.339 cm^2.

The electrode was first mechanically treated using various grades of grinding paper (up to 1200 grit) and then polished with the help of emery sheets with 1/0 to 4/0 grades to remove adhering impurities before every single corrosion test. Finally strips were cleaned by using double distilled water and ethanol.

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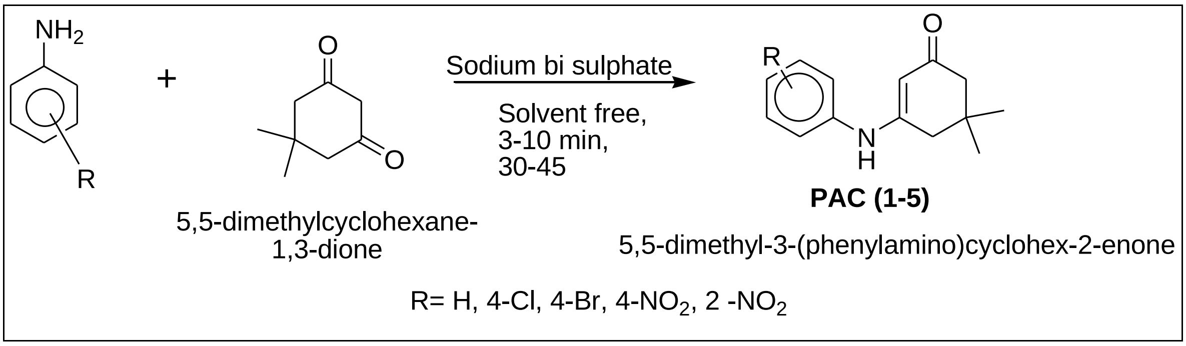

Scheme 1: The microwave assisted pathway of phenylamino cyclohex-2-enones.

Instruments: The skeleton structure of the organic inhibitor was confirmed by using Perkin-Elmer 1650 spectrometer and Bruker AMX 400 NMR spectrometers. The Perkin-Elmer 1650 was used for IR studies with the absorption unit cm^{-1}. Bruker AMX instrument was used to predict and carryout the ^1H and ^{13}C NMR values of the inhibitors with the unit ppm and the standard was TMS, $CDCl_3$ as solvent. The single-mode microwave reactor was used for synthesis purpose under control pressure, temperature and power. Maspec MSW 9629 spectrometer was used to obtain the mass spectra value of the inhibitor.

Organic Inhibitor: Organic inhibitor is a compound which reduces the corrosion effect of steel rod in acidic medium. It has a function either anodic or cathodic or both. Many of the organic compounds have to reduce the corrosion rate of the iron or steel rods in acidic medium. The inhibition activity was performed by additive adsorption between the metal-acid solution interfaces. This is known as potential difference of the interface. The changes occur in the size and properties of inhibitor at the interface due to formation of electrical double layer. The displacement reaction during adsorption process is written as:

$$\text{Org}_{(sol)} + nH_2O \longrightarrow \text{Org (ads)} + nH_2O$$

The number of removal of water molecules indicates the number of adsorbed inhibitors on metal surface. Adsorption of organic molecule occurs because the interaction energy is between the metal surface and inhibitor due to presence of ionization energy between them. Especially, there are three types of inhibition effect mode. (i) geometric blocking effect, (ii) blocking the active sites and (iii) electro-catalytic effect of the inhibitor or reaction products. In the first mode, inhibition occurs due to reduction of reaction and other modes occur due to change in activation energy barriers of the anodic or cathodic reaction. There is some deviation in electrochemical behaviour between interpreted and measured electrochemical data because there is presence of factors affecting inhibitors.

Effect of temperature of organic compounds on metal: Most of the organic inhibitors contain at least one polar group like N, S or Se, P in some cases. The inhibition properties of organic compounds were understood by the electron density of the reaction centre. The chemisorptions bond strengthened between metal surface and inhibitor with increases in electron density of the reaction centres in inhibitor. Electron density increases when unshared pair of electron in polar compounds is detached. The corrosion monitoring methods known as weight loss, electrochemical and potentiometric studies give adsorption details of inhibitor molecules. These tests are taken by using suitable method and instruments.

Corrosion monitoring method- (i) Weight loss tests: Weight loss measurements were performed at different temperatures (35°,45°,55° and 65°) of carbon steel under 20 ml of HCl and H_2SO_4 medium and the same studies were also done by different inhibitor concentrations with 20 ml of acids at room temperature. The blank value was also noted for every reading. At the end of the test, the specimens were cleared and finally weight loss were recorded. The corrosion rate, inhibition efficiency and surface coverage were determined by following equations:

$$V_{corr} = (8.76 \times 10^4\ W)/ATD$$
$$\Theta = (V_{corr,0} - V_{corr,i})/\ V_{corr,0}$$
$$I.E,\ \% = [(V_{corr,0} - V_{corr,i})/\ V_{corr,0}] \times 100$$

where W is weight loss (g), D is the density of steel (g cm^{-3}), A is the surface area (cm^2), T is the time in hours and $V_{corr,0}$, $V_{corr,i}$ are the weight loss values in the presence and absence of inhibitor.

Electrochemical tests: Electrochemical tests are mainly done by identify the kinetics of cathode and anode potentials in the electrode. The electrochemical tests were performed by using three electrode glass cells. 99.9% purity platinum electrode was considered as a counter electrode and the electrode was made up of mild steel ($0.339cm^2$) used as a working electrode and its electrode potential was measured against a standard calomel electrode (SCE).

The setup of electrochemical instrument, method of working and calculation of polarization resistance values are followed as given in the previous studies[11]. The inhibition of efficiency of the organic inhibitor was measured from its polarization resistance value by using following formulas:

$$[(I.E)_{R_p},\%] = \frac{R_p^i - R_p^0}{R_p^i} \times 100$$

$$\left[(I.E)_{T},\%\right] = \frac{i^{0}_{corr}-i^{i}_{corr}}{i^{0}_{corr}} \times 100$$

where R^0_p and R^i_p indicate the polarization resistance in the absence and presence of inhibitor respectively and i^i_{corr} and i^0_{corr} are the corrosion current density values in presence and absence of inhibitor. The corrosion densities (i_{corr}) from the Tafel extraplotations was also used to determine the inhibition efficiency.

Results and Discussion

Structural confirmation of Organic Inhibitor: The PAC target compounds were synthesized using Schiff reaction between substituted aniline and 5,5- dimethyl substituted cyclohexan-1,3-dione via microwave irradiation. Microwave method is one of the best and eco-friendly method to synthesise these type of organic inhibitors and is also time saving and economical method. The skeleton structures were confirmed by using elemental analysis spectral data are given as follows:

PAC-1 (5,5-dimethyl-3-(phenylamino)cyclohex-2-enone: Yield 70%, m.p. 100ºC, Molecular Formula $C_{14}H_{17}NO$; %Calcd. (Found); C%= 51.42 (78.10), H% =4.28 (7.96), N% = 7.8 (6.51), O%=9.16 (7.43). M/z (M) +:215.3; FT-IR (KBr, cm^{-1}): 3042.09 cm-1(Aromatic CH stretching), 2889.54cm^{-1} (Aliphatic CH stretching), 1656.67 cm^{-1}(Amide C=O stretching), 1418.05 cm^{-1}(C=N Stretching), 645.15, 735.42, 784.42 cm^{-1}(Aromatic ring stretching); ^{1}H NMR ($CDCl_3$, δ ppm, 400 MHz) 1.02-1.11 (m, 6H of CH_3), 1.88-2.86 (m, 4H of methylene in cyclohexanone), 3.62 (S, 1H of NH), 5.54 (d, 1H of C-2 of cyclohexanone), 6.48-7.15(Aromatic protons); ^{13}C NMR ($CDCl_3$, δ ppm,100 MHz): 198.93 (C=O), 27.21 (methyl group in cyclohexanone ring), 99.08 (C-2 of cyclohexanone), 162.35 (C-3 of cyclohexanone), 43.08 (C-4 of cyclohexanone), 31.59 (C-5 of cyclohexanone), 52.73 (C-6 of cyclohexanone),122.56-144.08 (Aromatic carbons).

PAC-2 (5,5-dimethyl-3-(4-chlorophenylamino)cyclohex-2-enone: Yield 70%, m.p. 100ºC, Molecular Formula $C_{14}H_{16}NOCl$; %Calcd. (Found); C%= 51.42 (67.33), H% =4.28 (6.46), N% = 7.8 (5.61) O%=9.16 (6.41), Cl% = (14.20). M/z (M) +:249.09; FT-IR (KBr, cm^{-1}): 3076.23 cm^{-1}(Aromatic CH stretching), 2888.45cm^{-1} (Aliphatic CH stretching), 1652.25 cm^{-1}(Amide C=O stretching), 1412.51 cm^{-1}(C=N Stretching), 654.15, 710.54, 783.91 cm^{-1}(Aromatic ring stretching); ^{1}H NMR ($CDCl_3$, δ ppm, 400 MHz) 1.03-1.25 (m, 6H of CH_3), 2.14-2.84 (m, 4H of methylene in cyclohexanone), 3.62 (S, 1H of NH), 5.68 (d, 1H of C-2 of cyclohexanone), 6.45-7.87(Aromatic protons); ^{13}C NMR ($CDCl_3$, δ ppm,100 MHz): 198.82 (C=O), 28.42 (methyl group in cyclohexanone ring), 97.43 (C-2 of cyclohexanone), 162.14 (C-3 of cyclohexanone), 43.48 (C-4 of cyclohexanone), 32.95 (C-5 of cyclohexanone), 51.25 (C-6 of cyclohexanone),117.71-142.53 (Aromatic carbons).

PAC-3 (5,5-dimethyl-3-(4-bromophenylamino)cyclohex-2-enone: Yield 70%, m.p. 100ºC, Molecular Formula $C_{14}H_{16}NOBr$; %Calcd. (Found); C%= 51.42 (57.16), H% =4.28 (5.48), N% = 7.8 (4.76) O%=9.16 (5.44), Br%= (27.16). M/z (M) +:350,352; FT-IR (KBr, cm^{-1}): 3066.11 cm^{-1}(Aromatic CH stretching), 2885.51cm^{-1} (Aliphatic CH stretching), 1658.78 cm^{-1}(Amide C=O stretching), 1417.68 cm^{-1}(C=N Stretching), 642.3, 709.8, 763.81 cm^{-1}(Aromatic ring stretching); ^{1}H NMR ($CDCl_3$, δ ppm, 400 MHz) 1.06-1.48 (m, 6H of CH_3), 2.18-2.58 (m, 4H of methylene in cyclohexanone), 3.12 (S, 1H of NH), 5.76 (d, 1H of C-2 of cyclohexanone), 6.97-7.53(Aromatic protons); ^{13}C NMR ($CDCl_3$, δ ppm,100 MHz): 198.52 (C=O), 28.61 (methyl group in cyclohexanone ring), 97.56 (C-2 of cyclohexanone), 162.84 (C-3 of cyclohexanone), 43.38 (C-4 of cyclohexanone), 33.09 (C-5 of cyclohexanone), 50.73 (C-6 of cyclohexanone),124.28-138.93 (Aromatic carbons).

PAC-4 (5,5-dimethyl-3-(4-nitrophenylamino)cyclohex-2-enone: Yield 70%, m.p. 100ºC, Molecular Formula $C_{14}H_{16}N_2O_3$; %Calcd. (Found); C%= 64.42 (64.60), H% =4.28 (6.20), N% = 7.8 (10.76) O%=9.16 (18.44). M/z (M) +: 260.12; FT-IR (KBr, cm^{-1}): 3065.23 cm^{-1}(Aromatic CH stretching), 2881.74cm^{-1} (Aliphatic CH stretching), 1657.15 cm^{-1}(Amide C=O stretching), 1417.88 cm^{-1}(C=N Stretching), 652.30, 712.57, 788.99 cm^{-1}(Aromatic ring stretching); ^{1}H NMR ($CDCl_3$, δ ppm, 400 MHz) 1.04-1.50 (m, 6H of CH_3), 2.14-2.64 (m, 4H of methylene in cyclohexanone), 3.09 (S, 1H of NH), 5.48 (d, 1H of C-2 of cyclohexanone), 6.72-7.94 (Aromatic protons); ^{13}C NMR ($CDCl_3$, δ ppm,100 MHz): 198.95 (C=O), 29.05 (methyl group in cyclohexanone ring), 98.18 (C-2 of cyclohexanone), 162.23 (C-3 of cyclohexanone), 43.14 (C-4 of cyclohexanone), 32.89 (C-5 of cyclohexanone), 50.83 (C-6 of cyclohexanone), 121.92-146.88 (Aromatic carbons).

PAC-5 (5,5-dimethyl-3-(2-nitrophenylamino)cyclohex-2-enone: Yield 70%, m.p. 100ºC, Molecular Formula $C_{14}H_{16}N_2O_3$; %Calcd. (Found); C%= 51.42 (64.60), H% =4.28 (6.20), N% = 7.8 (10.76) O%=9.16 (18.44); FT-IR (KBr, cm^{-1}): 3065.47 cm^{-1}(Aromatic CH stretching), 2882.12 cm^{-1} (Aliphatic CH stretching), 1657.85 cm^{-1}(Amide C=O stretching), 1417.56 cm^{-1}(C=N Stretching), 653.03, 713.61, 785.96 cm^{-1}(Aromatic ring stretching); ^{1}H NMR ($CDCl_3$, δ ppm, 400 MHz) 1.05-1.56 (m, 6H of CH_3), 2.09-2.46 (m, 4H of methylene in cyclohexanone), 3.11 (S, 1H of NH), 5.45 (d, 1H of C-2 of cyclohexanone), 6.74-7.96 (Aromatic protons); ^{13}C NMR ($CDCl_3$, δ ppm,100 MHz): 198.91 (C=O), 29.12 (methyl group in cyclohexanone ring), 98.16 (C-2 of cyclohexanone), 162.24 (C-3 of cyclohexanone), 43.18 (C-4 of cyclohexanone), 32.91 (C-5 of cyclohexanone), 50.85 (C-6 of cyclohexanone),121.98-145.93 (Aromatic carbons).

From the above data, carbon structures of the organic inhibitors (PAC 1-5) were confirmed and the common structure is shown in figure 1.

Weight loss measurement: The inhibition efficiency with different concentrations of the inhibitor PAC on the mild steel in 1M H_2SO_4 and 1M HCl has been evaluated by weight loss measurements and the results are summarized in table 1.

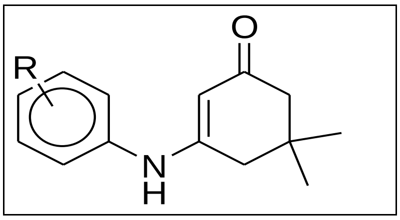

Figure 1: The common structure of PAC inhibitors

The data reveals that inhibition efficiency increases with increase in concentration of the inhibitors. The behavior may be attributed to an increase in surface coverage (θ) by the adsorption of inhibitor on the mild steel surface, in the aggressive solution which restricts the dissolution of the metal.

Effect of temperature: The effect of temperature on the inhibited acid-metal reaction is highly complex because many changes occur on the metal surface such as rapid etchings, desorption of the inhibitor and the inhibitor may undergo decomposition and/ or rearrangement. To evaluate the effect of temperature on the adsorption behaviour as well as to determine the activation parameters of the corrosion of mild steel in 1M H_2SO_4 solution and 1M H_2SO_4 solution containing the inhibitors, the weight loss measurements were carried out in the temperature range of (301-318K) and the results are presented in table 2.

The data reveals that as the temperature is increased, the corrosion rate increased and the inhibition efficiency decreased. The decrease in the inhibition efficiency with increase in temperature may be attributed to the increase in the solubility of the protective film or the reaction products precipitated on the surface of the metal that might otherwise inhibit the reaction. This is in accordance with Ergun et al[10].

The corrosion rate (CR) of the mild steel in acidic media is related to the temperature by the Arrhenius equation:

$$\text{Log CR} = \log A - E_a / 2.303\,RT$$

where CR is the corrosion rate, Ea is the apparent activation energy, R is the molar gas constant, T is the absolute temperature and A is the frequency factor. The plot of log CR vs 1/T is shown in fig. 2. Linear plots were obtained.

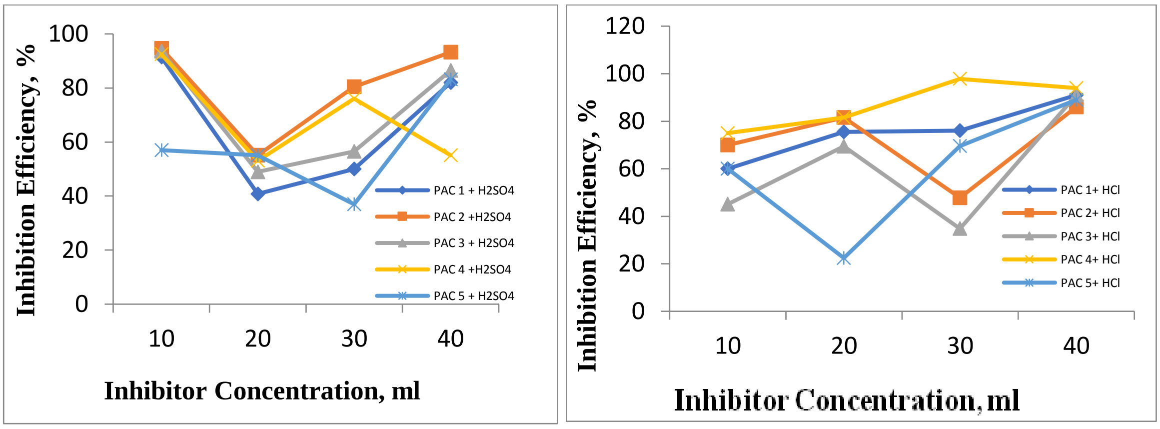

Figure 2: (a) plot of inhibition concentration against inhibition efficiency of mild steel in IM H_2SO_4 of inhibitor PAC (1-5), (b) plot of inhibition concentration against inhibition efficiency of mild steel in IM HCl of inhibitor PAC (1-5).

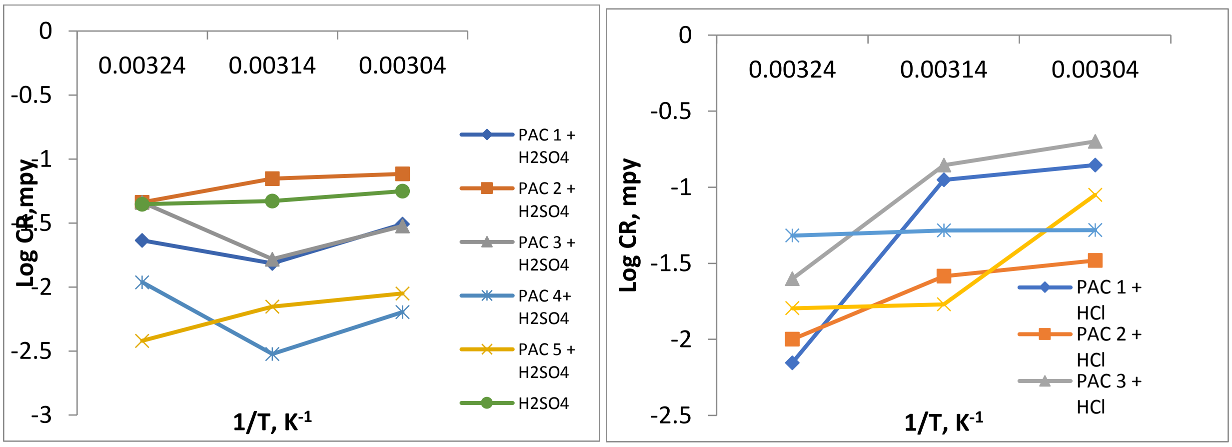

Figure 3: (a) plot of inhibition concentration against inhibition efficiency of mild steel in IM H_2SO_4 of inhibitor PAC (1-5), (b) plot of inhibition concentration against inhibition efficiency of mild steel in IM HCl of inhibitor PAC (1-5).

Table 1
Inhibition efficiency of PAC inhibitors at various concentration immersed at various concentrations of 1M HCl and H_2SO_4

Inhibitor concentration in %	Weight loss in mg	Inhibition Efficiency in %	Degree of coverage in θ	C/θ	Corrosion rate in mpy*10^{-3}
Blank (10 ml)	0.093	-	-	-	0.0478
H_2SO_4+ PAC 1	0.008	91.39	0.91	10.989	0.368
H_2SO_4 + PAC 2	0.005	94.62	0.94	21.276	0.832
H_2SO_4 + PAC 3	0.006	93.54	0.93	32.258	0.999
H_2SO_4 + PAC 4	0.007	92.47	0.92	43.478	1.165
H_2SO_4 + PAC 5	0.005	56.98	0.94	53.191	0.832
Blank (20 ml)	0.049	-	-	-	0.0251
H_2SO_4+ PAC 1	0.029	40.81	0.40	50	0.088
H_2SO_4 + PAC 2	0.022	55.10	0.55	36.36	0.028
H_2SO_4 + PAC 3	0.073	48.97	0.48	41.66	0.093
H_2SO_4 + PAC 4	0.023	53.06	0.53	37.73	0.029
H_2SO_4 + PAC 5	0.022	55.10	0.55	36.36	0.028
Blank (30 ml)	0.046	-	-	-	0.0021
H_2SO_4+ PAC 1	0.069	50	0.50	60	0.088
H_2SO_4 + PAC 2	0.009	80.43	0.80	37.5	0.011
H_2SO_4 + PAC 3	0.020	56.52	0.56	53.57	0.025
H_2SO_4 + PAC 4	0.011	76.08	0.76	39.47	0.014
H_2SO_4 + PAC 5	0.029	36.95	0.36	83.33	0.037
Blank (40 ml)	0.089	-	-	-	0.0457
H_2SO_4 + PAC 1	0.016	82.02	0.82	48.78	2.664
H_2SO_4 + PAC 2	0.006	93.25	0.93	43.01	10.825
H_2SO_4 + PAC 3	0.012	86.51	0.87	45.97	1.998
H_2SO_4 + PAC 4	0.040	55.05	0.55	72.72	6.662
H_2SO_4+ PAC 5	0.015	83.14	0.83	48.19	2.498
Blank (10 ml)	0.02	-	-	-	0.1027
HCl+ PAC 1	0.008	60	0.60	16.666	1.332
HCl + PAC 2	0.006	70	0.7	28.571	0.999
HCl + PAC 3	0.011	45	0.45	66.66	1.832
HCl + PAC 4	0.005	75	0.75	53.331	0.832
HCl + PAC 5	0.008	60	0.60	83.33	1.332
Blank (20 ml)	0.049	-	-	-	0.0096
HCl+ PAC 1	0.012	75.51	0.75	26.66	0.015
HCl + PAC 2	0.009	81.63	0.81	24.69	0.014
HCl + PAC 3	0.015	69.38	0.69	28.98	0.019
HCl + PAC 4	0.009	81.63	0.81	24.69	0.011
HCl + PAC 5	0.060	22.44	0.22	90.90	0.076
Blank (30 ml)	0.046	-	-	-	0.012
HCl+ PAC 1	0.011	76.0	0.76	39.47	0.014
HCl + PAC 2	0.024	47.8	0.47	63.82	0.030
HCl + PAC 3	0.03	34.78	0.35	85.71	0.070
HCl + PAC 4	0.001	97.82	0.97	30.92	0.012
HCl + PAC 5	0.013	69.56	0.69	43.47	0.016
Blank (40 ml)	0.058	-	-	-	0.298
HCl+ PAC 1	0.005	91	0.91	43.95	0.832
HCl + PAC 2	0.008	86	0.86	46.511	1.332
HCl + PAC 3	0.005	91	0.91	43.95	0.832
HCl + PAC 4	0.003	94	0.94	42.55	0.4979
HCl + PAC 5	0.006	89	0.89	44.94	0.9958

Table 2
Inhibition efficiency of PAC (1-5) inhibitors at various temperature 35ºC, 45ºC and 55ºC of 1M HCl and H_2SO_4

Inhibitor concentration in %	Weight loss in mg	Inhibition Efficiency in %	Degree of coverage in θ	C/θ	Corrosion rate in Mpy
Blank (35ºC)	0.034	-	-	-	0.0443
H_2SO_4+ PAC 1	0.018	55	0.55	1.8181	0.0231
H_2SO_4 + PAC 2	0.036	10	0.10	10	0.0459
H_2SO_4 + PAC 3	0.036	10	0.10	10	0.0459
H_2SO_4+ PAC 4	0.0038	90.5	0.90	1.111	1.0048
H_2SO_4 + PAC 5	0.003	92.5	0.92	1.086	0.0038
Blank (45ºC)	0.036	-	-	-	0.047
H_2SO_4+ PAC 1	0.012	67.73	0.67	1.492	0.0153
H_2SO_4 + PAC 2	0.06	62.16	0.62	1.6129	0.0765
H_2SO_4 + PAC 3	0.013	64.86	0.64	1.562	0.0165
H_2SO_4+ PAC 4	0.050	35.13	0.35	2.857	0.0638
H_2SO_4 + PAC 5	0.007	81.08	0.81	1.234	0.0089
Blank (55ºC)	0.043	-	-	-	0.0561
H_2SO_4+ PAC 1	0.025	41.86	0.41	2.439	0.031
H_2SO_4 + PAC 2	0.055	27.90	0.27	3.703	0.070
H_2SO_4 + PAC 3	0.024	44.18	0.44	2.272	0.030
H_2SO_4+ PAC 4	0.003	93.02	0.93	1.075	0.003
H_2SO_4 + PAC 5	0.006	86.04	0.86	1.162	0.007
Blank (35ºC)	0.04	-	-	-	0.052
HCl+ PAC 1	0.006	85.0	0.85	1.176	0.007
HCl + PAC 2	0.008	80.0	0.80	1.250	0.010
HCl + PAC 3	0.011	72.5	0.72	1.388	0.140
HCl + PAC 4	0.010	75	0.75	1.333	0.012
HCl + PAC 5	0.013	168.7	0.168	5.952	0.016
Blank (45ºC)	0.037	-	-	-	0.048
HCl+ PAC 1	0.011	70.27	0.70	1.428	0.140
HCl + PAC 2	0.021	43.24	0.43	2.325	0.026
HCl + PAC 3	0.002	94.59	0.94	1.063	0.025
HCl + PAC 4	0.004	89.18	0.89	1.123	0.051
HCl + PAC 5	0.014	62.16	0.62	1,612	0.017
Blank (55ºC)	0.040	-	-	-	0.0087
HCl+ PAC 1	0.006	85.0	0.85	1.176	0.007
HCl + PAC 2	0.003	92.0	0.92	1.086	0.003
HCl + PAC 3	0.157	292.5	0.292	3.424	0.200
HCl + PAC 4	0.009	77.5	0.77	1.298	1.011
HCl + PAC 5	0.007	82.5	0.82	1.219	0.089

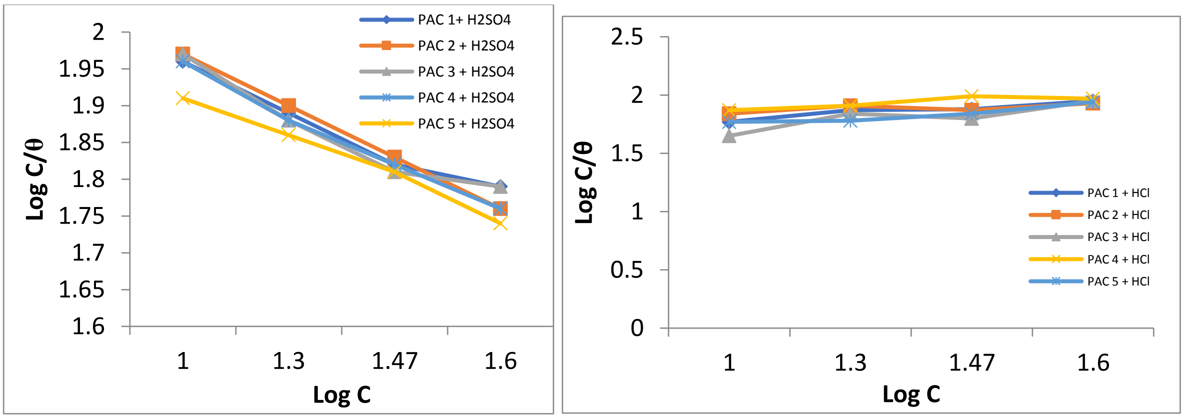

Figure 4: (a) Langumuir adsorption isotherms after the addition of PAC (1-5) inhibitor used for carbon steel in IM H_2SO_4, (b) Langumuir adsorption isotherms after the addition of PAC (1-5) inhibitor used for carbon steel in IM HCl.

Adsorption isotherm: Adsorption of the inhibitor molecules mainly depends on the charge and nature of the metal surface, electronic characteristics of the metal surface, temperature, adsorption of the solvent, ionic species and the electrochemical potential at the solution interface. The adsorption isotherm describes the adsorption behaviour of organic compounds. The most frequently used adsorption isotherms are Langmuir, Tempkin, Frumkin and Freundlich. To obtain the adsorption isotherm, the degree of surface coverage (θ) was calculated for various concentrations of PAC inhibitors from the weight loss data listed in table 1.

Adsorption behaviour of PAC inhibitors is best explained by Langmuir adsorption isotherm. Langmuir isotherm is an ideal isotherm for physical or chemical adsorption where there is no interaction between the adsorbate and adsorbent [11]. Assumption of Langmuir relates the concentration of the adsorbate in the bulk of the electrolyte (C) to the degree of surface coverage (θ) according to the equation:

$$C/\theta = 1/K + C$$

where 'K' is the equilibrium constant of adsorption.

Applicability of Langmuir adsorption isotherm to the adsorption of PAC inhibitors on mild steel confirms the formation of multimolecular layer of adsorption where there is no interaction between the adsorbate and the adsorbent.

Potentiometric polarization tests: In iron or steel corrosion, electrochemical reactions may take place as follows:

At the anodic areas:

$$Fe \longrightarrow Fe^{2+} + 2e^-$$

When iron corrodes, the rate is usually controlled by the cathodic reaction. There are several different cathodic reactions that are frequently encountered in metallic corrosion. The most common are:

Hydrogen evolution
$2H^+ + 2e^- \longrightarrow H_2$
Oxygen reduction (acid solution)
$O_2 + 4\,H^+ + 4e^- \longrightarrow 2H_2O$
Oxygen reduction (neutral or basic solution)
$O_2 + 4H_2O + 4e^- \longrightarrow 4OH^-$
Metal ion reduction
$M^{3+} + e^- \longrightarrow M^{2+}$
Metal deposition
$M^+ + e^- \longrightarrow M$

Hydrogen evolution is a common cathodic reaction since acidic media are frequently encountered. Oxygen reduction is very common, since any aqueous solution in contact with air is capable of reducing this reaction. Metal ion reduction and metal deposition are less common. All the above reactions are consuming electrons.

Since the anodic and cathodic reactions occurring during corrosion are mutually dependent, it is possible to reduce corrosion by reducing the rates of either reaction. So, if the surface of the metal is coated with paint or other conducting film, the rates of both anodic and cathodic reactions will be greatly reduced and corrosion will be retarded. The corrosion behaviour of metals and thus the corrosion-inhibiting processes depend greatly on the anion composition of the electrolyte.

The values of electrochemical parameters i.e. corrosion current density (i_{corr}), corrosion potential (Ecorr), Tafel slope (βc) and inhibitor efficiency (IET, %) obtained as functions are measured.

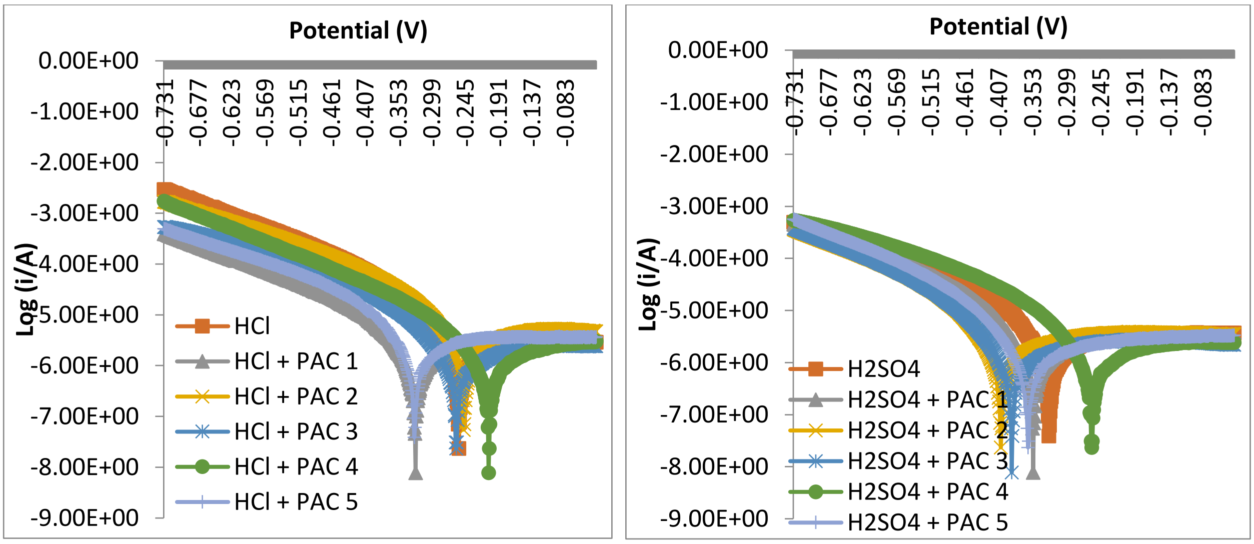

Figure 5: (a) Potentio dynamic polarization curves for carbon steel in 1M H_2SO_4 solution and after addition of PAC inhibitors, (b) Potentio dynamic polarization curves for carbon steel in 1M HCl solution and after addition of PAC inhibitors

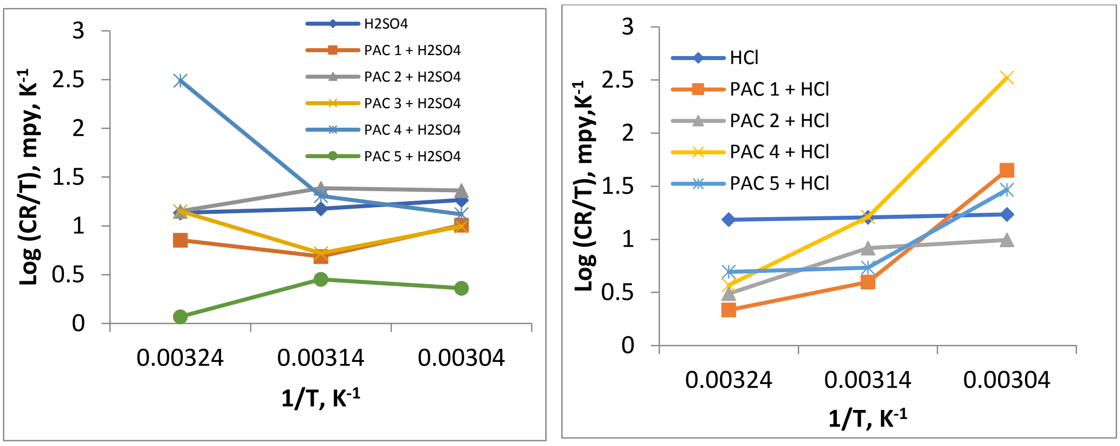

Figure 6: (a) log (corrosion rate/T) – (1/T) curves for dissolution in 1M H_2SO_4 in absence and presence of PAC (1-5) absence and presence of inhibitor, (b) log (corrosion rate/T) – (1/T) curves for dissolution in 1M HCl in absence and presence of PAC (1-5) absence and presence of inhibitor

Kinetic-thermodynamic corrosion parameters: The effect of temperature (28°C,35°C and 45°C) on the corrosion rate of iron in 1M HCl and H_2SO_4 at different concentrations of inhibitors was studied using weight loss measurements. Plots of log k (corrosion rate) against 1/T (Figure 6), for iron dissolution at different concentrations of inhibitors gave straight lines. The values of the slopes obtained at different temperatures permit the calculation of Arrhenius activation energy (Ea*). Activation parameters for corrosion of iron in 1M HCl and 1M H_2SO_4 were calculated from Arrhenius type plot:

$k=A \exp(-Ea^*/RT)$

and transition state type equation:

$k=RT/Nh \exp(\Delta S^*/R) \exp(-\Delta H^*/RT)$

The almost similar values of ΔEa^* suggested that the inhibitors are similar in the mechanism action and the order of the efficiency may be related with the pre-exponential factor A in equation (not shown).

The presence of investigated derivatives increases the activation energy of iron indicating strong adsorption of the inhibitor molecules on the metal surface. The presence of these additives induces energy barrier for the corrosion reaction and this barrier increases by increasing the additive concentration. The values of ΔH^* reported are positive. The positive sign of the enthalpy reflects the endothermic nature of Fe dissolution process.

Also, the values of entropy of activation are negative. The negative values of entropy imply that the activated complex in the rate determining step represents an association rather than dissociation step, meaning that a decrease in disordering takes place on going from reactants to activated complex. A decrease in inhibition efficiency with rise in temperature suggests a possible desorption of some adsorbed inhibitor molecules from the metal surface at higher temperatures. Such behaviour indicates that inhibitor molecules were physically adsorbed on the metal surface.

Conclusion

The PAC (1-5) inhibitors were synthesized in Schiff base mechanism by using eco-friendly microwave assisted method. All the PAC (1-5) inhibitors structures were characterized by using elemental analysis, IR, ^1H NMR and ^{13}C NMR. The inhibition efficiency of compounds PAC (1-5) was done by using weight loss method on 1M solution of HCl and H_2SO_4. The inhibition efficiency of the synthesized PAC (1-5) inhibitors increases with increase in inhibitor concentration and increase in temperature on 1M HCl and H_2SO_4 medium.

The PAC (1-5) inhibitors obey Langumuir adsorption isotherm and in the kinetic study, the mechanism is an endothermic one and Tafel polarization plot indicates the PAC (1-5) inhibitors behave mixed type.

References

1. Ahamad C., Gupta R., Prasad R. and Quraishi M.A., An experimental and theoretical investigation of adsorption characteristics of a Schiff base compound as corrosion inhibitor at mild steel/ hydrochloric acid interface, *J Appl. Electro Chem.*, **40**, 2171–2183 **(2010)**

2. Ahamad I., Prasad R. and Quraishi M.A., Thermodynamic, electrochemical and quantum chemical investigation of some Schiff bases as corrosion inhibitors for mild steel in hydrochloric acid solutions, *Corros. Sci*., **52**, 933–942 **(2010)**

3. Ahamad I. and Quraishi M.A., Bis(benzimidazol-2-yl) disulphide: An efficient water soluble inhibitor for corrosion of mild steel in acedic media, *Corros Sci.*, **51**, 2006–2013 **(2009)**

4. Ashassi-Sorkhabi H. and Eshaghi M., Corrosion inhibitor of mild steel in hydrochloric acid by betanin as a green inhibitor, *J. Solid State Electro Chem*., **13**, 1297–1301 **(2009)**

5. Ashassi-Sorkhabi H., Seifzadeh D. and Hosseini M.G., EN, EIS and polarization studies to evaluate the inhibition effect of 3H-

phenothiazin-3-one, 7-dimethylamin on mild steel corrosion in 1M HCl solution, *Corros Sci*., **50**, 3363–3370 **(2008)**

6. Bouklah M., Benchat N., Aouniti A., Hammouti B., Benkaddour M., Lagren´ee M., Vezin H. and Bentiss F., Effect of the substitution of an oxygen atom by sulphur in a pyridazinic molecule towards inhibition of corrosion steel in 0.5 M H_2SO_4 medium, *Prog. Org. Coat*., **51**, 118 **(2004)**

7. Dilek Demirezen Yilmaz, Koca Fatih Doğan and Nurhan Ertaş Onmaz, Comparison of antimicrobial activity of bio-synthesized silver and zinc oxide nanoparticles using Lavandula stoechas leaf extract, *Res. J. Biotech.*, **14(5)**, 24-29 **(2019)**

8. Ebenso E.E., Haliemichael Alemu, Umoren S.A. and Obot I.B., Inhibition of Mild Steel Corrosion in Sulphuric acid Using Alizarin Yellow GG Dye and Synergistic Iodide additive, *Int. J. Electrochem. Sci*., **3**, 1325-1339 **(2008)**

9. Emregul K.C. and Hayval M., Studies on the effect of vanillin and protocatechualdehyde on the corrosion of mild steel in hydrochloric acid, *Mater Chem. Phys.*, **83**, 209–216 **(2004)**

10. Ergun U., Yuzer D. and Emregul K.C., The inhibitory effect of bis-2,6-(3,5-dimethylpyrazolyl)pyridine on the corrosion behavior of mild steel in HCl solution, *Mater. Chem. Phy.*, **109**, 492 **(2008)**

11. Ezhilarasi M.R., Prabha B. and Santhi T., Corrosion inhibitive effect of pyrazole compounds towards the corrosion of mild steel in acidic medium, *Rasayan Journal of Chemistry*, **8(1)**, 71-83 **(2015)**

12. Govindaraju K.M., Gopi D. and Kavitha L., Inhibiting effects of 4-amino-antipyrine based Schiff base derivatives on the corrosion of mild steel in hydrochloric acid, *J Appl. Electro Chem*., **39**, 2345–2352 **(2009)**

13. Gupta N.K., Verma C., Quraishi M.A. and Mukherjee A.K., Schiff's bases derived from L-lysin and aromatic aldehydes as green corrosion inhibitors for mild steel: Experimental and theoretical studies, *J. Mol. Liq*., **215**, 47-57 **(2016)**

14. Hasanov R., Sadıkoglu M. and Bilgic S., Electrochemical and quantum chemical studies of some Schiff bases on the corrosion of steel in H_2SO_4 solution, *Appl Surf Sci.*, **253**, 3913–3921 **(2007)**

15. Huynh N., Bottle S.E., Notoya T., Trueman A., Hinton B. and Schweinsberg D.P., Studies on alkyl esters of carboxybenzotriazole as inhibitors for copper corrosion, *Corros. Sci*., **44**, 1257-1276**(2002)**

16. Nascimento R.C., Furtado L.B., Maria Jose, Guimaraes O.C., Peter R. Seidl and Rocha J.C., Synergistic effect of propargyl alcohol, octadecylamine and 1,3-dibutyl thiourea for API P110 alloys in acetic and formic acidic solutions used in oil well acidicing, *J. Mol. Liq.*, **256**, 548-557 **(2018)**

17. Quraishi M.A., Rawat J. and Ajmal M., Dithiobiurets: a novel class of acid corrosion inhibitors for mild steel, *J. Appl. Electrochem*., **30**, 745**(2000)**

18. Rajeev P., Surendranathan A.O. and Murthy C.S.N., Corrosion mitigation of the oil well steels using organic inhibitors-A review, *J. Mater. Environ. Sci.*, **3**, 856-869 **(2012)**

19. Tebbji K., Aouniti A., Benkaddour M., Oudda H., Bouabdallah I., Hammouti B. and Ramdani A., New bipyrazolic derivatives as corrosion inhibitors of steel in 1 M HCl, *Prog. Org. Coat*., **54**, 170-174 **(2005)**

20. Tebbji K., Faska N., Tounsi A., Oudda H., Benkaddour M. and Hammouti B., The effect of some lactones as inhibitors for the corrosion of mild steel in 1M hydrochloric acid, *Materials Chem. and Phy.*, **106**, 260-267 **(2007)**

21. Yadav M., Sinha R.R., Kumar S., Bahadur I. and Ebenso E.E., Synthesis and application of new acetohydrazide derivatives as a corrosion inhition of mid steel in acidic medium: Insight from electrochemical and theoretical studies, *J. Mol. Liq.*, **208**, 322-332 **(2015)**.

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