



ISSN: 0976-3376

Available Online at <http://www.journalajst.com>

ASIAN JOURNAL OF
SCIENCE AND TECHNOLOGY

Asian Journal of Science and Technology
Vol. 07, Issue, 09, pp.3489-3498, September, 2016

RESEARCH ARTICLE

CORROSION INHIBITION POTENTIAL OF PYRIMETHAMINE FOR MILD STEEL CORROSION IN ACIDIC MEDIUM

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ARTICLE INFO

Article History:

Received 27th June, 2016
Received in revised form
09th July, 2016
Accepted 04th August, 2016
Published online 30th September, 2016

Key words:

Corrosion inhibition,
Mild steel Pyrimethamine,
Hydrochloric acid.

ABSTRACT

Corrosion is a gradual degradation of materials, usually metals by chemical reaction with its environment. Corrosion of metals constitutes a major problem facing most construction firms. In recent years, more efforts are directed towards investigation of mild steel corrosion perhaps due to increased technologically related applications of mild steel and metals in general for industrial and domestic purposes. This study investigates corrosion inhibition of mild steel by pyrimethamine in 2.0M HCl, by gravimetric analysis. Essential parameters like corrosion rate, percentage inhibition efficiency and degree of surface coverage were obtained from data generated experimentally. Facts gathered from analysis of generated data and review of related literature, revealed that; pyrimethamine significantly ($p < 0.5$) reduced the corrosion rate of mild steel in 2.0M HCl. And that the reduction in corrosion rate significantly ($p < 0.5$) increased with increased in inhibitor concentrations, but reduced with rise in temperature to values that tested non-significant ($p < 0.05$) for temperatures $\geq 333K$ and inhibitor concentrations $< 5.0 \times 10^{-4}M$. Also, the corrosion rate increased with rise in temperature at all inhibitor concentrations. Percentage inhibition efficiency and degree of surface coverage were notice to increase with increase in inhibitor concentration but reduced with rise in temperature.

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INTRODUCTION

In recent years, more efforts are directed towards investigation of mild-steel corrosion, may be due to increased technologically related application of mild-steel and metals in general for industrial and domestic purposes.(Akpan et al., 2011). Corrosion is a gradual degradation of materials, usually metals, by chemical reaction with its environment, (Doner et al., 2012). In a related review, corrosion is referred to as the oxidation of a metal by its environment, resulting in the destruction of the metal lattice. (Williams et al., 2014) Corrosion in most cases occur in wet environment by electrochemical process where a cell is set up and the metal oxidized anodically (Akpan et al., 2011). Corrosion of metals is a major problem facing most construction companies and in the maritime subsector, corrosion constitute a basic setback as mild steel is considered most suitable material for ship, port and other facilities construction,(Kar and Singh, 2011; Williams et al., 2014).

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This process is highly influenced by the chemistry of the corroding environment; a factor that accounts for the corrosion rate of the material (Nahl'e, et al., 2012). Hence, the study of mild steel corrosion phenomena particularly in acidic media has become increasingly important due to increased industrial applications of acid solutions such as in pickling, chemical and electrochemical etching, industrial acid descaling, etc, (Arukalam, 2012; Eddy and Ebenso, 2010). In view of the vast industrial value of mild steel, the need to mitigate against adverse environmental consequences of corrosion, and increased avenues of aggressive corrodent into our environment, the need to device better technologies for corrosion inhibition is becoming more imperative, (Bhat and Alva, 2011; Ebenso et al., 2010; Williams et al., 2014): The use of corrosion inhibitors is one of the most practical methods for protection of metals against corrosion. (Akpan et al., 2011) Most well known inhibitors are organic compounds containing Nitrogen, Sulphur, Oxygen and Phosphorus in their functional groups, (Nasser and Sathiq, 2010; Paul et al., 2013; Sathiq et al., 2011). This study shall consider the potency of pyrimethamine as an inhibitor for mild steel corrosion in hydrochloric acid solution by gravimetric analysis. Useful parameters to be considered include Corrosion Rate (CR),

percentage Inhibition Efficiency (IE) and degree of surface coverage (θ). In view of the increasing environmental awareness and harmful effects of some inhibitors, research in recent times is directed towards developing cost effective and environmentally friendly corrosion inhibitors (Gatton, 2004; Ofoegbu and Ofoegbu, 2012; Parameswari *et al.*, 2011). Hence the choice of pyrimethamine for this study.

MATERIALS AND METHODS

Preparation of specimen

The mild steel material used for this study was identified and supplied by ken-Johnson Nigeria Limited, Uyo-Nigeria. The material was mechanically cut into 2.0 x 1.0 x 0.05 cm coupons. A small hole was drilled out at the centre of each coupon. These coupons were pre-cleaned using three different grades of sand paper (P60X, P220 and P450). Each coupon was washed in distilled water to remove dirt, washed in ethanol to remove grease and thereafter in acetone to remove oil. The cleaned coupons were stored over calcium chloride in a dessicator prior to use.

Preparation of reagents

All the reagents used in this experimental work were of analytical grade and were supplied by reputable companies as stated respectively;

- Acetone-BDH chemicals Ltd; Poole-England.
- Calcium Chloride –May and Baker Ltd., Dagenham-England.
- Hydrochloric acid – May and Baker Ltd., Dagenham-England.
- Ethanol - James Burrough Ltd., London.
- Sodium Hydroxide pellets – May and Baker Ltd., Poole-England.
- Zinc dust–BDH chemicals Ltd., Poole – England.
- Pyrimethamine (the inhibitor) was of Analar grade and was supplied by Healthway Pharmacy, Uyo, Akwa Ibom State, Nigeria.

Preparation of standard solution of HCl

The molarity of stock was first obtained using direct formula method as presented below:

$$\text{Molarity} = \frac{\% \text{ purity} \times \text{Specific gravity} \times 1000\text{cm}^3}{\text{Molar mass} \times \text{Volume of Solution}}$$

(Kar and Singh, 2011; Williams *et al.*, 2014), Basic information such as % purity, specific gravity and molar mass of the reagent were obtained from the assay on the stock bottle of concentrated HCl, as given below:

$$\begin{aligned} \% \text{ purity} &= 33.0 \\ \text{Specific gravity} &= 1.18\text{g} \\ \text{Molar mass} &= 36.46\text{gmol}^{-1} \end{aligned}$$

By appropriate substitution of the given values into the above formula, we have that;

$$\text{Molarity of stock HCl} = \frac{33.0 \times 1.18\text{g} \times 1000}{36.46\text{gmol}^{-1} \times 100} = 10.66\text{M}$$

The proposed 1000cm³ of 2.0M working solution of HCl was therefore obtained by dilution principle as shown below:

$$M_1V_1 = M_2V_2, V_2 = \frac{M_1V_1}{M_2} = \frac{2.0\text{M} \times 1000\text{cm}^3}{10.68} = 187.30\text{cm}^3$$

Therefore, 187.30cm³ of the concentrated HCl was carefully measured and transferred to a standard flask containing distilled water and the volume made up to 1000cm³ mark.

Preparation of standard solution of Pyrimethamine

1.0M stock solution of pyrimethamine was first prepared by carefully measuring the equivalent weight of the compound and dissolving it in 30ml of distilled water in appropriate flask, then making up the volume to 1000cm³ with distilled water. The respective concentrations (2.0 x 10⁻⁴M, 1.0 x 10⁻⁴M, 5.0 x 10⁻⁵M and 0.5 x 10⁻⁵M) of the working solutions were obtained from the stock solution by dilution principle as shown below:

Concentration of stock C_s x Volume of stock V_s = Conc. Of working Soln C_w x Volume of working soln V_w ; Volume of working solution $V_w = \frac{C_s V_s}{C_w}$

Where $C_s = 1.0\text{M}$, $V_s = 1000\text{cm}^3$,

$$C_w = 2.0 \times 10^{-4}\text{M} \text{ and } V_w = ?$$

By appropriate substitution, we have that

$$V_w = \frac{1.0\text{M} \times 1000\text{cm}^3}{2.0 \times 10^{-4}\text{M}} = 0.05\text{cm}^3$$

Hence, 0.05cm³ of stock solution of pyrimethamine was carefully measured and transferred into a standard flask and the volume was made up to 1000cm³. Other concentrations of the working solution were obtained in the same manner, using similar principle. The equivalent weight of pyrimethamine is 233.5g.

Gravimetric analysis

Gravimetric analysis was conducted on the prepared specimen (mild steel coupons). The coupons were totally immersed by means of glass rod and hook in 100ml of test solutions and blank each maintained at 303K. To determine weight loss with time, the coupons were retrieved from the test solutions and blank at two hours interval, immersed in 20% NaOH solution containing 200gL⁻¹ of Zinc dust, scrubbed with bristle brush, washed in distilled water, dried in acetone and reweighed. The weight loss was to be the difference between the initial and the final weights respectively of the coupon at a given time. The analysis was repeated with temperature of test solution and blank maintained at 313K, 323K and 333K respectively. For each temperature, the corresponding weight loss values were measured and recorded. From the weight loss values, useful parameters such as corrosion rate (CR), surface coverage (θ) and percentage Inhibition Efficiency (%IE) were evaluated using appropriate equations as shown below;

$$\text{CR} = \frac{W_i - W_f}{\text{ST}}, \theta = \frac{\text{CR}_0 - \text{CR}_i}{\text{CR}_0} \text{ and } \% \text{IE} = \frac{\text{CR}_0 - \text{CR}_i}{\text{CR}_0} \times 100$$

Where;

- W_i - Initial weight of coupon
- W_f - Final weight of coupon
- S - Total surface Area of coupon
- T - Corrosion Time,
- CR - Corrosion Rate
- CR_0 - Corrosion Rate of coupon in the absent of inhibitor
- CR_i - Corrosion Rate of coupon in the present inhibitor
- (θ) - Surface Coverage of inhibitor
- %IE - %age Inhibition Efficiency of the inhibitor (Begum *et al.*, 2010; Firdhouse and Nalini, 2013; Williams *et al.*, 2014).

RESULT AND DISCUSSION

Gravimetric studies

Gravimetric study of mild steel corrosion in 2.0M HCl and its inhibition by various concentrations of pyrimethamine at different temperatures was conducted. Data generated from the study is presented in three categories; The first category reports raw data of weight loss of mild steel from its corrosion in 2.0M HCl and its subsequent inhibition by various concentrations of pyrimethamine at the respective temperatures. The report is as presented on Tables I, II, III and IV respectively. The second category reports data of Corrosion Rate (CR), evaluated from raw data and presented in tables V, VI, VII and VIII respectively. The third category summarises the statistically analyzed data of corrosion rate and data generated from the evaluation of other relevant parameters like degree of surface coverage (θ) and percentage Inhibition Efficiency (%IE) at various temperatures and respective inhibitor concentrations. The report is as presented on table IX.

From the above tables, it was observed that weight loss of the mild steel in 2.0M HCl reduced with increase in inhibitor concentration, but rather increased with increase in exposure time, and temperature respectively. Data of Corrosion Rate above show that mean Corrosion Rate, $\bar{X}CR$ of mild steel in 2.0M HCl reduces in the present of pyrimethamine inhibitor. It was also observed that; the reduction in $\bar{X}CR$ of the mild steel in the test solution (Corrodent) increased with increase in the concentration of the inhibitor.

The $\bar{X}CR$ was also noticed to increase with increase in temperature of the corrodent. The increase in the successive reduction in $\bar{X}CR$ with corresponding inhibitor concentration tested significant ($p < 0.05$) for corrodent temperatures of 333K, the increase in the successive reduction in $\bar{X}CR$ tested non significant ($P < 0.05$) for inhibitor concentrations of $0.1 \times 10^{-4}M$, $0.5 \times 10^{-4}M$, $1.0 \times 10^{-4}M$, and $2.0 \times 10^{-4}M$. And tested weakly significant ($P < 0.5$) at inhibitor concentration of $5.0 \times 10^{-4}M$. The table above reveals that percentage inhibitor efficiency (%IE) of pyrimethamine for mild steel corrosion in 2.0M HCl increases with increase in inhibitor concentration and decreases with increase in corrodent temperature. Similarly, degree of surface coverage (θ) increases with inhibitor concentration and reduces with rise in corrodent temperature. A plot of the variations of the above parameters (Table IX) is as presented below in Figures I and II.

Table 1. Weight Loss Experiment for the Corrosion of Mild Steel Coupons in 2.0 M HCl Solution Containing Different Concentrations of Pyrimethamine at 303K

Time (hr)	Inhibitor Concentration $\times 10^{-4}(M)$	Initial weight Mild Steel Coupon (W_1)g	Final Weight wt of mild steel coupon (W_2)g	Weight loss ($\Delta W = W_1 - W_2$)g
2	Blank	1.900	1.745	0.155
	0.1	1.860	1.814	0.046
	0.5	1.845	1.802	0.043
	1.0	1.825	1.787	0.038
	2.0	1.700	1.663	0.037
	5.0	1.790	1.756	0.034
4	Blank	1.900	1.732	0.168
	0.0	1.860	1.795	0.050
	0.5	1.845	1.798	0.047
	1.0	1.825	1.784	0.041
	2.0	1.700	1.660	0.040
	5.0	1.790	1.753	0.037
6	Blank	1.900	1.723	0.177
	0.0	1.860	1.807	0.053
	0.5	1.845	1.795	0.050
	1.0	1.825	1.782	0.043
	2.0	1.700	1.658	0.042
	5.0	1.790	1.751	0.039
8	Blank	1.900	1.710	0.190
	0.0	1.860	1.803	0.057
	0.5	1.845	1.792	0.053
	1.0	1.825	1.778	0.047
	2.0	1.700	1.655	0.045
	5.0	1.790	1.748	0.042
10	Blank	1.900	1.705	0.195
	0.0	1.860	1.801	0.059
	0.5	1.845	1.790	0.055
	1.0	1.825	1.776	0.049
	2.0	1.700	1.654	0.046
	5.0	1.790	1.747	0.043

Table 2. Weight Loss Experiment for the Corrosion of Mild Steel Coupons in 2.0 M HCl Solution Containing Different Concentrations of Pyrimethamine at 313K

Time (hr)	Inhibitor Concentration $\times 10^{-4}$ (M)	Initial Weight Mild Steel Coupon (W_1)g	Final Weight of mild steel coupon (W_2)g	Weight loss ($\Delta W = W_1 - W_2$)g
2	Blank	2.040	1.888	0.152
	0.1	1.805	1.755	0.050
	0.5	1.790	1.740	0.050
	1.0	1.855	1.811	0.044
	2.0	2.090	2.048	0.042
	5.0	1.625	1.587	0.038
4	Blank	2.040	1.872	0.168
	0.0	1.805	1.750	0.055
	0.5	1.790	1.736	0.054
	1.0	1.855	1.807	0.048
	2.0	2.090	2.043	0.047
	5.0	1.625	1.583	0.042
6	Blank	2.040	1.864	0.176
	0.0	1.805	1.747	0.058
	0.5	1.790	1.734	0.056
	1.0	1.855	1.804	0.051
	2.0	2.090	2.041	0.049
	5.0	1.625	1.581	0.044
8	Blank	2.040	1.852	0.188
	0.0	1.805	1.743	0.062
	0.5	1.790	1.730	0.060
	1.0	1.855	1.802	0.053
	2.0	2.090	2.038	0.052
	5.0	1.625	1.578	0.047
10	Blank	2.040	1.843	0.197
	0.0	1.805	1.740	0.065
	0.5	1.790	1.727	0.063
	1.0	1.855	1.798	0.057
	2.0	2.090	2.035	0.055
	5.0	1.625	1.576	0.049

Table 3. Weight Loss Experiment for the Corrosion of Mild Steel Coupons in 2.0 M HCl Solution Containing Different Concentrations of Pyrimethamine at 323 K

Time (hr)	Inhibitor Concentration $\times 10^{-4}$ (M)	Initial Weight Mild Steel Coupon (W_1)g	Final Weight of mild steel coupon (W_2)g	Weight loss ($\Delta W = W_1 - W_2$)g
2	Blank	1.820	1.641	0.179
	0.1	1.760	1.690	0.070
	0.5	1.830	1.762	0.068
	1.0	1.940	1.876	0.064
	2.0	1.965	1.905	0.059
	5.0	1.840	1.788	0.052
4	Blank	1.820	1.627	0.193
	0.0	1.760	1.684	0.076
	0.5	1.830	1.757	0.073
	1.0	1.940	1.871	0.069
	2.0	1.965	1.902	0.063
	5.0	1.840	1.784	0.056
6	Blank	1.820	1.615	0.205
	0.0	1.760	1.679	0.081
	0.5	1.830	1.752	0.078
	1.0	1.940	1.868	0.072
	2.0	1.965	1.898	0.067
	5.0	1.840	1.780	0.060
8	Blank	1.820	1.610	0.210
	0.0	1.760	1.676	0.084
	0.5	1.830	1.748	0.082
	1.0	1.940	1.865	0.075
	2.0	1.965	1.894	0.071
	5.0	1.840	1.778	0.062
10	Blank	1.820	1.595	0.255
	0.0	1.760	1.567	0.090
	0.5	1.830	1.746	0.084
	1.0	1.940	1.859	0.081
	2.0	1.965	1.891	0.074
	5.0	1.840	1.775	0.065

Table 4. Weight Loss Experiment for the Corrosion of Mild Steel Coupons in 2.0 M HCl Solution Containing Different Concentrations of Pyrimethamine at 333K

Time (hr)	Inhibitor Concentration x 10 ⁻⁴ (M)	Initial Weight Mild Steel Coupon (W ₁)g	Final Weight of mild steel coupon (W ₂)g	Weight loss (ΔW = W ₁ - W ₂)g
2	Blank	1.930	1.686	0.244
	0.1	1.920	1.788	0.132
	0.5	1.745	1.627	0.118
	1.0	1.720	1.611	0.108
	2.0	1.775	1.678	0.097
	5.0	1.830	1.744	0.086
4	Blank	1.930	1.833	0.262
	0.0	1.920	1.780	0.140
	0.5	1.745	1.617	0.128
	1.0	1.720	1.604	0.116
	2.0	1.775	1.738	0.105
	5.0	1.830	1.830	0.092
6	Blank	1.930	1.654	0.276
	0.0	1.920	1.772	0.148
	0.5	1.745	1.610	0.135
	1.0	1.720	1.596	0.124
	2.0	1.775	1.668	0.107
	5.0	1.830	1.733	0.007
8	Blank	1.930	1.641	0.289
	0.0	1.920	1.764	0.156
	0.5	1.745	1.603	0.142
	1.0	1.720	1.591	0.129
	2.0	1.775	1.659	0.116
	5.0	1.830	1.729	0.101
10	Blank	1.930	1.628	0.302
	0.0	1.920	1.757	0.163
	0.5	1.745	1.596	0.149
	1.0	1.720	1.548	0.129
	2.0	1.775	1.654	0.121
	5.0	1.830	1.725	0.105

Table 5. Statistical Analysis of raw data presented on Table I

Inhibitor Concentration x 10 ⁻⁴ (M)	CR x 10 ⁻³ (Mgcm ⁻² h ⁻¹)	X̄CR x 10 ⁻³	SD x 10 ⁻³	Difference in X̄CR x 10 ⁻³	SEMD x 10 ⁻³	STATISTICAL TEST			
						df	TEST VALUES T _{cal.}	T _{tab} (p<0.05)	Significance (p<0.05)
Blank	18.0	8.94	4.89	-	-	8	2.70	2.31	S
	9.77								
	6.86								
	5.52								
	4.53								
	5.35								
0.1	2.91	2.67	1.44	6.27	2.28	8	2.70	2.31	S
	2.05								
	1.66								
	1.37								
	5.00								
	2.73								
0.5	1.94	2.50	1.35	6.44	2.27	8	2.84	2.31	S
	1.54								
	1.28								
	4.42								
	2.38								
	1.67								
1.0	1.37	2.20	1.18	6.74	2.25	8	3.00	2.31	S
	1.14								
	4.30								
	2.33								
	1.63								
	1.31								
2.0	1.31	2.13	1.16	6.81	2.25	8	3.03	2.31	S
	1.07								
	3.95								
	2.15								
	1.51								
	1.22								
5.0	1.00	1.97	1.09	6.93	2.24	8	3.09	2.31	S
	1.22								
	1.00								

Table 6. Statistical Analysis of raw data presented on Table 2

Inhibitor Concentration x 10 ⁻⁴ (M)	CR x 10 ⁻³ (Mgcm ⁻² h ⁻¹)	$\bar{X}CR \times 10^{-3}$	SD x 10 ⁻³	Difference in $\bar{X}CR \times 10^{-3}$	SEMD x 10 ⁻³	STATISTICAL TEST			
						df	TEST VALUES T _{cal.} T _{tab} (p<0.05)	Significance (p<0.05)	
Blank	17.67	8.86	4.75	-	-	8	2.54	2.31	S
	9.77								
	6.82								
	5.47								
	4.58								
0.1	5.81	2.91	1.56	5.96	2.34	8	2.54	2.31	S
	3.20								
	2.25								
	1.80								
	1.51								
0.5	5.81	2.87	1.58	5.99	2.24	8	2.67	2.31	S
	3.14								
	2.17								
	1.74								
	1.47								
1.0	5.12	2.55	1.38	6.31	2.21	8	2.86	2.31	S
	2.49								
	1.98								
	1.54								
	1.33								
2.0	4.88	2.46	1.31	6.40	2.20	8	2.91	2.31	S
	2.73								
	1.90								
	1.51								
	1.28								
5.0	4.42	2.22	1.19	6.64	2.19	8	3.03	2.31	S
	2.44								
	1.71								
	1.37								
	1.14								

Table 7. Statistical Analysis of raw data presented on Table 3

Inhibitor Concentration x 10 ⁻⁴ (M)	CR x 10 ⁻³ (Mgcm ⁻² h ⁻¹)	$\bar{X}CR \times 10^{-3}$	SD x 10 ⁻³	Difference in $\bar{X}CR \times 10^{-3}$	SEMD x 10 ⁻³	STATISTICAL TEST			
						df	TEST VALUES T _{cal.} T _{tab} (p<0.05)	Significance (p<0.05)	
Blank	20.81	10.40	5.54	-	-	8	2.38	2.31	S
	11.22								
	7.95								
	6.11								
	5.93								
0.1	8.14	4.05	2.20	6.35	2.67	8	2.38	2.31	S
	4.42								
	3.14								
	2.44								
	2.09								
0.5	7.91	3.90	2.15	6.50	2.66	8	2.44	2.31	S
	4.24								
	3.02								
	2.38								
	1.95								
1.0	7.44	3.66	2.03	6.74	2.64	8	2.55	2.31	S
	4.01								
	2.79								
	2.18								
	1.88								
2.0	6.86	3.38	1.86	7.02	2.61	8	2.69	2.31	S
	3.66								
	2.60								
	2.06								
	1.72								
5.0	6.02	2.99	1.64	7.41	2.58	8	2.87	2.31	S
	3.26								
	2.33								
	1.80								
	1.51								

Table 8. Statistical Analysis of raw data presented on Table 4

Inhibitor Concentration x 10 ⁻⁴ (M)	CR x 10 ⁻³ (Mgcm ⁻² h ⁻¹)	$\bar{X}CR \times 10^{-3}$	SD x 10 ⁻³	Difference in $\bar{X}CR \times 10^{-3}$	SEMD x 10 ⁻³	STATISTICAL TEST			
						df	T _{cal.}	T _{tab} (p<0.05)	Significance (p<0.05)
Blank	28.37	13.95	7.73	-	-	8	1.64	2.31	NS
	15.23								
	10.70								
	8.40								
	7.02								
0.1	15.35	7.51	4.19	6.44	3.93	8	1.64	2.31	NS
	8.14								
	5.74								
	4.53								
	3.49								
0.5	13.72	6.80	3.73	7.15	3.84	8	1.86	2.31	NS
	7.44								
	5.23								
	4.13								
	3.47								
1.0	12.56	6.17	3.43	7.78	3.78	8	2.06	2.31	NS
	6.74								
	4.81								
	3.75								
	3.00								
2.0	11.28	5.54	3.08	8.41	3.72	8	2.26	2.31	NS
	6.10								
	4.15								
	3.37								
	2.81								
5.0	10.00	4.90	2.74	9.05	3.67	8	2.47	2.31	S
	5.35								
	3.76								
	2.94								
	2.44								

Table 9. Summary of analyzed data of Corrosion Rate (CR) and evaluation of relevant parameters (Surface Coverage (θ) and Inhibition Efficiency (%IE) at various Temperatures and respective inhibitor concentrations)

Inhibitor Concentration x 10 ⁻⁴ (M)	303K		313K		323K		333K					
	CR x 10 ⁻³ (Mgcm ⁻² h ⁻¹)	%IE	θ	CR (Mgcm ⁻² h ⁻¹)	%IE	θ	CR (Mgcm ⁻² h ⁻¹)	%IE	θ			
Blank	8.9 ± 4.89			8.86 ± 4.75			10.40 ± 5.54			13.95 ± 7.73		
0.1	2.67 ± 1.44	70	0.7	2.91 ± 1.56	67	0.67	4.05 ± 2.20	60	0.60	7.51 ± 4.19	46	0.46
0.5	2.50 ± 1.35	72	0.72	2.87 ± 1.58	68	0.68	3.90 ± 2.15	63	0.63	6.80 ± 3.73	51	0.51
1.0	2.20 ± 1.18	75	0.75	2.55 ± 1.38	71	0.71	3.66 ± 2.03	64	0.64	6.17 ± 3.43	55	0.55
2.0	2.13 ± 1.16	76	0.76	2.46 ± 1.31	72	0.72	3.38 ± 1.86	67	0.67	5.54 ± 3.08	60	0.60
5.0	1.97 ± 1.09	78	0.78	2.22 ± 1.19	75	0.75	2.99 ± 1.64	71	0.71	4.90 ± 2.74	65	0.65

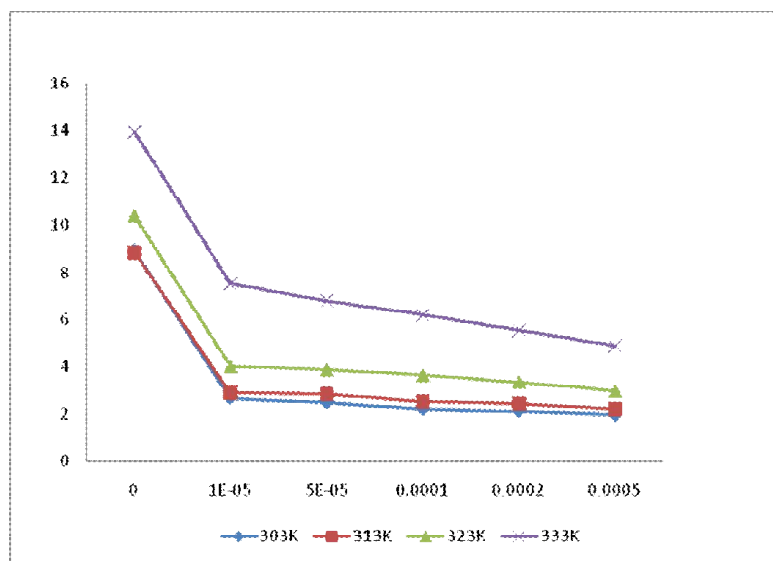


Fig. 1. A plot of $\bar{X}CR$ with inhibitor concentrations at various corrodent temperatures

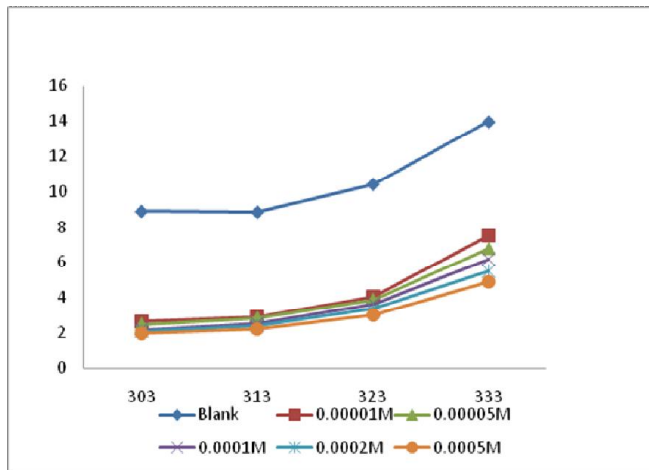


Fig. 2. A plot of $\bar{X}CR$ with inhibitor temperature at various inhibitor concentrations

Method of statistical analysis

Raw data generated from experimental work was statistically analyzed and changes in parameters of interest were tested using appropriate statistical method (t-test) and their significance measured at appropriate significance level ($p < 0.05$). The following statistical instruments were involved in the entire work;

$$\text{Mean, } \bar{X} = \frac{\sum fx}{\sum f} \quad \text{or} \quad \bar{X} = \frac{\sum fx}{N}$$

Where $\sum fx$ = Summation f of x and f = Frequency

$\sum f$ = Summation $f = N$. x = observation

$$SD = \sqrt{\frac{\sum f(x - \bar{x})^2}{\sum f}}$$

Where

SD = Standard Deviation

f = Frequency

\bar{X} = Mean

x = Observation

$$SEMD = \sqrt{\frac{S_1^2}{N_1} + \frac{S_2^2}{N_2}}$$

Where

SEMD - Standard Error of Mean Deviation

S_1 – Standard Deviation of the first group

S_2 – Standard Deviation of the second group

N_1 – Number of Observations of the first group

N_2 – Number of Observations of the second group

$$t = \frac{\bar{X}_1 - \bar{X}_2}{SEMD}$$

Where t = t-test

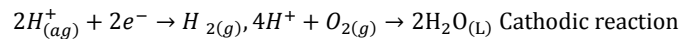
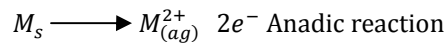
\bar{X}_1 - mean of the first group

\bar{X}_2 - mean of the second group

SEMD - Standard Error of Mean Deviation (Garai *et al.*, 2012; Khamis *et al.*, 2012)

Occurrence and mechanism of corrosion

Corrosion occurs by electrochemical process involving an electrolyte (where there is ionic transfer), anodic and cathodic reactions respectively and electrical currents to initiate its actions. It involves the formation of a chemical cell, in which a potential difference is set up between the points on the surface involved. The electrolytic reactions are as shown below:

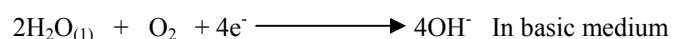
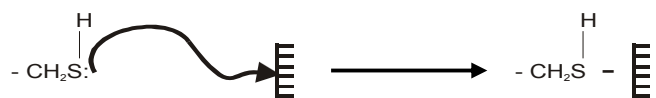


The reaction is characterized by the formation of reddish brown colouration of Fe^{3+} as the corrosion product also known as RUST and the process as RUSTING. (Chitra *et al.*, 2010; Ita *et al.*, 2013)

Proposed mechanism of corrosion inhibition

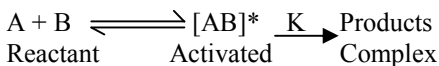
Most inhibitors are organic compound and Thiourea derivatives containing Nitrogen (N), Oxygen (O) and Sulphur (S) in their molecules which are all electron rich atoms. (Begum *et al.*, 2010) The compounds are hydrolysable and can easily adsorbed on the metal surface via the lone pair of electrons carried by their respective N, O and S atoms (Nasser and Sathiq, 2010; Paul *et al.*, 2013; Popova *et al.*, 2007). The bulky group that carries the functional groups containing the reacting atoms, covers the surface of the metal preventing further interaction of the metal with the corrosion environment and perhaps subsequent characteristic ionic transfer, as such preventing corrosion occurrence. The thin layer coverage formed, essentially blocks the discharge of H^+ and dissolution of metal ions, producing an electrostatic system where the protonated constituents molecules are adsorbed by process of physisorption, producing inhibition effect of very high efficiency (Paul *et al.*, 2013; Hyamala and Kashuri, 2011).

The schematic representation of the proposed mechanism is as shown below:



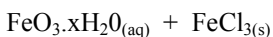
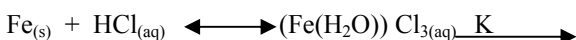
The reaction mechanism of corrosion follows the ‘absolute reaction rates theory’ also known as ‘transition state theory’.

which states that; 'molecules before undergoing reaction must form an activated complex in equilibrium with the reactants, and that the rate of any reaction is given by the rate of decomposition of the complex to form the reaction products. (Abdullah and Hameed, 2008; Akpan *et al.*, 2011) Generally, for a reaction between a molecule of A and B, the postulated steps can be represented schematically as below:



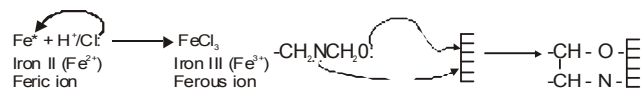
The activated complex has certain properties of an ordinary molecule and possess temporary stability (Akpan *et al.*, 2011).

Similarly, corrosion of mild steel in HCl solution follows a reaction mechanism as presented below:



The above reaction illustrates an oxidation of Fe from oxidation state of +2 to +3 by a lone pair of electron from chlorine (Cl⁻), (Obot and Obi-Egbedi, 2010; Rajalakshmi and Subhashini, 2011).

The reaction occurs by electrophilic addition as shown below:



From the above mechanism, corrosion inhibition can be explained on the basis of the concept of adsorption of inhibitors on the corroding metal surface. The inhibitive actions of these compounds have been attributed to the strong adsorption of these molecules on the positive metal surface, using the lone pairs of electron available on their hetero atoms, (Akpan *et al.*, 2011; Firdhouse and Nalini, 2013; Nalini *et al.*, 2011).

Pyrimethamine as corrosion inhibitor

Pyrimethamine is an organic compound having equivalent weight of 233.5g and with structural configuration rich in Nitrogen as presented below:

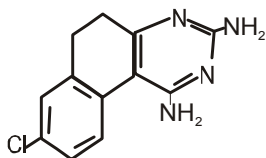
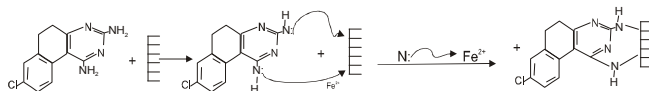


Fig. 3. Structural Configuration of Pyrimethamine

It is readily available as antibiotics generally for microbial infections. (Gatton, 2004; Ofoegbu and Ofoegbu, 2012) As antimicrobial Agent, pyrimethamine is found to be more potent in combination with sulfadoxine as sulfadoxine-pyrimethamine complex. (Gatton, 2004)

As corrosion inhibitor, pyrimethamine is proposed to operate with the mechanism presented below:



Pyrimethamine like other nitrogenous inhibitors records relatively high corrosion inhibition efficiency due to strong adsorption of the molecule on the positive metal surface using the lone pairs of electron from nitrogen. The bulky functional group attached to the molecule then spread on the surrounding metal surface and with its hydrophobic nature, prevent further interactions of the metal surface with the corroding environment (Gatton, 2004; Nalini *et al.*, 2011; Sathiq *et al.*, 2011).

Conclusion

Corrosion rate of mild steel in 2.0M HCl increased with increase in temperature, and reduced significantly ($p < 0.05$) in the present of as low as $0.1 \times 10^{-4}M$ concentration of pyrimethamine. The reduction in corrosion rate increased significantly ($p < 0.05$) with increase in inhibitor concentration, but reduce with rise in temperature to values that tested non-significant at $\geq 333k$ and conc. $< 5.0 \times 10^{-4}M$. Essential parameters like percentage inhibition Efficiency and degree of surface coverage increased relatively with increase in inhibitor concentration and decreased with rise in temperature. Thus making pyrimethamine not very effective corrosion inhibitor for mild steel corrosion at relative very high temperature ($T \geq 333k$) especially at very low inhibitor concentration (Conc. $< 5.0 \times 10^{-4}M$). The effectiveness of the inhibitor is accounted for by the structural configuration and composition of its molecules.

Acknowledgements

Authors are grateful to Akwa Ibom State College of Education for research grants to conduct the present study.

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