

# A Study on 4-(4-Aminobenzene-1-sulfonyl)piperazin-1-yl)(furan-2-yl)methanone for the Prevention of Corrosion on Mild Steel in Acidic Medium

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Synthesized [4-(4-aminobenzene-1-sulfonyl)piperazin-1-yl)(furan-2-yl)methanone (4-4-ABSPFM), a novel organic compound was used as inhibitor on prevention of mild steel corrosion. Experiments were performed in 1 N HCl acidic medium by weight loss method and electrochemical analysis. On comparing the results, it reveals that the novel organic compound shows better inhibition efficiency on mild steel corrosion, which is more effective in 1 N HCl at three different temperatures Electrochemical studies such as AC impedance and potentiodynamic polarization studies were proven the results by showing the inhibitor is a mixed type inhibitor in acidic medium. From the semi-micrograph obtained from SEM analysis shows a better efficiency of the inhibitor over the surface of the mild steel.

Keywords: Polarization, Impedance, Adsorption, Langmuir, Corrosion.

## **INTRODUCTION**

In majority of steel industries such as fabrication of reacting vessels, large storage tanks, petroleum refining industries and in many steel plants mild steel material plays a major role [1,2]. The main problem of utilizing mild steel material is its dissolution in acidic medium. Several remedies and methods are used at present for the prevention of corrosion. In reported methods using a new synthesized organic inhibitor is more efficient [3]. Many researchers reported that the organic compounds containing nitrogen, sulfur, oxygen and polar functional groups present in heterocyclic compounds inhibits mild steel corrosion [4-10]. Interaction of mild steel material and inhibitor takes places at the surface of the material via adsorption process. Factors such as nature of the material, type of hostile medium, structure of the inhibitor used and the nature of interaction between inhibitor molecule and the surface of the metal shows the influence of the adsorption of the inhibitor. In adsorption process there are two forms, one in physical adsorption and another one is chemical adsorption. In adsorption process, there may be sharing of charges or transfer of charges from the inhibitor molecule to the surface of the metal to form dative covalent bond formation [11].

Based on the literature, many organic inhibitors are reported. For example, indole-3-acetic acid on mild steel in

acidic medium (0.5 M HCl) shows a better result around 93% of inhibition efficiency [12]. On comparing the corrosion behaviour of mild steel in 1.11 N HCl with formazan of p-dimethylamino benzaldehyde (FD) and formazan of benzaldehyde (FB) show a better result in FD of inhibition efficiency 80% [13]. In sulphuric acid medium, effective inhibition of triazoles [14], azoles [15] and indoles [16] were reported of efficiency 65%. Around 95% of inhibition efficiency of Schiff based triazole in one molar HCl was reported [17]. Similarly on comparing 1 M HCl and 1 M H<sub>2</sub>SO<sub>4</sub> medium, the inhibition efficiency of a group of oxadiazoles compounds were reported shows an inhibition efficiency of more than 90% in 1 M HCl [18]. Therefore in this work, the inhibition efficiency of [4-(4-aminobenzene-1-sulfonyl)piperazin-1-yl)(furan-2-yl)methanone (4-4-ABSPFM) has been investigated on mild steel corrosion in 1 N HCl medium by weight loss method and electrochemical method at different temperature.

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# EXPERIMENTAL

**Preparation of mild steel specimens:** For weight loss method mild steel strips were cut into pieces of 5 cm  $\times$  1 cm. The metal has the following percentage composition Fe = 99.720, Ni = 0.017, Mo = 0.016, Cr = 0.049, S = 0.014, p =

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0.017, Si = 0.009, Mn = 0.142, C = 0.016. MS plate were cut into 1 cm  $\times$  1 cm  $\times$  0.3 cm dimension were used for electrochemical analysis. One surface which is not covered with araldite were immersed into acidic medium remaining part of the electrode is covered with araldite. Using various grade of emery sheet ranges from 400-1200 grit were used for polishing the surface of the metal and further degreased with acetone [19].

**A.C. Impedance cell:** Utilizing two-fold walled glass cell of limit which has an arrangements of bay for nitrogen gas, luggin slender, working anode and counter platinum terminal and. Through the luggin slender the capability of functioning terminal calomel anode (SCE) was estimated.

Preparation of inhibitor: Inhibitor solution of [4-(4aminobenzene-1-sulfonyl)piperazin-1-yl)(furan-2-yl)methanone (4-4-ABSPFM) was synthesized according to the reported method [20]. The reaction was carried out at a room temperature by adding compound 1-(2-furoyl)piperazine (3.0 g, 0.016 mol) was dissolved in ethylene dichloride (45 mL) with dry pyridine (4.1 mL, 0.053 mol) and 4-nitrobenzene-1-sulfonyl chloride (3.68 g, 0.016 mol). The mixture was allowed to stir for about 5 min for dissolution. The reaction mixture was heated for 8 h at 80 °C and the progress of reaction was monitored by TLC. The reaction mass was cooled and partitioned between ethyl acetate and water. The combined organic layer was washed with 2N HCl ( $2 \times 200$  mL), 5% NaHCO<sub>3</sub> ( $1 \times 250$  mL), brine solution (1  $\times$  250 mL) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> to afford [4-(4-nitrobenzene-1-sulfonyl)piperazin-1-yl](furan-2yl)methanone. Pale yellow solid; yield 85%; m.p.: 291-292 °C; IR (KBr, v<sub>max</sub>, cm<sup>-1</sup>): 3131, 3098 (CH *str.*, arom.), 2909, 2857 (CH str., aliph.), 1625 (C=O str.), 1535, 1294 (NO<sub>2</sub> str.), 1473, 1421 (CH bend.), 1332, 1166 (S=O str.), 1001 (CH bend.), 746 (CH bend, oop). <sup>1</sup>H NMR (DMSO- $d_6$ , 400 MHz)  $\delta$  ppm: 3.04 (t, 4H, J = 4.8 Hz), 3.72 (m, 4H), 6.56-6.57 (m, 1H), 6.94 (d, 1H, J = 3.2 Hz), 7.78 (d, 1H, J = 0.4 Hz), 7.98 (d, 2H, J =8.8 Hz), 8.40 (d, 2H J = 8.8 Hz); <sup>13</sup>C NMR (DMSO- $d_6$ , 400 MHz) δ ppm: 39.9, 46.2, 111.7, 116.5, 125.2, 129.5, 141.0, 145.0, 145.3, 146.9, 150.6, 158.7; LC-MS ESI m/z : 365.9 (M+1)+.

**Preparation of solution:** 1 N HCl solution was prepared using doubled distilled water. The aliquots of 4-4-ABSPFM in 100 mL of test solution were prepared by dissolving 1 g. Similarly various percentage of solutions have been prepared.

Weight loss measurement: In 1N HCl, mild steel specimens were immersed at a three different temperature range of 303 K, 318 K and 333 K in inhibitor at various concentrations. After 1 h, the specimen were detached and splashed with doubled distilled water and also using acetone. The difference in initial weight and final weight was calculated for weight loss data. Using this data rate of corrosion and efficiency of the inhibitor were calculated.

Corrosion rate (CR) = 
$$\frac{87.6 \times W}{D \times A \times T}$$

where, W = weight of the specimen, D = density of mild steel, A = area of the specimen and T = exposure time.

Similarly, inhibition efficiency:

$$\text{IE} (\%) = \frac{W_{o} - W_{i}}{W_{o}} \times 100$$

where  $W_o$  and  $W_i$  are the values of the weight loss (g) of mild steel in the absence and presence of inhibitor respectively.

Electrochemical studies: Electrochemical investigations were performed by setting up the coupons of mild steel material were cut into  $1 \text{ cm} \times 1 \text{ cm}$ . Subsequent the working anode electrode with analdite, 1 cm<sup>2</sup> space of the functioning terminal was uncovered into the test arrangement by cleaning the cathode with 400-1200 coarseness emery papers and degreased with acetone. In a three anode polarization cell 100 mL of the test arrangement was presented. The test arrangement in the polarization cell was permitted to accomplish a consistent possible incentive for 20 min [21,22]. By applying steady potential the resultant current was estimated. The exploratory setup were completed at an estimated voltage of  $\pm 200 \text{ mV}$  from consumption potential. With various temperature study the trial were done in the presence and non-appearance of the inhibitor. The determination of  $\beta_a$  and  $\beta_c$ , current thickness and Tafel curves were done by the extrapolation from the polarization bends. Hindrance productivity was from the accompanying equation:

IE (%) = 
$$\frac{I_{corr} - I_{corr(i)}}{I_{corr}} \times 100$$

where  $I_{corr}$  = Corrosion current density in the absence of inhibitor;  $I_{corr(i)}$  = Corrosion current density in the presence of inhibitor.

Likewise AC impedance study was completed in the recurrence scope of 10 kHz to 0.01 Hz. The impedance were plotted in Nyquist plots. The arrangement opposition ( $R_s$ ) and complete obstruction ( $R_t$ ) were acquired from the low recurrence and high-recurrence curves on Z' pivot of Nyquist plot separately. The distinction among  $R_t$  and  $R_s$  esteems give the charge move opposition  $R_{ct}$  esteem.

IE (%) = 
$$\frac{R_{ct(i)} - R_{ct}}{R_{ct(i)}} \times 100$$

**SEM analysis:** For SEM analysis, the mild steel material was cut into three cube shapes with a side length of 0.3 cm. The material was polished with 400-7000 lattice sandpaper until the testing surface is level. Two gentle steel cube pieces were independently immersed in 1 N HCl in absence and presence of the inhibitors for 24 h at three different temperatures.

### **RESULTS AND DISCUSSION**

Weight loss method: Mild steel material sample 5 cm  $\times$  1 cm were taken and numbered at the highest part of the plate. Presently, the plates were immersed in various concentration of the inhibitor in acidic medium and the study was performed at three different temperatures *viz.* 303 K, 318 K and 333 K. The rate of corrosion and efficiency of inhibitor were calculated (Table-1) and the graphs plotted for corrosion rate and inhibitor efficiency are shown in Figs. 1 and 2.

On comparing the data obtained the rate of corrosion decreases and efficiency of the inhibitor increases on the addition of inhibitor at three different temperatures. Based on the comparative result 303 K shows better efficiency of 87.21% in 1 N HCl medium.

#### TABLE-1 CORROSION INHIBITION BEHAVIOUR OF MILD STEEL IN 1 N HCI SOLUTION IN ABSENCE AND PRESENCE [4-(4-AMINOBENZENE-1-SULFONYL)PIPERAZIN-1-YL)(FURAN-2-YL) METHANONE INHIBITOR

Concentration of - inhibitor (%)	303 K		31	3 K	333 K			
	Corrosion rate	Inhibition	Corrosion rate	Inhibition	Corrosion rate	Inhibition		
	(mmpy)	efficiency (%)	(mmpy)	efficiency (%)	(mmpy)	efficiency (%)		
Blank	19.838	-	29.974	-	32.081	-		
10	7.133	64.04	28.654	59.24	31.823	53.60		
20	6.464	67.41	27.214	63.61	29.564	54.53		
40	5.461	72.47	24.587	69.21	28.325	57.21		
60	4.123	79.21	21.020	74.82	25.189	60.63		
80	2.897	85.39	24.541	76.63	21.365	62.47		
100	2.536	87.21	18.243	77.82	20.879	64.73		



Fig. 1. Comparison of corrosion rate of mild steel in 1 N HCl at various concentration of [4-(4-aminobenzene-1-sulfonyl)piperazin-1-yl) (furan-2-yl) methanone at different temperature at 1 h



Fig. 2. Comparison of inhibition efficiency of mild steel in 1 N HCl at various concentration of [4-(4-aminobenzene-1-sulfonyl)piperazin-1-yl)(furan-2-yl) methanone at different temperatures at 1 h

**Electrochemical studies:** For various corrosion framework highlights of EIS spectra were shown dependent on their charge transfer control, dispersion control or a mixed type of inhibitor. From EIS information (Nyquist plot), the component of corrosion can be distinguished [23]. Inhomogeneity of the surface and roughness of the cathodes are regularly suggested the recurrence scattering. The "depressed" half circle with the middle under the real axis of Nyquist plot shows the characteristic for the solid electrodes [24].

Nyquist plots for interface of mild steel electrode and electrolyte in the absence and presence of various concentrations of inhibitors at different temperatures are shown in Fig. 3a-c. Impedance parameters are represented in Table-2. The presence of N-H group in the inhibitor compound shows a better efficiency on prevention of mild steel material.

**Potentiodynamic polarization studies:** Efficiency on corrosion rate on mild steel material in 1 N HCl with inhibitory impact of [4-(4-aminobenzene-1-sulfonyl)piperazin-1-yl)-(furan-2-yl)methanone at three distinctive temperature was envisaged utilizing the potentiodynamic polarization studies and shown in Fig. 4a-c.

Tafel slope shows bot anodic and cathodic shift ( $\beta_a$  and  $\beta_c$ ) with different potentiodynamic boundaries. From the graph  $E_{corr}$  and  $I_{corr}$  was calculated. There is shift in the cathodic side because of the adsorption factor of the inhibitor over the mild steel surface which is seen from the  $E_{corr}$ . This shows the controlling idea of the inhibitor which effectively obstructing the destinations on the outside of the metal in the acidic medium. This proof clarifies that there is an extensive polarization access at cathode. The inhibitive activity of the



Fig. 3. A.C. Impedance curves of mild steel electrode immersed in 1 N HCl in the absence and presence of the inhibitor at (a) 303 K, (b) 318 K and (c) 333 K

A.C. IMPEDANCE PARAMETERS OF MILD STEEL ELECTRODE IMMERSED IN 1 N HCI IN THE ABSENCE AND PRESENCE OF THE INHIBITOR AT DIFFERENT TEMPERATURES									
Inhibitor	303 K			318 K			333 K		
concentration (ppm)	$R_{ct} (ohm cm^2)$	$C_{dl}$ ( $\mu$ F/cm <sup>2</sup> )	Inhibition efficiency (%)	$R_{ct} (ohm cm^2)$	$C_{dl}$ ( $\mu$ F/cm <sup>2</sup> )	Inhibition efficiency (%)	$R_{ct} (ohm cm^2)$	$\frac{C_{al}}{(\mu F/cm^2)}$	Inhibition efficiency (%)
Blank	22.54	805.22	-	22.54	127.99	-	22.17	1344.40	-
10	26.12	630.16	13.70	39.12	83.04	42.34	28.37	619.33	21.85
20	26.12	563.45	13.70	39.87	82.91	43.46	36.43	120.36	39.14
40	40.12	532.23	43.81	49.42	71.25	54.39	37.86	88.94	41.44
60	48.25	430.75	53.28	56.23	67.43	59.91	43.12	82.72	48.58
80	53.62	360.52	57.96	77.42	64.89	70.88	44.58	42.82	50.26
100	119.32	245.65	81.10	107.12	51.24	78.95	57.34	30.31	61.33

TABLE-2



Fig. 4. Potentiodynamic polarization curves of mild steel in 1 N HCl in the absence and presence of the inhibitor at (a) 303 K, (b) 318 K and (c) 333 K

inhibitor particle on mild steel material in acidic medium at various temperatures is a cathodic sort of inhibitor.

From Table-3, the potentiodynamic polarization boundaries were presented, which shows the fluctuation on Tafel slopes exposes that inhibitor at all fixation at various temperature shows the consumption component measure at cathode. At three unique temperatures on examination shows that  $I_{\mbox{\scriptsize corr}}$  were diminished.

**SEM studies:** Fig. 5 shows the component of mild steel surfaces at various conditions. Fig. 5a is the element of the mild steel surface in the wake of granulating, whereas Fig. 5b shows the surface element at 303 K dipping in a test solution

TABLE-3 POLARIZATION PARAMETERS OF MILD STEEL ELECTRODE IMMERSED IN THE ABSENCE AND PRESENCE OF THE OF THE INHIBITORS AT THREE DIFFERENT TEMPERATURES								
Temperature (K)	Inhibitor concentration (ppm)	$\beta_{c}  (V  dec^{-1})$	$\beta_{a}(Vdec^{\text{-1}})$	$E_{Corr}(V)$	$I_{\text{Corr}} \times 10^{-4} (\text{A})$	Corrosion rate (mmpy)	Inhibition efficiency (%)	
	Blank	7.016	5.900	-570	18.103	210.36	-	
	10	16.773	7.914	-512	10.523	90.502	41.87	
	20	12.139	7.636	-522	9.812	70.410	45.79	
303	40	10.021	4.745	-491	9.348	64.692	48.36	
	60	10.135	4.627	-443	8.142	52.243	55.02	
	80	10.090	4.015	-388	6.724	47.891	62.85	
	100	9.759	4.049	-361	3.432	91.700	81.04	
318	Blank	23.359	7.709	-576	29.852	196.52	-	
	10	7.590	3.905	-508	17.153	107.65	42.53	
	20	11.756	5.205	-491	15.825	98.78	46.98	
	40	20.791	8.240	-483	15.063	97.93	49.54	
	60	11.433	3.858	-465	13.297	94.65	55.45	
	80	10.135	4.627	-441	11.002	91.87	63.14	
	100	18.159	7.515	-434	6.345	68.46	78.74	
333	Blank	5.326	4.917	-542	18.646	216.67	-	
	10	9.103	5.905	-534	11.835	188.95	36.52	
	20	12.186	4.417	-501	11.023	174.25	40.88	
	40	10.021	4.754	-493	10.018	152.45	46.27	
	60	5.470	4.241	-482	8.898	132.54	52.27	
	80	6.077	3.735	-480	7.594	107.65	59.27	
	100	16.573	5.593	-411	5.172	76.54	72.26	



Fig. 5. Surface feature of mild steel in the different condition: (a) the surface of the mild steel after the sanding, (b) the mild steel after the addition of the inhibitor molecule is immersed in 303 K at 1 N HCl for 24 h and (c) mild steel surface after soaking for 24 h in 1 N HCl with inhibitor at 318 K for 24 h and (d) mild steel surface after soaking for 24 h in 1 N HCl with inhibitor at 333 K

for 24 h in 1 N HCl with 4-4-ABSPFM. Figs. 5c and 5d shows the element of mild steel surface inundated in 1 N HCl with 100 ppm of 4-4-ABSPFM at the temperature of 318 K and 333 K for 24 h with corrosion inhibitor.

From the semi micro pictures the outcome revealved that more pits were happened when the mild steel were soaked in test blank solution. No clear corrosion openings were found and a few scratches left in the surface of the mild steel. Along these lines, by contrasting the SEM pictures of Fig. 5b-d it shows that the inhibition efficiency of 4-4-ABSPFM in 1 N HCl corrosive arrangement can viably hinder the mild steel consumption.

### Conclusion

In this work, an efficiency of a novel organic corrosion inhibitor [4-(4-aminobenzene-1-sulfonyl)piperazin-1-yl)-(furan-2-yl)methanone] on mild steel in 1 N HCl were determinded by weight loss method as well as by electrochemical studies. The inhibitor was used for the investigation of consumption restraint of mild steel in 1 N HCl arrangements at three unique temperatures specifically 303 K, 318 K and 333 K. The effectiveness of the inhibitor was acceptable on every one of the three diverse temperature tested. On looking at the effectiveness of the inhibitor it keeps up at around 80% of productivity at low temperature. The inhibitor goes about as best inhibitor because of the presence of heteroatoms, O and N which shows higher basicity and electro thickness. As per the EIS information on expanding the centralization of the inhibitor, the proficiency increments yet relatively the effectiveness get diminishes on expanding temperature. The SEM morphology displayed that the inhibitor particle structure a solid film over the surface of the mild steel material which viably repressed the mild steel corrosion.

# **CONFLICT OF INTEREST**

The authors declare that there is no conflict of interests regarding the publication of this article.

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