

Pyrimidine Amines As Inhibitors For The Acid Corrosion of Mild Steel

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Abstract-Three Pyrimidine amines (PA1, PA2 & PA3) have been synthesized and investigated for corrosion inhibition activity towards mild steel in 1M H₂SO₄. Weight loss, potentiodynamic polarisation and electrochemical impedance spectral techniques have been used. Thermodynamic parameters [ΔG°_{ads} , ΔH° and ΔS°] have been evaluated. The compounds act through physisorption mechanism on the mild steel surface and obeyed Langmuir adsorption isotherm. Polarisation studies showed that the compounds behave as cathodic type.

Keywords: Pyrimidine amines, Mild steel, Corrosion inhibition, Potentiodynamic polarisation, Electrochemical impedance, Adsorption.

I. INTRODUCTION

The corrosion of iron and steel and methods of reducing the rate at which corrosion of these materials takes place have been the subject of much investigation. A large number of organic compounds particularly those containing nitrogen, oxygen, or sulphur in a conjugated system are known to be applied as inhibitors to control acid corrosion of iron and steel. Schram et al have systematically investigated the efficiency of large number of aliphatic and aromatic amines in inhibiting the corrosion of mild steel by acid ^[1]. These inhibitors form readily ionizable onium compounds and get adsorbed on the cathodic areas and reduced the corrosion rate. In this work an attempt has been made to synthesize three pyrimidine amines and to evaluate their corrosion inhibition characteristics for mild steel in 1M H₂SO₄.

II. EXPERIMENTAL INHIBITORS

The pyrimidine amines have been synthesized by the reported procedure^[2]. They were purified by crystallisation. The compounds were characterised by IR spectra.

III. WEIGHT LOSS MEASUREMENTS

Mild steel containing 0.08% C, 0.36% Mn, 0.12% Si, 0.02% P, 0.02% Cr and the remainder Fe, were used in all experiments. For weight loss method, rectangular specimens having size 5cm x 2cm x 0.05cm were used. The specimens were washed, dried and polished successively using emery

sheets of 1/0, 2/0, 3/0 and 4/0 grades to remove adhering impurities, degreased with trichloroethylene and dried. Pre-weighed mild steel specimen (in triplicate) were suspended for 3hrs in 1M H₂SO₄ with and without the inhibitors in different concentrations. After 3hrs the specimens were removed from the test solution, washed with running water, dried well and then weighed. The percentage inhibition efficiency for various concentration of the inhibitors were calculated as,

$$\text{Efficiency of Inhibitor} = \frac{(\text{Weight loss without inhibitor}) - (\text{Weight loss with inhibitor})}{\text{Weight loss without inhibitor}} \times 100$$

The effect of temperature on the inhibitory action of the inhibitor was determined by weight loss method at 1mM concentration at different temperatures (303K, 313K, 323K and 333K) after immersing for 1hr.

IV. POLARIZATION AND IMPEDANCE MEASUREMENTS

Electrochemical measurements were carried out using potentiostat (1280 B Solartron, U.K.). Measurements were carried out in a glass cell with a capacity of 100ml. A platinum electrode and a saturated calomel electrode (SCE) were used as counter electrode and reference electrode respectively. Mild steel rod having the same composition, embedded in Teflon with an exposed area of 0.785cm² was used as working electrode. The polarisation measurements were performed at a scan rate of 1mv/sec in the potential range of -200mV to +200mV vs corrosion potential of the working electrode measured against SCE. The impedance measurements were done in the frequency range 10kHz to 0.01 Hz with a signal amplitude of 10mV at OCP after a stabilisation period of 30 minutes. The AC impedance measurements are shown as Nyquist plots and polarization data as Tafel plots. The I_{corr} , E_{corr} , R_t and C_{dl} values were obtained from the data using the corresponding "corr view" and "Z view" softwares.

V. RESULTS AND DISCUSSION WEIGHT LOSS STUDIES

The results of weight loss measurements at 30°C, after 3hours of immersion of the mild steel specimen for compounds PA1 to PA3 in 1M H₂SO₄ have been reported in table-1. It is evident from the table-1 that all the compounds showed > 80% efficiency at 1mM concentration. The corrosion rate decreases and inhibition efficiency increases with increase in concentration of inhibitors. The surface coverage values θ increase with concentration. Therefore it is evident that the corrosion inhibition is due to the

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adsorption of inhibitors on the metal surface forming a barrier film protecting the metal from corrosion.

VI. EFFECT OF TEMPERATURE

The influence of temperature at the optimum concentration (1mM) on inhibition efficiency was studied by weight loss method and the data are given in table-2. It is evident that the inhibition efficiency decreases with increase in temperature which may be attributed to an increase in the solubility of the protective adsorbed film and of any reaction products precipitated on the surface of the metal that inhibit the reaction. Ergun et al^[3] has attributed the decrease in inhibition efficiency with rise in temperature to be due to an enhanced effect of temperature on the dissolution process of steel in acidic media and or the partial desorption of the inhibitor from the metal surface. In an acidic solution, the corrosion rate is related to the temperature by the Arrhenius equation,

$$\text{LogCR} = \frac{-Ea}{2.303RT} + \text{log } A$$

Activation energy (Ea) and thermodynamic data, such as change in free energy ($\Delta G^{\circ}_{\text{ads}}$), enthalpy (ΔH°) and entropy (ΔS°) for mild steel in 1M H₂SO₄ in the presence and in the absence of the inhibitors were calculated and are listed in table-3. The activation energy at different concentration of the inhibitor in H₂SO₄ is calculated by plotting Log CR Vs 1/T [Fig-1]. Linear plots were obtained for all the inhibitors. It is clear from the table-3 that Ea values in the presence of the additives are higher than that in the absence. The higher activation energies imply a slow reaction and that the reaction is very sensitive to temperature. Similar results have been reported by Ebenso et al in the corrosion inhibition of steel by Alizarin yellow^[4]. The increase in activation energy in the presence of inhibitor signifies physical adsorption^[5]. Enthalpy and entropy of activation ΔH° and ΔS° were obtained by applying the transition state equation:

$$CR = \frac{RT}{Nh} \exp \left[\frac{\Delta S^{\circ}}{R} \right] \exp \left[\frac{-\Delta H^{\circ}}{RT} \right]$$

An endothermic adsorption process ($\Delta H^{\circ} > 0$) is attributed to chemisorption, an exothermic adsorption ($\Delta H^{\circ} < 0$) may involve either physisorption or chemisorption or a mixture of both^[6]. In the present study negative ΔH° values are obtained indicating physisorption. The ΔS° values presented in table-3 are negative which means that the process of adsorption is accompanied by a decrease in entropy. The negative value of ΔS° decreases in the presence of inhibitor as compared to that in their absence i.e there is an increase in entropy in the presence of inhibitor. This indicates that the adsorption process is spontaneous and there is an increase in randomness or disorder on the surface due to the adsorption process and also desorption at higher

temperature. ΔG° values listed in table-3 are all negative suggesting the spontaneity of the adsorption process. But the values are all within -20KJ/mole indicating physisorption of the inhibitors on the steel surface.

VII. ADSORPTION ISOTHERMS

Surface coverage θ values for the compounds as determined by weight loss measurements for various concentrations of the inhibitors were used to find the best adsorption isotherm between those more frequently used i.e Langmuir, Temkin, and Frumkin. The best fit was obtained with Langmuir isotherm according to the equation,

$$\frac{\theta}{1-\theta} = KC$$

on rearranging it gives,

$$\frac{C}{\theta} = \frac{1}{K} + C$$

Plots of C/ θ against C gives the straight line with unit slope [Fig-2]. This indicates that the adsorption of the pyrimidine amines on mild steel surface in 1M H₂SO₄ solution follows Langmuir isotherm and consequently there is no interaction between the molecules adsorbed at the metal surface.

VIII. POTENTIODYNAMIC POLARISATION STUDIES

Polarization curve for mild steel in 1M H₂SO₄ at various concentrations of PA1 is shown in fig-3. The values of corrosion current densities (I_{corr}), corrosion potential (E_{corr}), the cathodic and anodic Tafel slopes (b_a and b_c) are calculated from the curves and are given in table-4. The data reveals that the corrosion current I_{corr} decreases substantially and inhibition efficiency increases with the inhibitor concentration. It is also evident that the inhibitor adsorption shifted the corrosion potential E_{corr} in the negative direction with respect to the blank signifying that the suppression of the cathodic reaction is the main effect of these inhibitors. Moreover the presence of these inhibitors enhanced the value of cathodic Tafel slopes showing that the inhibitors behave as cathodic type getting adsorbed on the cathodic sites to decrease the evolution of hydrogen.

IX. IMPEDANCE STUDIES

Fig-4 show the Nyquist plot for mild steel specimen immersed in 1M H₂SO₄ containing various concentrations of inhibitors PA1. The equivalent circuit parameters obtained are tabulated in table-5. The Nyquist plots are all semicircles and correspond to a capacitive loop. The diameter of the semicircle increases with increasing concentration of inhibitors. The R_t values increase with concentration of inhibitor. Since R_t is inversely proportional to the corrosion current and it can be used to calculate the inhibition efficiency from the relation

$$\text{Inhibition efficiency (\%)} = \frac{R_t(\text{inh}) - R_t(\text{blank})}{R_t(\text{inh})} \times 100$$

The C_{dl} value decreases with increase in concentration which indicates the formation of a surface film on the metal and thereby decreasing the dissolution reaction.

X. MOLECULAR STRUCTURE AND INHIBITION EFFICIENCY

Organic inhibitors contain atleast one polar group with an atom of N,S or O each of them might be an adsorption centre. The inhibitive properties of such compounds depend on the electron densities around the adsorption centre, the higher the electron densities around the adsorption centre, the more effective the inhibitor is.

The pyrimidine amines are organic bases and in acid solution they get protonated at the NH_2 group. The adsorption of these compounds on the mild steel surface occurs by two ways

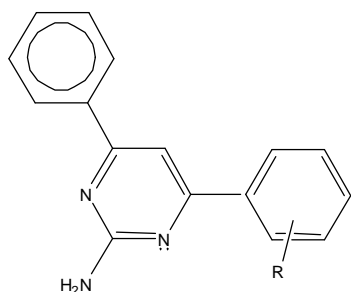
a) Electrostatic interaction between the protonated amines ($-\text{NH}_3^+$) and negatively charged Fe surface in acid medium – physisorption.

b) Interaction of lone pairs of electron on N as well as Πe^- of the rings with the Fe atom – chemisorption.

The physisorption mechanism has been proved to be predominant by higher temperature studies. The order of inhibition efficiency of the pyrimidine amines is found to be,

PA1>PA3> PA2.

The general structure of the inhibitors is (Table-7),



PA1 shows maximum efficiency of > 95% and PA2 shows 83% efficiency. PA2 has a $-\text{OH}$ group in the ortho position, which is closer to the main adsorption centre. The lower I.E of PA2 may be attributed to the formation of intramolecular hydrogen bonding of the $-\text{OH}$ hydrogen with the N-atom via the lone pair of electrons. The lone pair of electrons is therefore less readily available for protonation in acid medium. This hinders the electrostatic adsorption leading to lower inhibition. This phenomenon of ortho effect has been discussed by Popova et al^[7] in their work in attempting to explain adsorption of molecules with ortho, meta and para substituents by Hammett equation. PA3 has substituents in the meta and para position showing higher inhibition efficiency. But the efficiency is somewhat lower than the unsubstituted compound which may be due to the ready solubility of the vanillin compounds in aqueous acid medium.

XI. SYNERGISM INFLUENCE OF HALIDE IONS

It is reported that the surface of iron is found to be positively charged in sulphuric acid media and the protonated inhibitor species would be less strongly adsorbed on to the metal surface resulting in lesser inhibition efficiencies. However the addition of halide ions in acid media has been found to increase the adsorption of amines and hence inhibition. This method is therefore effective to get better performance and to decrease the amount of usage of the inhibitor. The synthesized pyrimidine amines show 80-90% inhibition at 1mM concentration and somewhat lesser inhibitory activity at lower concentration. In order to improve the performance of the inhibitor at lower concentration and to reduce the cost, the synergistic effect on the addition of halide ions has been attempted by weight loss method. The values of inhibition efficiency obtained by weight loss method with and without addition of 1mM KCl, KBr, & KI are given in table-6. It is apparent that inhibition efficiency increases with the addition of halide ions at all concentrations of the inhibitors tested. With the addition of iodide ion the inhibition efficiency of all the three inhibitors has been increased to > 90% even at 0.1mM concentration of the inhibitors. This synergism effect can be explained as follows. Amines in aqueous acidic solutions may exist as either neutral molecules or in the form of cations depending on the concentration of H^+ ions in the solutions. The potential of zero charge (PZC) of iron in sulphuric acid is about -650 mV Vs SCE^[8]. Therefore the amines can interact through the Π electrons of benzene ring with the positively charged metal surface and through the positively charged ammonium ions on the cathodic surface and offer marginal corrosion inhibition. But the presence of halide ions show very good synergism. The synergistic effect is due to the co-adsorption of halide ions on the surface which forms oriented dipoles with their negative ends toward the solution thus increasing the adsorption of protonated organic inhibitor ions. Fouda et al^[9] have reported similar findings in their study on synergistic influence of iodide ions with some aliphatic amines on the inhibition of corrosion of carbon steel in sulphuric acid. It can also be inferred from this study that the order of synergism of halide ions with pyrimidine amine molecules is $\text{I}^- > \text{Br}^- > \text{Cl}^-$ the reason for the better synergism with iodide ions may be due to the large size and ease of polarizability of I^- ions which facilitates electron pair bonding with iron surface.

XII. CONCLUSION

- 1) The synthesized pyrimidine amines are a good inhibitors for the corrosion of mild steel in 1M H_2SO_4 .
- 2) The inhibitors are an adsorption type inhibitors and adsorption follows the Langmuir adsorption isotherm.
- 3) Adsorption of the inhibitor on mild steel surface is exothermic and spontaneous.

- 4) The inhibition efficiency of the inhibitor decreases with the rise of the temperature.
- 5) The results obtained from the polarization study revealed that the inhibitor under study behaved as a cathodic type inhibitor.

XIII. REFERENCES

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Table-1. Inhibition efficiencies of selected concentrations of the inhibitors for the corrosion of mild steel in 1M H₂SO₄ obtained by weight loss measurement at 30±1°C

Name of the inhibitor	Inhibitor concentration (mM)									
	Blank	0.02	0.04	0.06	0.08	0.1	0.15	0.25	0.5	1
PA1	-	88.86	90.57	90.74	90.90	91.31	92.56	94.73	95.81	96.26
PA2	-	36.84	42.80	51.60	55.28	62.63	68.98	73.33	79.57	83.08
PA3	-	49.29	59.34	60.66	61.49	63.96	69.13	75.12	88.98	91.77

Table-2. Inhibition efficiency (%) of 1mM concentration of inhibitors for mild steel corrosion in 1M H₂SO₄ at different temperatures

Temperature (K)	Inhibition efficiency (%)		
	PA1	PA2	PA3
303	96.26	83.08	91.77
313	94.28	79.63	86.79
323	90.38	70.19	78.99
333	88.58	66.62	70.18

Table-3. Thermodynamic parameters for mild steel corrosion in 1M H₂SO₄.

Name of the inhibitor	-ΔH° (KJ/mole)	-ΔS° (KJ/mole)	E _a (kJ)	ΔG° _{ads} at various temperatures (kJ)			
				303 k	313k	323k	333 k
Blank	0.01887	0.10542	43.46	-	-	-	-
PA1	0.01390	0.15247	51.10	-18.30	-17.74	-18.89	-19.61
PA2	0.03006	0.09893	74.90	-14.12	-15.90	-16.69	-16.23
PA3	0.03350	0.08679	79.84	-16.19	-15.35	-14.33	-13.48

Table-4. Polarisation parameters for mild steel in 1M H₂SO₄ solution with different concentrations of the inhibitors.

Name of the inhibitor	Inhibitor concentration (mM)	Tafel slopes (mv/dec)		E _{corr} (mV)	I _{corr} (μAmp/cm ²)	Inhibition efficiency (%)
		b _a	b _c			
PA1	Blank	84.482	133	-474.0	500.47	-
	0.02	56	102	-501.2	143.99	71.22
	0.1	63	191	-491.1	120.16	75.99
	1	64	243	-487.3	65.06	87.0
PA2	0.02	66	193	-501.0	261.46	47.75
	0.1	71	244	-498.4	156.48	68.73
	1	62	173	-492.6	118.13	76.39
PA3	0.02	54	166	-504.7	66.92	86.62
	0.1	65	305	-484.5	62.43	87.52
	1	56	258	-488.3	47.264	90.55

Table-5. Impedance parameters for mild steel in 1M H₂SO₄ solution with different concentrations of the inhibitors

Name of the inhibitor	Inhibitor concentration (1mM)	R _t (ohmcm ²)	C _{dl} (μF/cm ²) × 10 ⁻⁶	Inhibition efficiency (%)
PA1	Blank	10.5299	34.2381	-
	0.02	89.54	12.208	88.24
	0.1	150.29	11.977	92.99

	1	189.73	10.948	94.45
PA2	0.02	80.74	12.175	86.95
	0.1	143.40	10.875	92.65
	1	165.46	10.083	93.63
PA3	0.02	122.16	9.2132	91.38
	0.1	133.54	6.5106	92.11
	1	170.72	5.8705	93.83

Table-6. Synergistic influence of halide ions on the inhibition efficiency of the inhibitor for mild steel corrosion in 1M H₂SO₄ at 30±1°C.

Name of the inhibitor	Inhibitor concentration on mM	Inhibition efficiency (%)			
		Without KCl, KBr & KI	With 1mM KCl	With 1mM KBr	With 1mM KI
PA1	0.02	88.86	89.95	93.32	95.56
	0.06	90.74	91.30	94.59	97.77
	0.1	91.31	92.56	98.50	99.30
PA2	0.02	36.84	46.49	76.70	81.34
	0.06	51.60	73.20	84.67	88.86
	0.1	62.63	79.59	85.17	89.13
PA3	0.02	49.29	60.70	83.32	95.88
	0.06	60.66	70.33	89.91	97.65
	0.1	63.96	73.16	89.99	98.50

Table-7. Structure of the inhibitors.

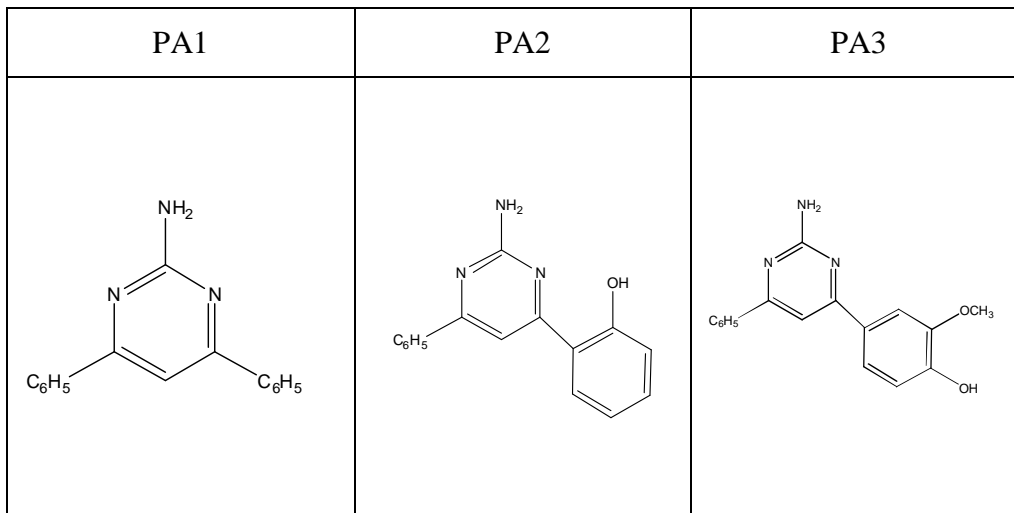


Figure-1. Arrhenius plot of corrosion rate of mild steel in 1M H₂SO₄ solution in the absence and presence of inhibitors.

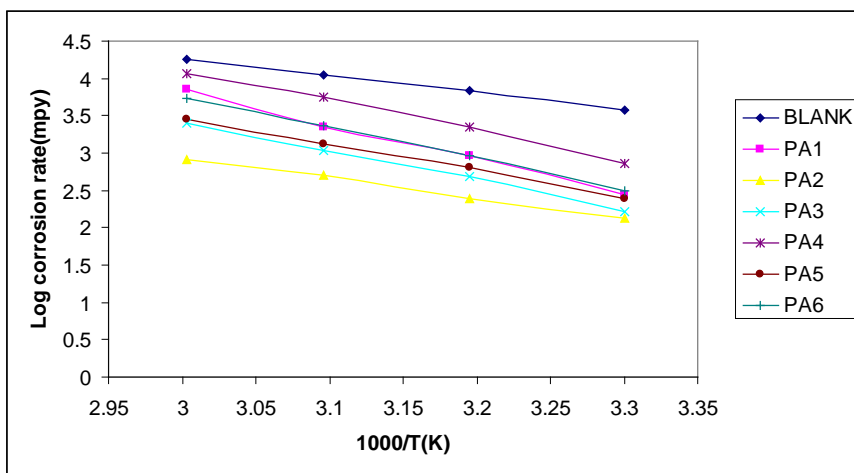


Figure -2. Langmuir plot of inhibitors for mild steel in 1M H₂SO₄

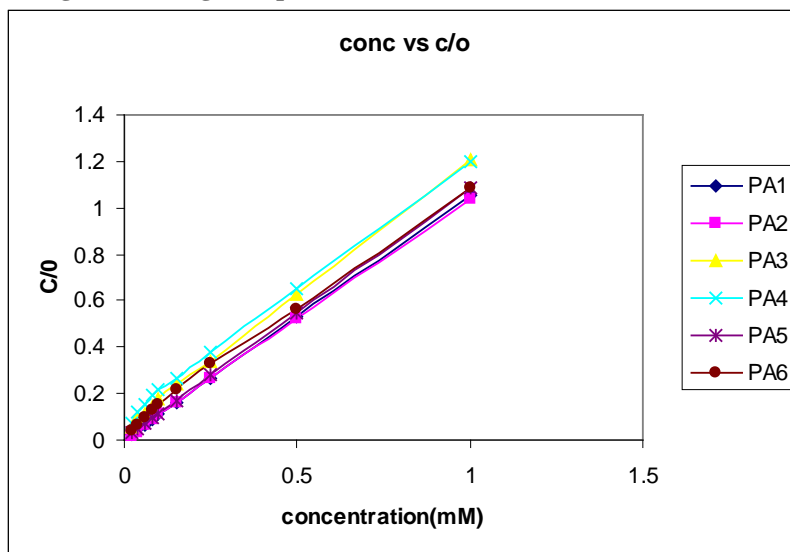


Figure-3. Polarization curves for mild steel recorded in 1M H₂SO₄ for selected concentrations of inhibitor (PA1)

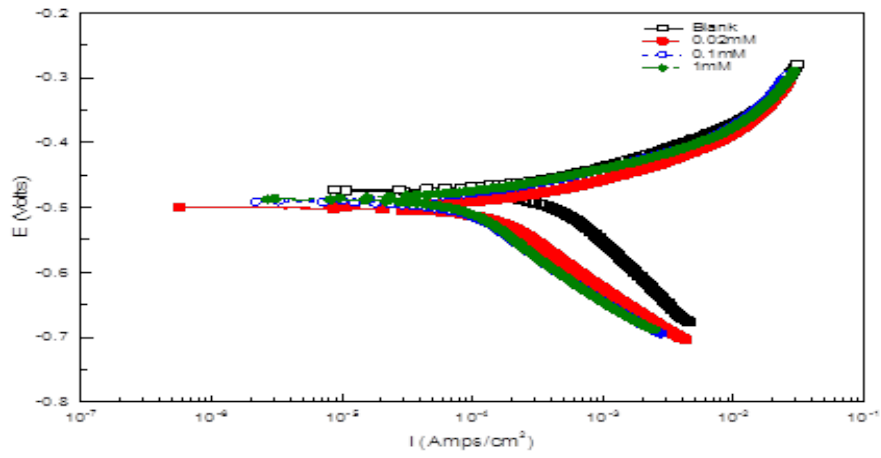


Figure-4. Nyquist diagram for mild steel in 1M H₂SO₄ for selected concentrations of inhibitor (PA1)

