

# THERMODYNAMIC AND SORPTION STUDIES OF 5 - PHENYLISOXAZOLE ON MILD STEEL IN 2 M HCl SOLUTIONS



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## ABSTRACT

Thermodynamic and sorption studies of 5 - phenylisoxazole (P) for mild steel in 2 M HCl solutions were undertaken. From weight loss technique. Results showed that inhibition efficiency increased with inhibitor concentration to a maximum of 66% in  $10 \times 10^{-4}$  M at 303 K. The negative values of Gibb's free energy ( $\Delta G^{\circ}_{\text{ads}}$ ) ranging from -12.62 kJ/mol to -24.00 kJ/mol for the inhibitor indicate spontaneous adsorption of the inhibitor on mild steel surface; and the adsorption mechanism was physi-sorption. The positive values of  $\Delta H^{\circ}$  reflected the endothermic behaviour of the adsorption of the inhibitor on the mild steel surface. The negative values of  $\Delta S^{\circ}$  suggested that the adsorption process was accompanied by a decrease in entropy.

## INTRODUCTION

Hydrochloric acid is often used for industrial metal scale removal and cleaning as well as other practices such as acid de-scaling and oil well acidizing (Nataraja *et al*, 2011). Due to these practices, metal corrosion is promoted, and if the corrosion process is not abated, failure is inevitable. The most effective way of metal corrosion control is the use of corrosion inhibitors (Umoren and Solomon, 2014a). Hence, it is advisable that metal corrosion inhibitors be added to the acid solutions before use. Organic (those with N, O, S, P, and  $\pi$ -electrons in their structure) (Xhanari and Finsger, 2016) and inorganic (nitrites, nitrates, phosphates and lanthanides) (Umoren and Solomon, 2017a) compounds are the common acid corrosion inhibitors. The demand for organic metals corrosion inhibitor stands at 70% presently; while that of the inorganic counterpart is remarkably low (Umoren and Solomon, 2017b) due to their negative influence on the ecosystem. Organic compounds have long been known to inhibit the corrosion of mild steel in acidic media. Organic compounds previously studied as inhibitors include triazole derivatives, bipyrazolic derivatives, aromatic hydrazides, organic dyes, poly (4 - vinylpyridine) and thiosemicarbazide (NACE, 2000; Hosseini *et al*, 2010). These compounds can adsorb onto the mild steel surface and block active sites, thus decreasing the corrosion rate. In the present work, 5 - phenylisoxazole (P) is used as inhibitor because it possesses heteroatoms, it is highly available, it is cost effective and eco-friendly, and has not been used as mild steel corrosion inhibitor in acidic medium in any available literature. With the multiple adsorption sites, complexes will be formed with the metal ions on the metal surface. This organic compound is a product of Sigma Aldrich.

## MATERIALS AND METHOD

The gravimetric (weight loss) experiments were conducted on mild steel coupons of dimension 5cm x 4cm after being polished and degreased in absolute ethanol, dried in acetone, and stored in moisture free desiccators prior to use. After  $10 \times 10^{-4}$  M of the inhibitor was prepared, the other concentrations were prepared by serial dilution. The pre-cleaned and weighed coupons were immersed in beakers containing the test solutions maintained at 303 K – 333 K. To determine weight loss with respect to time, the coupons were retrieved from test solutions at 2 h intervals progressively for 10 h, washed in distilled water, scrubbed with bristle brush, dried in

acetone and re-weighed. The weight loss was the difference between the initial weight and weight of the coupons at a given time (NACE, 2000).

## RESULTS AND DISCUSSION

### Weight loss studies

The results showed that weight loss increased with time, but decreased with increase in concentration of 5-phenylisoxazole (P). To ascertain the ability of the inhibitor to mitigate the free corrosion of mild steel in the acidic medium, gravimetric experiments were conducted over a total immersion period of 10 h in 2 M HCl solutions with and without the inhibitor. The plots revealed two major relationships: an increase in corrosion rate with exposure time for all systems (especially in the uninhibited acid) and a pronounced mitigation of corrosion rate due to addition of the inhibitor, signifying that the compound inhibited the corrosion of the mild steel in 2 M HCl solutions. Similar results had been reported by Hosseini *et al*, 2010; James, 2009 and Khaled, 2012. A maximum inhibition efficiency of 66 %, at the optimum concentration of  $10 \times 10^{-4}$  M was obtained.

### Adsorption Isotherm

In order to confirm the adsorption of the inhibitor on mild steel surface, adsorption isotherms were studied and the degree of surface coverage values ( $\theta$ ) at different inhibitors concentrations in 2 M HCl solutions were also evaluated from weight loss measurements at 303 K – 333 K, and tested graphically for fitting to a suitable adsorption isotherm (Table 1).

Table 1: Calculated values of corrosion rate (CR), surface coverage ( $\theta$ ) and inhibition efficiency (%I) of mild steel corrosion in different concentration of P

Inhi-bitor	Conc (M) x 10 <sup>-4</sup>	303 K			313 K			323K			333K		
		CR (mg/cm <sup>2</sup> h) x 10 <sup>-3</sup>	I (%)	$\theta$	CR (mg/cm <sup>2</sup> h) x 10 <sup>-3</sup>	I (%)	$\theta$	CR (mg/cm <sup>2</sup> h) x 10 <sup>-3</sup>	I (%)	$\theta$	CR (mg/cm <sup>2</sup> h) x 10 <sup>-3</sup>	I (%)	$\theta$
	Blank	3.00	-	-	4.96	-	-	6.34	-	-	8.41	-	-
	2	2.04	32	0.32	3.52	29	0.29	4.69	26	0.26	6.64	21	21
	4	1.56	48	0.48	2.78	44	0.44	3.80	40	0.40	5.80	31	31
P	6	1.47	51	0.51	2.53	49	0.49	3.61	43	0.43	5.47	35	35
	8	1.26	58	0.58	2.33	53	0.53	3.42	46	0.46	5.05	40	40
	10	1.02	66	0.66	1.79	64	0.64	2.47	61	0.61	4.46	47	47

The model considered was Temkin isotherm (Obot and Obi-Egbedi, 2009; Tang *et al*, 2006)

$$\exp(f\theta) = K_{ads}C \quad (4)$$

where  $K_{ads}$  is the equilibrium constant of the adsorption process, C the inhibitor concentration and f, the factor of energetic inhomogeneity. The best fitted straight line was obtained for the plot of surface coverage ( $\theta$ ) against logarithm of inhibitor concentration ( $\log C$ ) in Figure 1. The experimental data fitted best for the Temkin adsorption isotherm as the correlation co-

efficient ( $R^2$ ) were in the range  $0.9993 \geq R^2 \geq 0.9157$ . This suggests that the adsorption of the inhibitor on the metal surface obeyed Temkin adsorption isotherm. The calculated values of molecular interaction parameter 'a' and the equilibrium constant of adsorption process  $K_{ads}$  deduced from Temkin adsorption plots are also shown in Table 2. It is observed that the values of 'a' are negative in all cases showing that attraction exists in the adsorption layer (Umoren, 2008). It is a known fact that  $K_{ads}$  denotes the strength between adsorbate and adsorbent. Large values of  $K_{ads}$  imply more efficient adsorption and better inhibition efficiency (Tang *et al*, 2006). It is clear from the results in Table 2 that values of  $K_{ads}$  are very low indicating weak interaction between the inhibitor and the mild steel surface. This suggests that electrostatic interaction (Physisorption) occurred between the inhibitor molecule and the metal surface rather than molecular interaction which often results in strong interactions (Chemisorption) (Yurt *et al*, 2006)

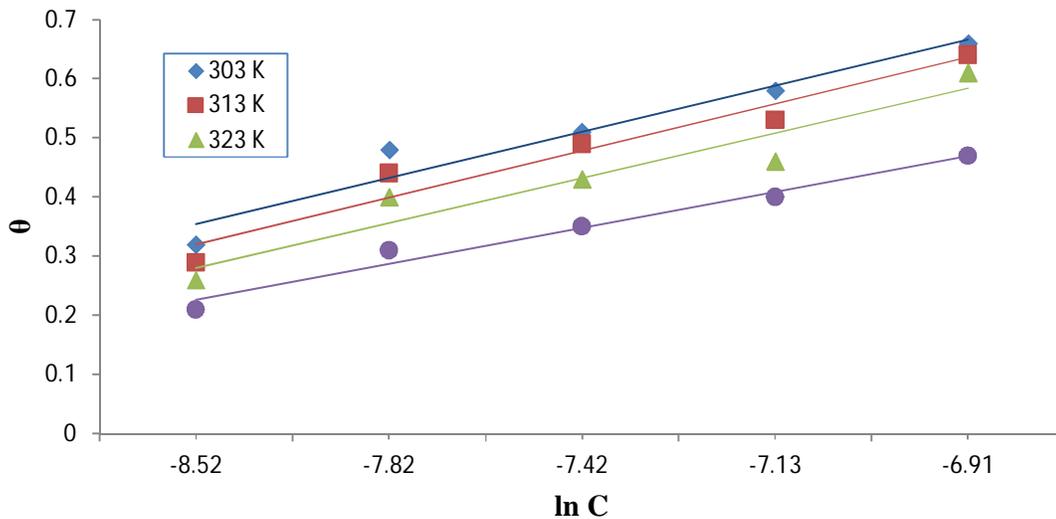


Figure 1: Temkin adsorption isotherm:  $\theta$  against  $\ln C$  for corrosion of mild steel coupons in 2 M HCl solutions containing different concentrations of 5 – Phenylisoxazole.

Table 2: Adsorption parameters from Temkin isotherm for corrosion of mild steel coupons in 2 M HCl containing different concentrations of P at 303 K – 333 K.

Inhibitor	Temp (°C)	ADSORPTION PARAMETERS						
		Intercept	Slope	K (mol/l)	f	A	-ΔG (kJ/mol)	R <sup>2</sup>
P	303	0.276	0.078	34.47	12.82	-6.41	19.03	0.9447
	313	0.241	0.079	21.12	12.66	-6.33	18.39	0.9473
	323	0.204	0.076	14.59	13.16	-6.58	17.98	0.9157
	333	0.165	0.061	15.03	16.39	-8.20	18.62	0.9772

The values of activation energies were calculated and given in Table 4. These values indicate that the presence of studied inhibitor (P) increased the activation energy of the metal dissolution reaction. The adsorption of the inhibitor is assumed to occur on the higher energy sites and the presence of the inhibitor, which resulted in the blocking of the active sites. The higher value of  $E_a$  in the presence of inhibitor compared to that in the absence of the inhibitor, and the decrease in the inhibition efficiency (%) with rise in temperature were indications of physisorption (Umoren, 2008). The computed values of the thermodynamics parameters of activation for the dissolution of mild steel at different temperatures are presented in Table 3.

Table 3: Activation parameters from Arrhenius equation for Mild steel coupons in 2 M HCl containing different concentration of the inhibitor at 303 K – 333K.

Inhibitor	Conc.(M) x 10 <sup>-4</sup>	ACTIVATION PARAMETERS				
		Intercept	Slope	$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ (J/mol.K)	R <sup>2</sup>
P	Blank	5.654	-3023.3	25.136	-150.530	0.9657
	2	6.877	-3511.9	29.198	-140.365	0.9768
	4	8.006	-3937.8	32.739	-130.978	0.9837
	6	8.207	-4021.4	33.434	-129.305	0.9920
	8	8.777	-4233.0	35.193	-124.565	0.9833
	10	9.181	-4434.5	36.868	-121.208	0.9868

The positive values of  $\Delta H^\circ$  reflect the endothermic behavior of the adsorption of the inhibitor (P) on the mild steel surface as reported by Umoren, 2008. The  $\Delta S^\circ$  values are negative, which are the usual expectation that the adsorption is an endothermic process and always accompanied by a decrease of entropy as reported by Umoren, 2008. The reason is that the adsorption of organic inhibitor molecules from the aqueous solution can be regarded as a quasi-substitution process between the organic compound in the aqueous phase [org (sol)] and water molecules at the electrode surface [H<sub>2</sub>O<sub>(ads)</sub>] (Founda *et al*, 2006). Here, the adsorption of the inhibitor was accompanied by desorption of water molecules from the electrode surface. The thermodynamic parameters obtained are the algebraic sum of the adsorption of organic inhibitor molecules and desorption of water molecules.

Table 4: Activation parameters from Transition state equation for mild steel coupons in 2 M HCl solutions containing different concentrations of 5 - Phenylisoxazole at 303 K – 333 K.

Inhibitor	Conc. (M) x 10 <sup>-4</sup>	Intercept	Slope	Activation parameters		R <sup>2</sup>
				E <sub>a</sub> (kJ/mol)	A x 10 <sup>-3</sup> (mgcm <sup>-2</sup> h <sup>-1</sup> )	
P	Blank	12.407	-3337.9	27.751	2.445 x 10 <sup>5</sup>	0.9713
	2	13.630	-3826.9	31.817	8.306 x 10 <sup>6</sup>	0.9801
	4	14.759	-4252.7	35.357	2.569 x 10 <sup>6</sup>	0.9851
	6	14.960	-4336.1	36.050	3.140 x 10 <sup>6</sup>	0.9930
	8	15.529	-4547.3	37.806	5.548 x 10 <sup>6</sup>	0.9853
	10	15.934	-4749.2	39.485	8.318 x 10 <sup>6</sup>	0.9885

The gain in entropy is attributed to the increase in solvent entropy (Emranuzzaman *et al*, 2004; Xianghong *et al*, 2009). The negative values of  $\Delta S^\circ$  suggest that the adsorption process was accompanied by a decrease in entropy, which is the driving force for the adsorption of the inhibitor on the mild steel surface.

### CONCLUSION

5 - Phenylisoxazole was found to be an effective inhibitor of mild steel corrosion in 2 M HCl solutions. The corrosion process was inhibited by adsorption of the organic molecules on the steel surface. Inhibition efficiency increased with increase in concentration of the inhibitor, but decreased with increase in temperature. The adsorption obeyed Temkin adsorption isotherm.

Phenomenon of physical adsorption was proposed from the values of kinetic/thermodynamics parameters ( $E_a$ ,  $\Delta G^{\circ}_{ads}$ ) obtained.

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