



Evaluation of Corrosion Resistance of 5-Pyrazolones on Mild Steel in Acid Media

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The effects of 5-pyrazolone derivatives have been investigated as corrosion inhibitor for mild steel in 1M HCl and 1M H₂SO₄ using electrochemical and non-electrochemical techniques. The efficiency of inhibitor increases with increase in inhibitor concentration and decreases with rise in temperature. The adsorption of these inhibitors on mild steel surface has been found to obey Langmuir isotherm. Potentiodynamic polarization results show that the inhibitors behave as a mixed type. Some thermodynamic parameters such as enthalpy (ΔH°), entropy (ΔS°) and free energy (ΔG°) have been calculated.

Key Words: Corrosion inhibitor, 5-Pyrazolones, Mild steel.

INTRODUCTION

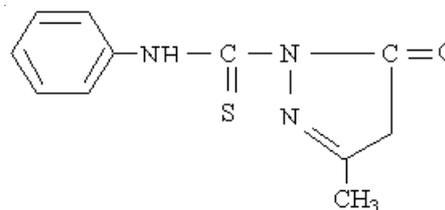
Mild steel is widely used as a constitutional material in many industries due to its good mechanical properties and low cost¹. The corrosion of mild steel is of fundamental academic and industrial concern that has received a considerable amount of attention. Inhibitors are often added in industrial processes to secure metal dissolution from acid solutions². A survey of literature reveals that the applicability of organic compounds as corrosion inhibitors for mild steel in acid media has been recognized for a long time. The organic molecules can adsorb on the metal surface because they form a bond between π -electron cloud and the metal thereby reducing the corrosive attack on metals in acidic media³. It has been observed that adsorption depends mainly on certain physico-chemical properties of the inhibitor group, functional groups, electron density at the donor atom, π -orbital character and the electro structure of the molecule⁴⁻⁶.

The present work is devoted to study the corrosion behaviour of different 5-pyrazolones for mild steel in 1M H₂SO₄ and 1M HCl by weight loss, potentiodynamic polarization and impedance methods.

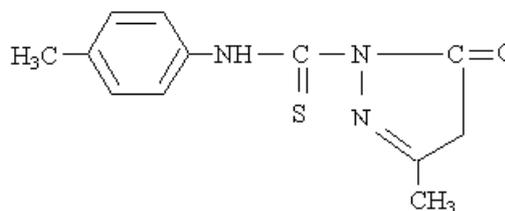
EXPERIMENTAL

Mild steel specimen of the size [(3.5 × 1.5) - 0.5] was used for investigation. The strips were mechanically polished using 1/0, 2/0, 3/0 and 4/0 emery papers and finally degreased with the organic solvent trichloroethylene and dried before use. The acid solutions were made from AR grade HCl and H₂SO₄ and the appropriate concentrations of the acids were

prepared with double distilled water. The compounds have been synthesized in two steps. The structural formula of the investigated compounds are given below



P1



P2

Weight loss measurements: Weight loss measurements were carried out by weighing the specimens in triplicate before and after immersion in 100 mL acid solution for 3 h in the absence and presence of inhibitors for various concentrations. From the initial and final masses of the specimen the weight loss was calculated. From this weight loss value, inhibition efficiency and corrosion rate were determined. Inhibitor efficiency has been determined by using the following relationship.

$$\text{Inhibitor efficiency (\%)} = \frac{W_b - W_i}{W_b}$$

where, W_b and W_i are the weight loss of mild steel in absence and presence of inhibitor.

Electrochemical measurements: Both cathodic and anodic polarization curves were recorded potentiodynamically at a scan rate of 1.66 mV/s using Parstat (Model 2723). A platinum electrode and a saturated calomel electrode were used as a counter electrode and reference electrode, respectively. The mild steel rod embedded in Teflon with an exposed area of 0.1257 cm² electrode was placed in the test solution before electrochemical measurements. Experiments were carried out at open circuit potential for the frequency range of 2-100 MHz. Charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) were obtained using AC impedance measurements.

RESULTS AND DISCUSSION

Weight loss studies: The inhibition efficiency with different concentrations of the inhibitors (P1 and P2) on mild steel has been evaluated by weight loss measurements and the results are given in Table-1. In all cases, the value of inhibition efficiency increases with increase in inhibitor concentration, suggesting an increase of the number of molecules adsorbed on mild steel surface³, blocking the active sites of acid attack and thereby protecting the metal from corrosion. The maximum efficiency of P1 and P2 are 91.88 and 61.76 %, respectively in HCl while in H₂SO₄, the maximum efficiency is found to be 96.70 and 3.97 %, respectively. The corrosion inhibition of these compounds is due to the presence of heteroatoms (O, N, S) and aryl group⁷.

Effect of temperature: To understand the effect of temperature on corrosion rate and inhibition efficiency, weight loss method was carried out at various temperatures from 303-

Name of the inhibitor	Inhibitor concentration (ppm)	Inhibition efficiency (%)	
		HCl	H ₂ SO ₄
P1	0.5	80.71	42.10
	1.0	86.80	73.48
	1.5	89.31	93.03
	2.0	90.86	94.98
	2.5	91.88	96.70
P2	0.5	29.41	37.31
	1.0	40.20	47.29
	1.5	46.08	56.83
	2.0	53.92	69.41
	2.5	61.76	73.97

333 K in the presence of the inhibitors. The results are given in Table-2. It can be seen from the table, inhibition efficiency decreases with rise of temperature in both acid medium. This may be due to the enhanced effect of temperature on the dissolution process of mild steel in acidic media and/or the partial desorption of inhibitor from the metal surface⁸. The result from temperature studies revealed that increasing temperature increases the corrosion rate and indicates that metal dissolution occurs on the metal surface⁹.

The activation energies were calculated from the slopes of Arrhenius plots (Fig. 1) for uninhibited and inhibited systems. It is apparent from the values of E_a (Table-3) that the activation energy is higher in the presence of inhibitor, suggesting that higher energy barrier for the corrosion process in the inhibited solution and also implies¹⁰ a slow reaction.

Thermodynamic parameters: The thermodynamic functions such as the free energy of adsorption (ΔG°), the heat of adsorption (ΔH°) and the entropy of adsorption (ΔS°) are very important to explain the adsorption phenomenon of inhibitor

TABLE-2
INHIBITION EFFICIENCIES OF INHIBITORS FOR THE CORROSION OF MILD STEEL OBTAINED BY WEIGHT LOSS MEASUREMENTS AT VARIOUS TEMPERATURES

Concentration of the inhibitor (ppm)	Temperature (K)	Inhibition efficiency (%)			
		HCl		H ₂ SO ₄	
		P1	P2	P1	P2
0.5	303	76.47	25.00	45.13	19.54
	313	75.56	16.33	35.95	15.94
	323	50.61	13.07	17.11	14.49
	333	18.08	07.57	5.46	12.47
1.0	303	83.53	36.11	59.73	25.50
	313	82.22	29.59	52.94	20.77
	323	70.12	22.11	26.56	18.82
	333	53.33	17.97	8.19	16.51
1.5	303	88.24	44.44	88.93	30.46
	313	85.56	38.78	86.60	26.57
	323	77.44	35.68	37.79	19.35
	333	67.56	29.31	18.89	17.99
2.0	303	89.41	47.22	89.82	65.23
	313	87.78	45.92	86.93	54.59
	323	83.54	40.20	62.92	32.62
	333	80.67	34.52	61.79	29.99
2.5	303	90.59	58.33	92.92	68.54
	313	90.00	53.06	90.20	63.77
	323	86.59	50.25	75.22	55.17
	333	83.11	47.04	75.11	51.01

TABLE-3
ACTIVATION ENERGIES (E_a) AND FREE ENERGY OF ADSORPTION (ΔG°) FOR
THE CORROSION OF MILD STEEL IN 1M HCl AND 1M H₂SO₄

Name of the inhibitor	E_a (kJ mol ⁻¹)		$-\Delta G^\circ$ at various temperatures (kJ mol ⁻¹)							
	HCl	H ₂ SO ₄	HCl				H ₂ SO ₄			
			303 K	313 K	323 K	333 K	303 K	313 K	323 K	333 K
Blank	68.05	50.40	–	–	–	–	–	–	–	–
P1	69.50	79.76	13.49	13.76	13.31	12.97	14.27	13.82	11.28	11.62
P2	74.60	63.36	8.63	8.36	8.33	8.23	9.75	9.51	8.86	8.67

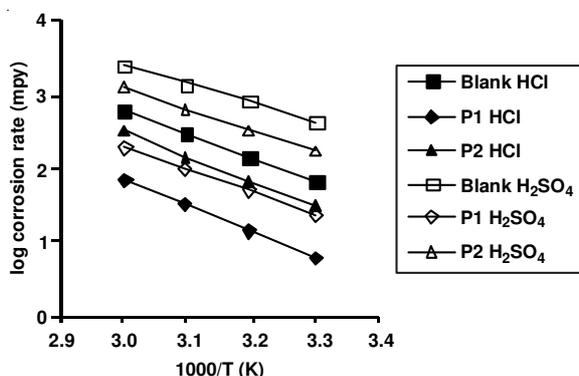


Fig. 1. Arrhenius plot for the corrosion of mild steel in 1M HCl and 1M H₂SO₄ in the absence and the presence of inhibitors

molecules. The free energy adsorption (ΔG°) were calculated using the following equation,

$$-\Delta G^\circ = 2.303 \times RT \left\{ 1.74 + \log \left[\frac{\theta}{(1-\theta)} \right] - \log C \right\}$$

The negative values¹¹ of ΔG° in all cases ensure the spontaneity of the adsorption process and stability of the adsorbed layer on the metal surface. Enthalpy of adsorption (ΔH°) and entropy of adsorption (ΔS°) were obtained from intercept and slope of the plot $-\Delta G^\circ$ against T depicted in Fig. 2 and are given in Table-4. The negative sign of the ΔH° reflects the exothermic nature of the mild steel adsorption process in the presence of P1 and P2 in both the acid media¹². The values of ΔH° obtained in this study are low, confirming that the inhibitors were physically adsorbed onto the mild steel surface. The ΔS° values in the presence of these three inhibitors are positive, indicating that an increase in disordering takes place in going from reactants to the metal adsorbed species reaction complex¹³.

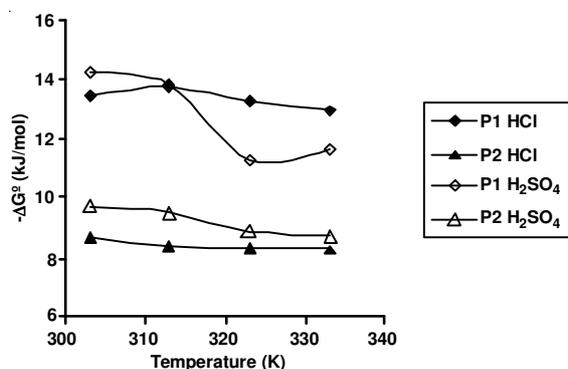


Fig. 2. Variation of $-\Delta G^\circ$ versus temperature on mild steel in 1M HCl and 1M H₂SO₄

TABLE-4
SOME THERMODYNAMIC PARAMETERS ΔS° AND ΔH° FOR
THE CORROSION OF MILD STEEL IN 1M HCl AND 1M H₂SO₄

Name of the Inhibitor	ΔS° (J/mol/K)		$-\Delta H^\circ$ (kJ/mol)	
	HCl	H ₂ SO ₄	HCl	H ₂ SO ₄
P1	19.81	46.17	0.02	0.11
P2	12.36	21.58	0.01	0.04

Adsorption isotherm: The degree of surface coverage (θ) has been used from weight loss data to explain the best isotherm to determine the adsorption process. The plotting (C/θ) against C gives straight line (Fig. 3). This indicates that the adsorption of P1 and P2 on mild steel in both HCl and H₂SO₄ solutions follow Langmuir's adsorption isotherm and consequently, there is no interaction between the molecules adsorbed at the metal surface.

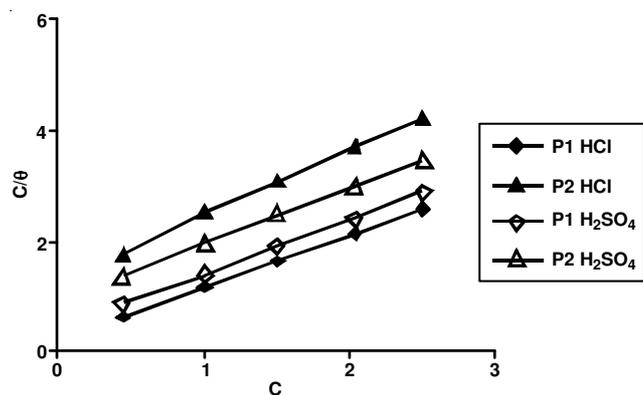


Fig. 3. Langmuir adsorption isotherm for inhibitors in 1M HCl and 1M H₂SO₄

Potentiodynamic polarization studies: The electrochemical parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}), Tafel slope (β_c and β_a) derived from polarization curves (Figs. 4-7) are listed in Table-5. Inspection of tables reveals that, (i) The addition of P1 and P2 shifted the E_{corr} to less negative values and no definite trend was observed in the shift of E_{corr} values in the presence of various concentrations of inhibitors. (ii) The values of I_{corr} of mild steel in the inhibited solution were smaller than those for the inhibitor free solution. The decrease of corrosion current may be explained by the action of inhibitor on both cathodic and anodic reactions¹⁴. (iii) In the case of P1 in H₂SO₄ and P2 and P1 in HCl medium the anodic (β_a) Tafel slope value was slightly affected compared to the cathodic (β_c) Tafel slope value, indicates that these compounds behave as a mixed type but slightly anodic in nature.

TABLE-5
CORROSION PARAMETERS FOR CORROSION OF MILD STEEL OF THE INHIBITORS IN
1M HCl AND 1M H₂SO₄ BY POTENTIODYNAMIC POLARIZATION METHOD

Name of the Inhibitor	Inhibitor concentration (ppm)	I_{corr} ($\mu A/cm^2$) $\times 10^{-2}$	E_{corr} (mV versus SCE)	β_c (mV/dec)	β_a (mV/dec)	Inhibition efficiency (%)
	Blank	1.621	-478.186	163.474	129.022	–
P1 HCl	0.5	1.352	-486.819	155.168	101.986	16.59
	1.0	0.660	-486.102	132.913	89.502	59.28
	1.5	0.535	-487.877	149.568	90.603	67.00
	2.0	0.515	-485.115	115.550	72.981	68.23
	2.5	0.234	-480.662	127.451	79.224	85.56
P2 HCl	0.5	1.381	-488.736	141.270	112.197	14.81
	1.0	1.343	-490.753	141.433	110.797	17.15
	1.5	1.105	-493.014	137.554	101.187	31.83
	2.0	1.009	-489.528	137.759	89.545	37.75
	2.5	0.707	-489.706	145.175	93.373	56.38
	Blank	2.713	-480.583	150.774	88.435	–
P1 H ₂ SO ₄	0.5	1.347	-473.356	146.333	78.016	50.35
	1.0	1.273	-460.176	156.350	71.023	53.08
	1.5	1.107	-456.867	143.075	66.728	59.20
	2.0	0.764	-459.790	147.534	58.174	71.84
	2.5	0.670	-457.245	149.192	57.765	75.30
P2 H ₂ SO ₄	0.5	1.381	-488.746	141.270	112.197	49.10
	1.0	1.343	-490.753	141.433	110.797	50.50
	1.5	1.105	-493.014	137.554	101.187	59.27
	2.0	1.009	-489.528	137.759	89.545	62.81
	2.5	0.902	-489.706	145.175	93.373	66.75

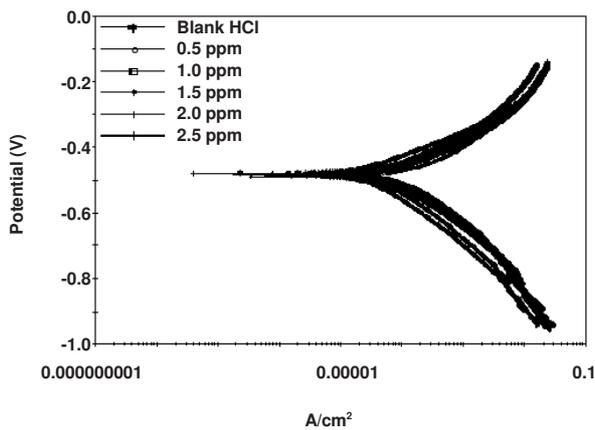


Fig. 4. Potentiodynamic polarization curves of P1 for mild steel in 1M HCl

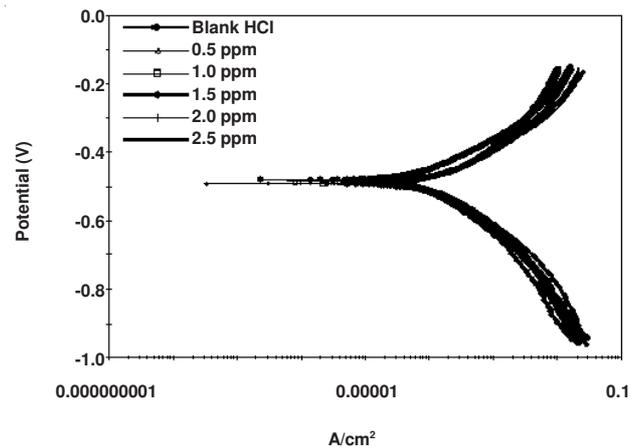


Fig. 6. Potentiodynamic polarization curves of P2 for mild steel in 1M HCl

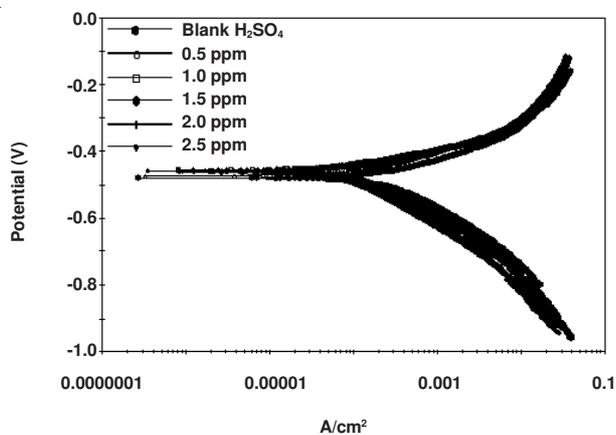


Fig. 5. Potentiodynamic polarization curves of P1 for mild steel in 1M H₂SO₄

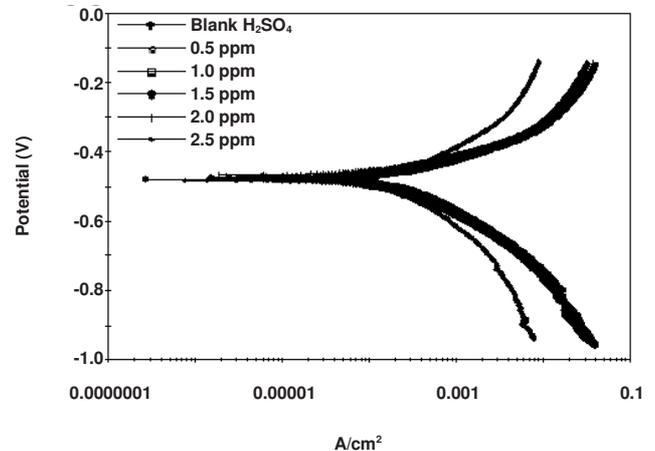


Fig. 7. Potentiodynamic polarization curves of P2 for mild steel in 1M H₂SO₄

Impedance measurements: The corrosion kinetic parameters such as charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) have been derived from Nyquist plot and percentage of inhibition efficiency are given in Table-6. The existence of semicircle in the Nyquist plot (Figs. 8-11) indicates that the corrosion of inhibitors is mainly controlled by a charge transfer process¹⁵. The presence of inhibitors enhances the values of R_{ct} . This indicates that the inhibitors does not alter the electro chemical reaction responsible for corrosion but inhibits corrosion primarily through its adsorption onto the metal surface. The decrease in C_{dl} values could be attributed to the adsorption of the inhibitor molecules at the metal surface¹⁶.

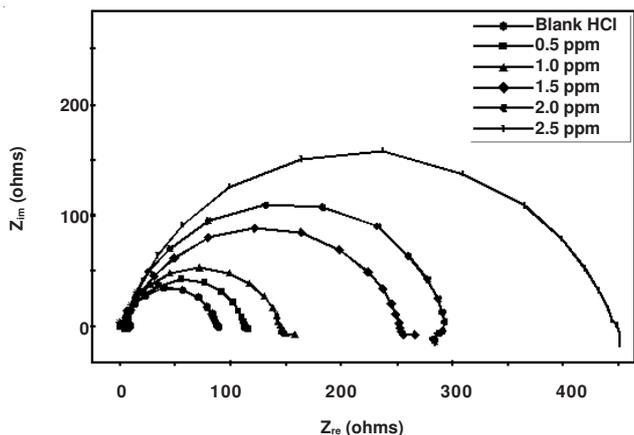


Fig. 8. Nyquist plots of P1 for mild steel in 1M HCl

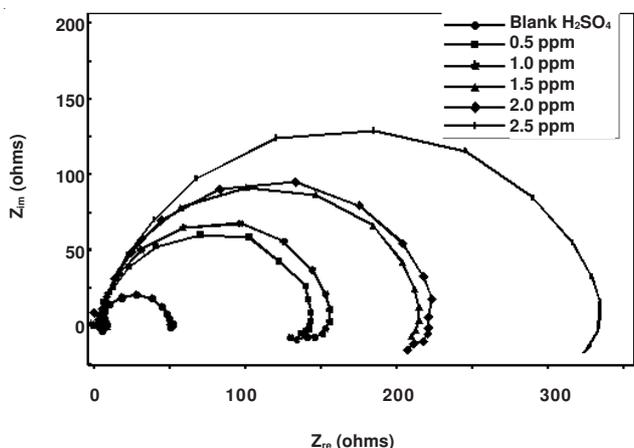


Fig. 9. Nyquist plots of P1 for mild steel in 1M H₂SO₄

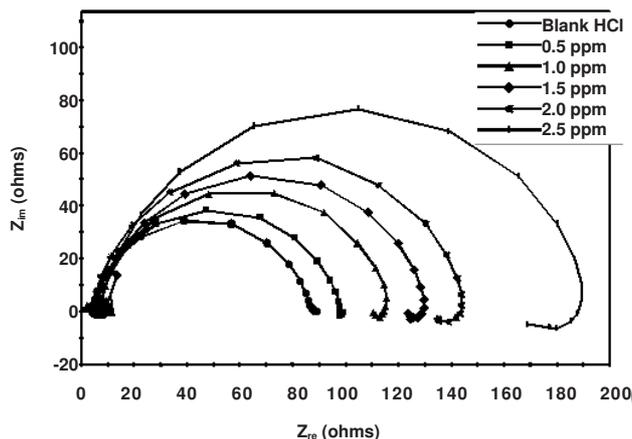


Fig. 10. Nyquist plots of P2 for mild steel in 1M HCl

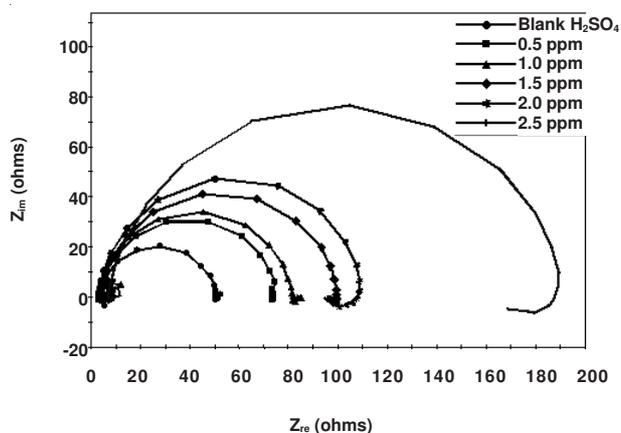


Fig. 11. Nyquist plots of P2 for mild steel in 1M H₂SO₄

The results obtained from impedance show a similar trend for the tested compounds as those obtained from potentiodynamic polarization and weight loss measurement but yielded different value of inhibition efficiency due to different experimental conditions.

Conclusion

- All investigated 5-pyrazolones are effective inhibitors for corrosion of mild steel in 1M HCl and 1M H₂SO₄.
- The inhibition efficiency increases with increase in the concentration of these inhibitors but decreases with rise in temperature.

Name of the inhibitor	Inhibitor concentration (ppm)	R_{ct} (ohms)		C_{dl} ($\times 10^{-5}$ μ farads)		Inhibition efficiency (%)	
		HCl	H ₂ SO ₄	HCl	H ₂ SO ₄	HCl	H ₂ SO ₄
Blank	–	77.81	42.79	2.130	1.753	–	–
P1	0.5	101.4	130.6	1.231	1.032	23.26	67.24
	1.0	129.9	142.4	0.973	1.2	40.10	69.95
	1.5	229.5	202.5	0.780	1.187	66.10	78.87
	2.0	269.3	208.8	0.792	0.798	71.11	79.51
	2.5	402.6	309.6	0.664	0.503	80.67	86.18
P2	0.5	89.07	65.44	1.577	1.572	12.64	34.61
	1.0	100.5	72.86	0.182	1.724	22.58	41.27
	1.5	115.3	88.74	0.161	1.834	32.52	51.78
	2.0	128.3	98.45	0.130	1.507	39.35	56.54
	2.5	168.1	132.5	0.122	1.273	53.71	67.71

- The inhibition is due to the presence of heteroatoms (O, N, S) and an aryl group.
- The adsorption of these compounds on the metal surface follows Langmuir adsorption isotherm in both acid media.
- The activation energy (E_a) is higher for inhibited acids than for uninhibited acids.
- Phenomenon of physical adsorption is proposed from the obtained value of thermodynamic parameters.
- The Tafel constants obtained from potentiodynamic polarization curves indicate that they are mixed type inhibitors but slightly anodic in nature.
- There is a good agreement between the results by electrochemical and non-electrochemical techniques.

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