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Corrosion Inhibition Study of Proguanil Hydrochloride for Mild Steel Corrosion in 2.0 m HCl by Weight Loss Method

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Abstract This study considers proguanil hydrochloride for inhibition of mild steel corrosion in 2.0M HCl by weight loss method. Useful parameters like mean Corrosion Rate (XCR), Percentage Inhibition Efficiency (%IE) and degree of Surface Coverage (θ) were evaluated from raw data generated experimentally. Analysis of generated data and available literature show that; XCR decreased in the present of proguanil hydrochloride inhibitor. The decrease in XCR increased with increased in inhibitor concentration but tested non-significant (P<0.05) for all inhibitor concentrations while showing continuous appreciation to values approaching significance level at high (5.0 x 10⁻⁴M) inhibitor concentrations and low (303K and 313K) corrodent temperatures. Useful parameters (%IE and θ) increased with increase in inhibitor concentration and decreased with rise in corrodent temperature.

Keywords Corrosion Inhibition, Mild Steel, Proguanil Hydrochloride, Hydrochloric acid, Weight loss.

Introduction

Despite numerous efforts to mitigate against the effects of corrosion on production materials in recent years, corrosion still remains basic challenge facing most construction firms worldover [1-2]. By context of definition, corrosion is known to be an environmentally initiated phenomenon, whose rate of occurrence is influenced by the composition of the environment some of which may naturally abound or come as a result of anthropogenic influences on the environment.

Increased application of acids in industrial operations such as pickling, chemical and electrochemical etching, industrial acid descalling, etc leads to increased abundance of acids in the environment [2]. Thus, distorting its physicochemistry, ecology, and enhancing its metallic corrosion potential. Consequently, the study of metallic corrosion specifically in acidic medium is considered essential.

Among several methods available for control of metallic corrosion, the use of corrosion inhibitors is one of the most practical methods [3]. Most well known inhibitors are organic compounds containing Nitrogen, Sulphur, Oxygen and Phosphorus in their functional groups [4-6]. In view to achieving cost effective and environmentally friendly inhibition of metallic corrosion by the environment, recent studies consider pharmaceutical products rich in Nitrogen, Sulphur and Phosphorus for metallic corrosion inhibition [7-9]. The present study shall consider Proguanil Hydrochloride as inhibitor for mild steel corrosion in 2.0 M HCl.

Materials and Methods Materials

All the reagents used for this study were of analytical grade and were identified alongside with the mild steel material and supplied by reputable companies as stated below:

Mild steel material (specimen) – Ken-Johnson Nigeria Ltd



- 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.
- Proguanil Hydrochloride (the inhibitor) was of Analar grade and was supplied by Healthway Pharmacy, Uyo, Akwa Ibom State, Nigeria.

Preparation of Specimen

The mild steel 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 Standard Solution of HCl

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

Molarity = $\frac{\% \text{ purity x Specific gravity x 1000cm}}{[1,10]}$

Molar mass x Volume of Solution

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:

%	purity	=	33.0

/0	Puny			55.0
Sr.	Acific	arguity	_	1 1 8

Specific gravity = 1.18gMolar mass = $36.46gmol^{-1}$

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

Molarity of stock HCl = $\underline{33.0 \times 1.18g \times 1000}$ = **10.66M**

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

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

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 Proguanil Hydrochloride

1.0M stock solution of Proguanil Hydrochloride 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 1000 cm^3 with distilled water. The respective concentrations (2.0 x 10^{-4} M, 1.0 x 1.0^{-4} M, 5.0 x 10^{-5} M and 0.5 x 10^{-5} M) of the working solutions were obtained from the stock solution by dilution principle as shown below:

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

Where
$$C_s = 1.0M$$
, $V_s = 1000 \text{ cm}^3$, $C_w = 2.0 \times 10^{-4} \text{M}$ and $V_w = ?$
By appropriate substitution, we have that $V_w = \frac{1.0M \times 1000 \text{ cm}^3}{2.0 \times 10^{-4} \text{M}} = 0.05 \text{ cm}^3$

Hence, 0.05cm³ of stock solution of Proguanil Hydrochloride was carefully measured and transferred into a standard flask and the volume is made up to 1000 cm³. Other concentrations of the working solution were obtained in the same manner, using similar principle. The equivalent weight of Proguanil Hydrochloride is 252.5g [11].

Weight Loss Analysis

Weight Loss 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 los 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 (%1E) were evaluated using appropriate equations as shown below;

$$CR = \frac{W_{i} - W_{f}}{ST}, \qquad \theta = \frac{CR_{0} - CR_{i}}{CR_{0}} \text{ and } \%IE = \frac{CR_{0} - CR_{i}}{CR_{0}} x 100$$

Where; W_i - Initial weight of coupon

- $W_{\rm f}~$ Final weight of coupon
- S Total surface Area of coupon
- T Corrosion Time,
- CR Corrosion Rate
- \mbox{CR}_0 Corrosion Rate of coupon in the absent of inhibitor
- $\ensuremath{\text{CR}}_i$ Corrosion Rate of coupon in the present inhibitor
- (θ) Surface Coverage of inhibitor
- %IE %age Inhibition Efficiency of the inhibitor [10,12-13]

Result and Discussion

Weight Loss Study

Weight loss study of mild steel corrosion in 2.0M HCl and its inhibition by various concentrations of Proguanil Hydrochloride was studied at various temperatures. Results obtained from the study are presented on tables I–IX. Raw data generated from weight loss of mild steel from its corrosion in 2.0M HCl and its inhibition by the various concentrations of Proguanil Hydrochloride at the respective temperatures are presented on tables I, II, III, IV. The corrosion rate (CR) is subsequently evaluated from the weight loss data and presented on tables V, VI, VII and VIII, representing the respective temperatures.

The corrosion rates obtained were statistically analyzed and other useful parameters like Percentage Inhibition Efficiency (% IE) and degree of Surface Coverage (θ) were evaluated and presented on table IX.

Containing Different Concentrations of Proguanil Hydrochloride at 303K.								
Time	Inhibitor Concentration	Initial Mild	Steel Final wt of mild steel coupon	Weight loss				
(hr)	x 10 ⁻⁴ (M)	Coupon (W ₁)g	$(\mathbf{W}_2)\mathbf{g}$	$(\Delta W = W_1 - W_2)g$				
	Blank	1.900	1.745	0.155				
	0.1	1.990	1.849	0.141				
2	0.5	1.885	1.763	0.122				
	1.0	1.965	1.871	0.094				
	2.0	1.830	1.752	0.078				
	5.0	1.955	1.889	0.066				
	Blank	1.900	1.732	0.168				
	0.0	1.990	1.837	0.153				
4	0.5	1.885	1.753	0.132				
	1.0	1.965	1.864	0.101				
	2.0	1.830	1.746	0.084				
	5.0	1.955	1.884	0.071				
	Blank	1.900	1.723	0.177				
	0.0	1.990	1.829	0.161				
	0.5	1.885	1.745	0.140				
6	1.0	1.965	1.857	0.108				
	2.0	1.830	1.741	0.089				
	5.0	1.955	1.879	0.076				
	Blank	1.900	1.710	0.190				
	0.0	1.990	1.818	0.177				
	0.5	1.885	1.735	0.150				
8	1.0	1.965	1.850	0.115				
	2.0	1.830	1.735	0.095				
	5.0	1.955	1.875	0.080				
	Blank	1.900	1.705	0.195				
	0.0	1.990	1.813	0.177				
10	0.5	1.885	1.731	0.154				

 Table 1: Weight Loss Experiment for the Corrosion of Mild Steel Coupons in 2.0 M HCl Solution



1.0	1.965	1.846	0.119
2.0	1.830	1.732	0.098
5.0	1.955	1.870	0.085
		: C) (110, 10	

 Table 2: Weight Loss Experiment for the Corrosion of Mild Steel Coupons in 2.0 M HCl Solution

 Containing Different Concentrations of Proguanil Hydrochloride at 313K.

Time	Inhibitor Concentration	Initial Mild Steel Coupon	Final wt of mild steel coupon	Weight loss
(hr)	x 10 ⁻⁴ (M)	(W ₁)g	(W ₂)g	$(\Delta W = W_1 - W_2)g$
	Blank	2.040	1.888	0.152
	0.1	1.980	1.839	0.141
2	0.5	1.830	1.705	0.125
	1.0	1.835	1.735	0.100
	2.0	1.905	1.822	0.083
	5.0	1.865	1.796	0.069
	Blank	2.040	1.872	0.168
	0.0	1.980	1.824	0.056
4	0.5	1.830	1.694	0.136
	1.0	1.835	1.725	0.110
	2.0	1.905	1.814	0.091
	5.0	1.865	1.788	0.077
	Blank	2.040	1.864	0.176
	0.0	1.980	1.816	0.164
6	0.5	1.830	1.686	0.144
	1.0	1.835	1.718	0.117
	2.0	1.905	1.808	0.097
	5.0	1.865	1.785	0.080
	Blank	2.040	1.852	0.188
	0.0	1.980	1.806	0.174
8	0.5	1.830	1.679	0.154
	1.0	1.835	1.711	0.124
	2.0	1.905	1.802	0.103
	5.0	1.865	1.779	0.086
	Blank	2.040	1.843	0.197
	0.0	1.980	1.797	0.183
10	0.5	1.830	1.668	0.162
	1.0	1.835	1.705	0.130
	2.0	1.905	1.797	0.108
	5.0	1.865	1.774	0.091

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

Time	Inhibitor	Initial Mild S	teel Final wt of mild steel	Weight loss
(hr)	Concentration	Coupon (W ₁)g	coupon (W ₂)g	$(\Delta W = W_1 - W_2)g$
	x 10 ⁻⁴ (M)			
	Blank	1.820	1.641	0.179
	0.1	1.830	1.170	0.170
2	0.5	1.715	1.559	0.156
	1.0	1.935	1.795	0.140
	2.0	2.025	1.901	0.124
	5.0	2.045	1.942	0.103
	Blank	1.820	1.627	0.193
	0.0	1.830	1.647	0.183
4	0.5	1.715	1.548	0.167
	1.0	1.935	1.784	0.151
	2.0	2.025	1.892	0.133
	5.0	2.045	1.934	0.111



	Blank	1.820	1.615	0.205
	0.0	1.830	1.637	0.193
6	0.5	1.715	1.537	0.178
	1.0	1.935	1.776	0.158
	2.0	2.025	1.884	0.141
	5.0	2.045	1.928	0.117
	Blank	11.820	1.610	0.210
	0.0	1.830	1.631	0.199
8	0.5	1.715	1.532	0.183
	1.0	1.935	1.771	0.164
	2.0	2.025	1.879	0.146
	5.0	2.045	1.923	0.122
	Blank	1.820	1.595	0.255
	0.0	1.830	1.616	0.214
10	0.5	1.715	1.739	0.196
	1.0	1.935	1.759	0.176
	2.0	2.025	1.870	0.155
	5.0	2.045	1.914	0.131

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

Time	Inhibitor	Initial Mild	Steel Final wt of mild steel	Weight loss
(hr)	Concentration	Coupon (W ₁)g	coupon (W ₂)g	$(\Delta W = W_1 -$
	x 10 ⁻⁴ (M)			\tilde{W}_2)g
	Blank	1.930	1.686	0.244
	0.1	1.865	1.628	0.237
2	0.5	1.810	1.590	0.220
	1.0	1.790	1.590	0.200
	2.0	1.825	1.644	0.181
	5.0	1.845	1.694	0.151
	Blank	1.930	1.668	0.262
	0.0	1.865	1.611	0.254
4	0.5	1.810	1.574	0.236
	1.0	1.790	1.576	0.214
	2.0	1.825	1.1632	0.193
	5.0	1.845	1.683	0.162
	Blank	1.930	1.654	0.276
	0.0	1.865	1.585	0.267
6	0.5	1.810	1.553	0.248
	1.0	1.790	1.564	0.226
	2.0	1.825	1.621	0.204
	5.0	1.845	1.674	0.171
	Blank	1.930	1.641	0.289
	0.0	1.865	1.585	0.280
8	0.5	1.810	1.550	0.260
	1.0	1.790	1.553	0.237
	2.0	1.825	1.611	0.214
	5.0	1.845	1.666	0.179
	Blank	1.930	1.628	0.302
	0.0	1.865	1.572	0.293
10	0.5	1.810	1.538	0.272
	1.0	1.790	1.542	0.248
	2.0	1.825	1.602	0.223
	5.0	1.845	1.658	0.187



<u> </u>		Concentrati	ions of Pro	guanil Hydro	chloride at	303K.			
Inhibitor	CD 10-3	T op (0, 2)	ab	Difference	SEMD			STATISTIC	CAL TEST
Concentration	$\begin{array}{c} \mathbf{CR} \mathbf{x} 10^{\circ} \\ \mathbf{CR} \mathbf{x}^{2} 1 \end{array}$	$XCR \ge 10^{-3}$	SD x	in XCR	$x 10^{-3}$	10	TES	Т	VALUES
$x 10^{-4} (M)$	(Mgcm ² h ²)		10 5	<i>x</i> 10 ⁻³		df	Signific	cance	
							T _{cal.}	T _{tab} (p<0.05)	(p<0.05)
	18.02						cuir		
Blank	9.77								
	6.86	8.94	4.87	-	-				
	5.52								
	4.53								
	16.39								
	8.90								
0.1	6.24	8.16	4.41	0.78	2.94	8	0.27	2.31	NS
	5.15								
	4.12								
	14.19								
	7.67								
0.5	5.43	6.33	3.89	2.61	2.79	8	0.94	2.31	NS
	4.36								
	3.58								
	10.93								
1.0	5.87								
	4.19	5.42	2.95	3.52	2.25	8	1.38	2.31	NS
	3.34								
	2.77								
	9.07								
2.0	4.88								
	3.45	4.49	2.45	4.45	2.44	8	1.82	2.31	NS
	2.76								
	2.28								
	7.67								
5.0	4.13								
	2.95	3.81	2.06	5.13	2.36	8	2.17	2.31	NS
	2.33								
	1.98		-						
	Table 6: Evaluat	ion of Corrosio Concentrati	n Rate of I	Mild Steel in 2 oguanil Hydro	2.0M HCl a chloride at	and its 313K.	inhibitio	n by various	
Inhibitor				Difference	SEMD			STATISTIC	CAL TEST
Concentration	CR x 10 ⁻³	\overline{X} CR x 10 ⁻³	SD x	in XCR	x 10 ⁻³	df	TES	т	VALUES
x 10 ⁻⁴ (M)	$(Mgcm^{-2}h^{-1})$		10 ⁻³	x 10 ⁻³			Signifi	cance	
							T _{cal.}	T _{tab} (p<0.05)	(p<0.05)
	17.67								
Blank	9.77								
	6.82	8.86	4.84	-	-				
	5.47								
	4.58								
	16.40								
	9.07								
0.1	6.36	8.23	4.40	0.63	2.93	8	0.22	2.31	NS
	5.06								
	4.26								
	14.53								

Table 5: Evaluation of Corrosion Rate of Mild Steel in 2.0M HCl and its inhibition by various

 Concentrations of Proguanil Hydrochloride at 303K.



	7.91		• • • •						
0.5	5.58	7.25	3.90	1.61	2.78	8	0.58	2.31	NS
	4.48								
	3.//								
1.0	11.63								
1.0	6.40	5.94	2.11	2.02	2.57	0	1 10	0.21	NC
	4.53	5.84	3.11	3.02	2.57	8	1.18	2.31	INS
	3.60								
	3.02								
2.0	9.65								
2.0	5.29	4.0.4	2 50	4.02	2.45	0	1 < 4	0.01	NG
	3.70	4.84	2.58	4.02	2.45	8	1.64	2.31	NS
	2.99								
	2.51								
5.0	8.02								
5.0	4.48	4.04	2.14	4.92	2 27	0	2.02	0.21	NC
	3.10	4.04	2.14	4.82	2.37	8	2.05	2.31	INS
	2.50								
	Z.1Z	ion of Correctio	n Doto of	Mild Steel in	2 OM UCI	and its	inhihitio	hu vorious	
	Table 7: Evaluat	Concentrat	ions of Pro	oguanil Hydro	2.01vi HCi chloride at	+ 323K	minomo	n by various	
Inhibitor		Concentrat		Difference	SFMD	. 52511.		STATISTIC	AL TEST
Concentration	CR x 10 ⁻³	$\overline{\mathbf{X}}$ CR v 10 ⁻³	SD v	in $\overline{\mathbf{X}}\mathbf{C}\mathbf{R}$	$r 10^{-3}$	df	TES	Т	VALUES
$x 10^{-4}$ (M)	$(Mgcm^{-2}h^{-1})$	ACK X IU	10^{-3}	$r 10^{-3}$	x 10	ui	Signifi	cance	i viilelo
	(ingen n)		10	x 10			Jigiiii	Т.	(n<0.05)
							T _{col}	(p < 0.05)	(p (010 C)
	20.81						Cal.	(I and)	
Blank	11.22								
	7.95	10.26	5.65	-	-				
	6.10								
	5.93								
	19.77								
	10.64								
0.1	7.48	9.73	5.46	0.53	3.51	8	0.15	2.31	NS
	5.78								
	4.98								
	18.14								
	9.71								
0.5	6.70	8.93	4.99	1.33	3.37	8	0.39	2.31	NS
	5.32								
	4.56								
	16.28								
1.0	8.78								
	6.12	8.01	4.44	2.25	3.21	8	0.70	2.31	NS
	4.77								
	4.09								
	14.42								
2.0	7.73								
	5.47	7.09	3.93	3.17	3.08	8	1.03	2.31	NS
	2.24								
	2 (0								
	3.00								
	3.60 11.98								
5.0	5.60 11.98 6.45								
5.0	5.60 11.98 6.45 4.53	5.91	3.25	4.35	2.91	8	1.47	2.31	NS



	3.05								
	Table 8: Evaluation of Corrosion Rate of Mild Steel in 2.0M HCl and its inhibition by various								
Inhibitor		Concentrati	ons of Pro	Difference	chloride at	333K.		STATISTIC	AT TEST
Concentration	CR x 10^{-3}	$\overline{\mathbf{X}}$ CR x 10 ⁻³	SD x	in $\overline{\mathbf{X}}\mathbf{C}\mathbf{R}$	$x 10^{-3}$	df	TES	T	VALUES
x 10 ⁻⁴ (M)	$(Mgcm^{-2}h^{-1})$	non n 10	10 ⁻³	$x 10^{-3}$	<i>n</i> 10		Signifi	cance	
							T _{cal.}	T _{tab} (p<0.05)	(p<0.05)
	28.37								
Blank	15.23								
	10.70	13.94	7.73	-	-				
	8.40								
	7.02								
	27.56								
	14.77								
0.1	10.35	13.53	7.52	0.41	4.83	8	0.08	2.31	NS
	8.14								
	6.81								
	25.58								
	13.72								
0.5	9.61	12.56	6.98	1.38	4.66	8	0.30	2.31	NS
	7.56								
	6.33								
	23.26								
1.0	12.44								
	8.76	11.42	6.33	2.52	4.47	8	0.56	2.31	NS
	6.89								
	5.77								
	21.05								
2.0	11.22								
	7.91	10.32	5.74	3.62	4.31	8	0.84	2.31	NS
	6.22								
	5.19								
	17.56								
5.0	9.42								
	6.63	8.63	4.78	5.31	4.07	8	1.30	2.31	NS
	5.20								
	4.35								

From tables V, VI, VII, and VII, data on corrosion rate show that XCR of mild steel in 2.0M HCl reduces in the present of proguanil Hydrochloride Inhibitor. It was also observed that the reduction in XCR of the mild steel in the test solution increased with increase in inhibitor concentration. XCR was also observed to increase with rise in corrodent temperature even in the present of inhibitor. The increase in successive reduction in XCR with corresponding increase in inhibitor concentration tested non-significant (P<0.05) for all concentrations of proguanil Hydrochloride inhibitor. Statistical test also reveals that the tested significance (P<0.05) gradually appreciated to values approaching significant levels at higher concentrations (5.0×10^{-4} M) of inhibitor and lower temperatures (303K and 313K).

Table 9: Summary of analyzed data of Corrosion Rate (CR) and evaluation of relevant parameters (Surface

Coverage,	$\boldsymbol{\theta}$ and Percentage	Inhibition	Efficiency,	%IE) at various	Temperatures	and respective
		1.1	11.14.1			

	inhibitor concentrations.											
303K		313K				323K			333K			
Inhibitor	$CR \times 10^{-3}$	%I	θ	CR	%	θ	CR	%	θ	CR	%I	θ
Concentratio	(Mgcm ⁻² h ⁻¹)	Е		$(Mgcm^2 h^2)$	IE		$(Mgcm^2 h^1)$	IE		(Mgcm ⁻² h ⁻¹)	Е	
n x 10 ⁻⁴ (M)	$\overline{x} \pm SD$											
Blank	8.94 ± 4.87			8.86 ± 4.84			10.26 ± 5.65			13.94 ± 7.73		
0.1	8.16 ± 4.41	9	0.09	8.23 ± 4.40	7	0.07	9.73 ± 5.46	5	0.05	13.53 ± 7.52	3	0.03



0.5	6.33 ± 3.89	21	0.21	7.25 ± 3.90	18	0.18	8.93 ± 4.99	13	0.13	12.56 ± 6.98	10	0.10
1.0	5.42 ± 2.95	39	0.39	5.84 ± 3.11	34	0.34	8.01 ± 4.44	22	0.22	11.42 ± 6.33	18	0.18
2.0	4.49 ± 2.45	50	0.5	4.84 ± 2.58	45	0.45	7.09 ± 3.93	31	0.31	10.32 ± 5.74	26	0.26
5.0	3.81 ± 2.06	56	0.56	4.04 ± 2.14	54	0.54	5.91 ± 3.25	42	0.42	8.63 ± 4.78	38	0.38

Data on table IX shows that %IE of Proguanil Hydrochloride for mild steel corrosion in 2.0M HCl increases with increase in inhibitor concentration and decreases with rise in corrodent temperature. Similarly, θ increases with increase inhibitor concentration and decreases with rise in corrodent temperature. Variations in the above parameters are shown in the plots below.







Figure 1: Plot of Mean Corrosion Rate ($\overline{X}CR$) against Inhibitor Concentrations at Various Corrodent Temperature

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;

Mean,
$$\overline{X} = \sum fx$$
 or $\overline{X} = \sum fx$
 $\sum f$ or $\overline{X} = \sum fx$
Where $\sum fx$ = Summation f of x and f = Frequency
 $\sum f$ = Summation f = N. x = observation
 $SD = \sqrt{\sum f(x - \overline{x})^2}$
Where SD = Standard Deviation
f = Frequency
 \overline{X} = Mean
x = Observation
SEMD $\sqrt{\frac{S_1^2 + S_2^2}{N_1 N_2}}$

Where SEMD - Standard Error of Mean Deviation

- S_1 Standard Deviation of the first group
- S₂ Standard Deviation of the second group
- N_1 Number of Observations of the first group
- N_2 Number of Observations of the second group

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

Where t = t-test

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

- \overline{X}_2 mean of the second group
- SEMD Standard Error of Mean Deviation [14-15]

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:

 $M_s \longrightarrow H_{(aq)}^{++}$ 2e⁻ Anadic reaction 2H⁺ + 2e⁻ \longrightarrow $H_{2(g)}$ Cathodic reaction

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 [16-17].

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 [12]. 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 [4,5,18]. 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 [5, 19]. The schematic representation of the proposed mechanism is as shown below;



$$4H^+_{(aq)} + O_{2(g)} \longrightarrow 2H_2O_{(1)}$$
 In acidic medium
 $2H_2O_{(1)} + O_2 + 4e^- \longrightarrow 4OH^-$ In basic medium

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 [3,13]. Generally, for a reaction between a molecule of A and B, the postulated steps can be represented schematically as below:

$$A + B \leftarrow [AB]^* K$$
 Products
Reactant Activated
Complex

The activated complex has certain properties of an ordinary molecule and possess temporary stability [13] Similarly, corrosion of mild steel in HCl solution follows a reaction mechanism as presented below:

 $Fe_{(s)} + HCl_{(aq)} \leftarrow Fe(H_2O) Cl_{3(aq)} K FeO_3.xH_2O_{(aq)} + FeCl_{3(s)}$ The above reaction illustrates an oxidation of Fe from oxidation state of +2 to +3 by a lone pair of election from chlorine (Cl⁻) [20-21.

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 election available on their hetero atoms [5.13,22].

Proguanil Hydrochloride as Corrosion Inhibitor

Proguanil Hydrochloride is an organic compound with equivalent weight of 252.5g. It is rich in Nitrogen and has a chemical structure as presented below.

Proguanil Hydrochloride

It is readily available as a pharmaceutical with high potency for microbial infections [11]. As corrosion inhibitor, proguanil hydrochloride is proposed to operate with the mechanism below.



Proguanil hydrochloride like other nitrogeneous inhibitors shows sufficient evidence of inhibition of mild steel corrosion in 2.0M HCl with non-significant (P<0.05), efficiency at its lower concentrations ($\leq 5.0 \times 10^{-4}$ M). It corrosion inhibition property is accounted for by strong adsorption of its molecules on the positive metal surface using the lone pairs of electron from its nitrogen. The bulky functional group spread on the metal surface preventing its further interactions with the corroding environment [6,7,22].

Conclusion

XCR of mild steel in 2.0M HCl decrease in the present of proguanil hydrochloride inhibitor. The successive decrease in the XCR increased with corresponding increase in inhibitor concentration. XCR increases with rise in corrodent temperature with or without inhibitor. Useful parameters like %IE and θ both increased with increase in inhibitor concentration and decreased with rise in corrodent temperature. Reduction in XCR tested non-significant (P<0.05) for all inhibitor concentrations, but showing gradual appreciation to values approaching significant level at higher (5.0x10⁻⁴M) inhibitor concentration and lower (303K and 313K) temperatures. Thus, making proguanil



hydrochloride better inhibitor for mild steel corrosion in 2.0M HCl at high $(5.0 \times 10^{-4} \text{M})$ inhibitor concentrations and low (T \leq 313K) corrodent temperatures.

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References

- 1. Kar, P. K. and Singh, G. (2011). Evaluation of Nitrilotrimethylene Phosphonic Acid and Nitrilotriacetic Acid as Corrosion inhibitors of Mild Steel in sea water. *Materials Science*, 5402, 1-6.
- 2. Khamis, A., Saleh, M. M. and Awad, M. I. (2012). Synergistic Inhibitor effect of Cetylpyridinium Chloride and other Halides on the Corrosion of Mild Steel in 0.5M H₂SO₄. *Corrosion Science*, 66, 343 349.
- Akpan, I. A., Onuchukwu, A. I., Ayuk, A. A. and Ejike, E. N. (2011); The Study of Cathodic Protection of Selected Electroactive anions on Galvanized Steel in acidic medium by Weight loss and hydrogen evolution techniques. Bulletin of Pure and Applied Sciences 30C (1,2), 1 – 5.
- Nasser, A. J. A. and Sathiq, M. A. (2010). Adsorption and Corrosion Inhibition of Mild Steel in Hydrochloric Acid Medium by N-[morpholin-4-yl(phenyl)methyl] benzamide. *International Journal of Engineering Science and Technology*, 2(11), 6417 – 6426.
- Paul, A., Joby, T. K., Vinod, P. R. and Shaju, K. S. (2013). 3-Formylindole-4-aminobenzoic Acid: A Potential Corrosion Inhibitor for Mild Steel and Copper in Hydrochloric Acid Media. *International Scholarly Research Network (ISRN):* Corrosion, 5402, 1-9.
- 6. Sathiq, M. A., Nasser, A. J. A. and Sirajudeen, P. M. (2011). Adsorption and Corrosion Inhibition Effect of N-(1-Morpholonobenzyl) urea on Mild Steel in Acidic medium. *E-Journal of Chemistry*, 8(2), 621 628.
- 7. Gatton, M. L. (2004); Evolution of Resistance to Sulfadoxine-pyrimethamine in Plasmodium Falciparum. Antimicrob Agents Chemother, 48(6), 2116 – 2123. *International Journal of Corrosion*, 1155, 1-7.
- 8. Ofoegbu, S. U. and Ofoegbu, P. U. (2012). Corrosion Inhibition of Mild Steel in 0.1M Hydrochloric Acid Media by Chloroquine Diphosphate. *ARPN Journal of Engineering and Applied Sciences*, 7(3), 272 276.
- Parameswari, K., Chitra, S., Kavitha, S., Rajpriya, J. and Selvaraj, A. (2011). Adsorption and Inhibitive properties of Triazolo-pyrimidine Derivatives in Acid Corrosion of Mild Steel. *E-Journal of Chemistry*, 8(3), 1250 – 1257.
- 10. Williams, E. E., Akpan, I. A. and Francis, A. J. (2014); Corrosion Inhibition potential of ethylamine for mild steel corrosion in saline water environment. MSAIJ, 10(5) 2014 [173 181].
- 11. Sutherland, C. J., Laundy, M. and Price, N. (2008). Mutations in the Plasmodium Falciparum Cytochrome b. Gene are Associated with delayed parasite Recrudescence in Malaria Patients Treatment Atovaquone Proguanil. Malaria Journal 7(1), 240-251.
- 12. Begum, A. S., Mallika, J. and Gayathri, P. (2010). Corrosion Inhibition Property of Some 1, 3, 4-Thiadiazolines on Mild Steel in Acidic Medium. *E-Journal of Chemistry*, 7(1), 185 – 197.
- 13. Firdhouse, M. J. and Nalini, D. (2013). Corrosion Inhibition of Mild Steel in Acidic Media by 5'-Phenyl-2',4'-dihydrospiro[indole-3,3'-pyrazol]-2(III)-one. *Journal of Chemistry*, 1155, 1-9.
- Garai, S., Garai, S., Jaiasankai, P., Singh, J. K. and Elango, A. (2012). A Comprehensive Study on crude Methanolic Extract of *Artemisia pallens* (Asteraceae) and its Actives Component as Effective Corrosion Inhibitors of Mild Steel in Acid Solution. *Corrosion Science*, 60, 193 – 204.
- 15. Khamis, A., Saleh, M. M. and Awad, M. I. (2012). Synergistic Inhibitor effect of Cetylpyridinium Chloride and other Halides on the Corrosion of Mild Steel in 0.5M H₂SO₄. *Corrosion Science*, 66, 343 349.
- 16. Chitra, S., Parameswari, K., Sivakani, C. and Selvaraj, A. (2010); Sulpha Schiff Bases as Corrosion Inhibitors for Mild Steel in IM Sulphuric Acid. Chemical Engineering Research Bulletin, 14, 1-6.
- 17. Ita, B. I., Abakedi, O. U. and Osabor, V. N. (2013). Inhibition of Mild Steel Corrosion in Hydrochloric Acid by 2-Acetylpyridine and 2-Acetylpyridine Phosphate. *Global Advanced Research Journal of Engineering, Technology and Innovation.* 2(3), 84-89.
- Popova, A., Christov, M. and Zwetanora, A. (2007); Novel Calixarene Derivatives as Inhibitor of Mild Steel Corrosion in 1M HCl. Corrosion Science 49, 2131 – 2136.
- 19. Shyamala, M. and Kashuri, P. K. (2011); The Inhibitory Action of the Extracts of *Adathoda vasica*, *Edipta alba* and *Centella asiatica* on the Corrosion of Mild Steel in Hydrochloric Acid medium: A Comparative Study. International Journal of Corrosion, 2012: 1-13.



- Obot, I. B. and Obi-Egbedi, N. O. (2010). Adsorption Properties and inhibition of Mild Steel Corrosion in Sulphuric Acid Solution by Ketocanazole: Experimental and theoretical Investigation. *Corrosion Science*, 52, 198 – 204.
- 21. Rajalakshmi, R. and Subhashini, S. (2011). Corrosion Inhibition Effect of Dicycloimine Hydrochloride (DCl) on Mild Steel in 1.0M HCl. *Journal of Chemistry*, 7(1), 323-330.
- 22. Nalini, D., Rajalakshmi, R. and Subhasini, S. (2011). Corrosion Inhibition of Mild Steel in Acid Solution by 3,4,5-Trimethoxyphenyl-2-imidazolines. *E-Journal of Chemistry*, 8(2), 671-679.

