

A Potential Corrosion Inhibitor for Acid Corrosion of Mild Steel

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Abstract

1-Phenyl-3-methylpyrazol-5-one (HPMP) was evaluated as corrosion inhibitor for mild steel in hydrochloric, nitric and perchloric acid solutions, using weight loss measurements at room temperature. HPMP was found to retard the corrosion rate of mild steel in hydrochloric and nitric acid solutions, while it aided the corrosion of same metal in perchloric acid solution. Corrosion rate decreased linearly with degree of surface coverage, and higher values of half-life were obtained for the coupons coated with HPMP inhibitor. The thicker the film of the HPMP coating on the metal, the more protection it gave to it, giving rise to the increase in inhibition efficiency.

Keywords

Corrosion, Mild Steel, Film Thickness, 1-Phenyl-3-Methylpyrazol-5-One (HPMP), Weight Loss, Surface Coverage

1. Introduction

Metals are the pre-eminent important materials used in structural and decorative applications. Most metals and alloys when used in different human activities are susceptible to different mechanisms of corrosion due to their exposure to different corrosive media. In petroleum industries, mild steel is regularly used in the construction of pipe lines. Many corrosion problems arise in these pipelines due to the aggressiveness of the liquids carried by them [1].

Corrosion, deterioration or destruction of metals generally, is an unavoidable but controllable process. One of the methods used to reduce the rate of metallic corrosion is the use of inhibitors [2]. Many studies have been carried out to find suitable organic and inorganic compounds to be used as corrosion inhibitors for mild steel in different aqueous solutions, for example, 1H-1,2,4-triazol-l-yl-methyl-2-(4-chlorophenoxy) acetate, methocarbamol, Potassium Iodide, Pyridoxal and Pyridoxal hydrochlorides, etc. [3] [4] [5] [6] [7]. These compounds were all found to be good Inhibitors of mild steel. The inhibition of metal corrosion by these compounds is attributed to either the adsorption of inhibitor molecule or the formation of a layer of insoluble complex of the metal on the surface which acts as a barrier between the metal surface and the corrosive medium [8].

The present study is aimed at investigating the inhibitive properties of 1-phenyl-3-methylpyrazol-5-one on mild steel in different acid solutions such as Hydrochloric acid, Nitric and perchloric acid, using weight loss and coating methods. Parameters such as half-life and film thickness of HPMP on the metal surface will be calculated to determine the inhibition efficiency of the inhibitor.

2. Experimental Method

2.1. Material Preparation

Mild steel sheets were obtained from the Engineering workshop of University of Port Harcourt, Port Harcourt. The optical image of the as-received metal is as shown in **Figure 1**. The sheets were mechanically press cut into 5 cm \times 5 cm coupons. The two faces had 50 cm² total geometric surface area. Each coupon was perforated with a hole at the side to allow the passage of thread for ease of handling. The metal coupons were mechanically cleaned and polished with emery paper of varying surface finish to expose clean shinning surfaces. Thereafter, the coupons were washed in distilled water to remove dirt and rust, degreased in ethanol, dipped in acetone and finally blown dry with a hand drier. The coupons were stored in a desiccator free of moisture prior to their coating with the inhibitor and their use in corrosion studies.

1-Phenyl-3-methylpyrazol-5-one (HPMP) used as inhibitor was synthesized using the method by Vogel [10]. It is insoluble in water, but soluble in a mixture

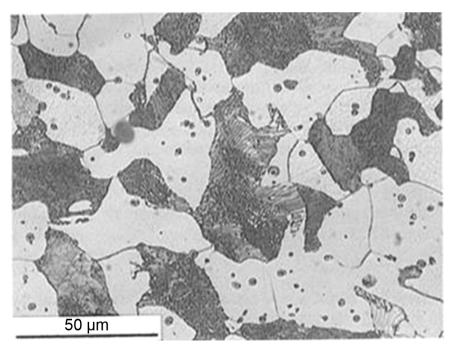


Figure 1. Microstructure of mild steel-courtesy Sun et al. [9].

of ethanol and water. The mild steel coupons were coated with HPMP as discussed in the previous works [11].

2.2. Weight Loss Measurements

Weight loss measurements were carried out as described in previous works [12] [13]. All the chemicals used were of the analytical grade. The sodium hydroxide pellets, hydrochloric acid, nitric acid, perchloric acid, ethanol and acetone, were products of May and Baker Limited, Dagenham, England. Distilled water was used for the preparation of all solutions.

3. Experimental Results and Discussion

3.1. Analysis of Weight Loss Measurement Results

The HPMP inhibitor was coated on the mild steel coupons at room temperature, and exposed to three different acidic environments. Their corresponding weight loss data are presented on Table 1. HPMP inhibited the corrosion of mild steel in HCI and HNO₃ environments, as lower values of weight loss were recorded for the coated coupons. However, in the perchloric acid environment, the coated samples had higher values of weight loss than the uncoated samples. This signifies that the inhibitor coating on the coupons dissolved, thereby aiding the corrosion of the metal. This behavior is attributed to the fact that HCIO₄ is one of the strongest acids known. It is a stronger acid than sulfuric and nitric acid. Perchloric acid is dangerously corrosive and readily forms potentially explosive mixtures [14]. It is a powerful oxidizing agent and thus causes fast dissolution of the metals.

3.2. Corrosion Kinetics

To characterize the corrosion reaction, the application of the principles of chemical kinetics to corrosion reaction is being explored. Calculated values of Log (W1- Δ W) obtained from the weight loss measurements were plotted against

Time (Days)	Weight loss (g)							
	HCI		HN	O ₃	HCIO ₄			
	Uncoated coupon	Coated coupon	Uncoated coupon	Coated coupon	Uncoated coupon	Coated coupon		
1	0.3490	0.1346	2.4677	1.7040	0.2975	0.3067		
2	0.4573	0.2091	2.5144	1.7855	0.4853	0.5600		
3	0.6057	0.2841	2.7345	2.0199	0.6836	0.7929		
4	0.8257	0.4256	2.9570	2.2336	0.8984	1.0541		
5	1.0074	0.5360	3.0669	2.4968	1.0916	1.4532		
6	1.1764	0.6340	3.1332	2.7459	1.2454	1.7359		
7	1.2813	0.7888	3.1890	2.9865	1.3822	2.0380		

Table 1. Weight loss (g) of coated and uncoated Mild Steel coupons in various acid solutions.



time as shown in **Figure 2**. The straight lines obtained from the plots in **Figure 1** with or without inhibitor coating confirm a first order reaction kinetics with respect to mild steel in the various acidic medium. A similar result was reported earlier for the corrosion of mild steel in HCI solution [15].

The first rate equation was used to evaluate the rate constant since the dissolution of mild steel for both the uncoated and coated samples in the acid solutions obey the first order rate equation. The rate constants (k) at room temperature were used to calculate the half-life ($t_{1/2}$) of the system by making use of the first order reaction equation [16].

$$t_{1/2} = 0.693/k \tag{1}$$

where k is the rate constant calculated using Equation (1).

$$k = 1/t \ln W_i / W_f \tag{2}$$

where W_i is the initial weight of the sample, W_f is the final weight of the sample and t is the immersion time (days). The calculated values of rate constants (k)

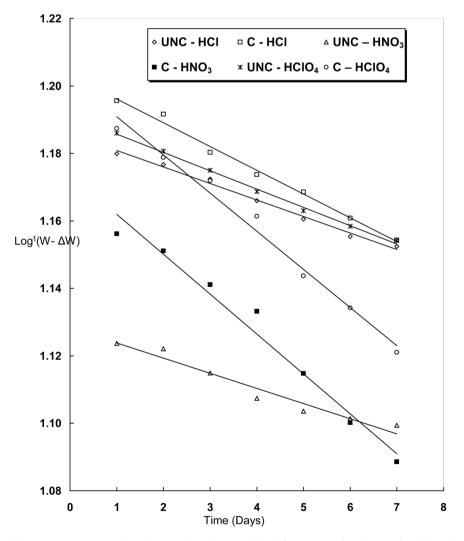


Figure 2. Variation of log (W_1 - ΔW) with time (days) for uncoated and coated mild steel in 0.5 m HCl, HNO₃ and HClO₄ solutions.

and half-life $(t_{1/2})$ obtained from Equation (1) are presented on **Table 2**. The results further confirm the inhibition of the metal by HPMP as higher values of half-life were obtained for the coated samples. For instance, for the uncoated mild steel coupon in HCI solution, it will take about 56.3 days for half of the coupon to decay (deteriorate) while for the coupon coated with HPMP, It will take about 113.3 days for half of the coupon to decay or corrode. This is a proof that HPMP is an effective corrosion inhibitor for mild steel. HPMP must have retarded corrosion by adsorption to form a thin invisible film only a few micrometers thick.

3.3. Variation of Corrosion Rate with Surface Coverage

The plot of the results of corrosion rate evaluated by Equation (3) is as shown on **Figure 3**.

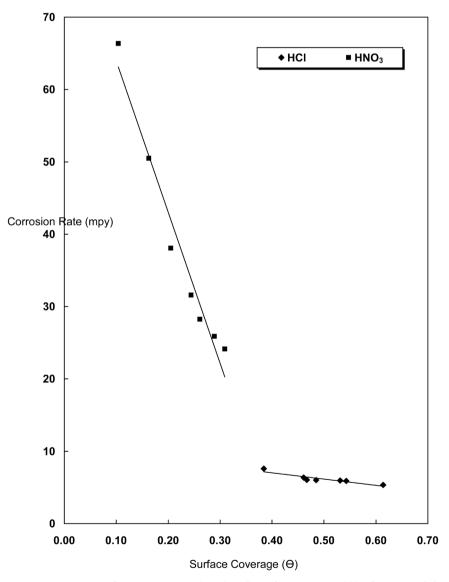
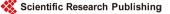


Figure 3. Variation of corrosion rates (mpy) with surface coverage (Θ) of HPMP inhibitor on mild steel in 0.5 m acid solution.



Nature of coupon	Acid	Rate Constant K (day ⁻¹)	Half-life, $t_{1/2}$ (days)
Uncoated	0.05M HCl	0.0123	56.3
Coated	0.05M HCl	0.0052	113.3
Uncoated	0.05M HNO ₃	0.0323	21.5
Coated	0.05M HNO ₃	0.0169	41.0
Uncoated	$0.05M \text{ HClO}_4$	0.0133	52.1
Coated	0.05M HClO ₄	0.0205	43.6

Table 2. Kinetic parameters for uncoated and coated mild steel in acid solutions.

Corrosion Rate (mpy) = 534w/DAT (3)

where w = weight loss (g) D = density of specimen (g/cm³) A = area of specimen (cm²) and *T* is exposure time (hours).

It is seen from the plot that corrosion rate decreases linearly with the degree of surface coverage for the metal studied. The straight lines confirm that the inhibition is due to the adsorption of HPMP on the metal surface.

3.4. Film Thickness (µm) and Inhibition Efficiency (%)

Variation of film thickness with inhibition efficiency is presented on **Table 3**. The result reveal that the thicker the film of the coating, the more protection it gives to the metal, giving rise to the increase in inhibition efficiency. The negative values of inhibition efficiency obtained for the metal in $HClO_4$ environment is a further proof that there was no inhibition of the metal in perchloric acid environment. A film thickness of 13.904 µm was obtained for mild steel, which yielded inhibition efficiency of 61.43%. The film forms a blanket over the surface of the metal, blocking the reaction sites (surface defects), thereby protecting the metal from direct attack of the acid.

The results of Inhibition Efficiency as shown on **Table 3** are evaluated using Equation (4).

Inhibition Efficiency (IE)% =
$$\left[1 - W_1/W_2\right] \times 100$$
 (4)

where W_1 is weight loss of coated sample with inhibitor, and W_2 is weight loss of uncoated sample. **Table 3** reveals that inhibition efficiency decreases with time in the various acidic solutions. The negative values of inhibition efficiency obtained for mild steel signify that there was no inhibition of the metal in HCIO₄ solution. The results also show that the thicker the film of the coating, the more protection it gives to the metals, giving rise to inhibition efficiency. The inhibition of the corrosion process by HPMP can be attributed to adsorption of its molecules at the metal-acid solution interface. This is usually observed by the decrease in corrosion loss as measured by weight loss.

4. Conclusions

From the present study, it is concluded that HPMP is a potential inhibitor for

Time (dave)	Film Thickness (µm)			Inhibition Efficiency (%)		
Time (days)	HCl	HNO ₃	$HClO_4$	HCl	HNO ₃	$HClO_4$
1	13.904	12.746	13.209	61.43	30.95	-3.09
4	7.879	9.965	11.355	48.51	24.46	-17.34
7	6.025	7.647	6.025	38.44	6.35	-47.45

Table 3. Film thickness (μ m) and inhibition efficiency (%) in 0.5 m acid concentration.

mild steel corrosion in HCI and HNO3 solutions. All parameters evaluated showed that there was no inhibition in HCIO₄, as negative values were obtained. Higher values of half-life were obtained for the coated samples, which is a proof that HPMP inhibited the mild steel samples.

Also the thicker the film of the coating, the more protection it gives to the metals, giving rise to higher inhibition efficiency. The corrosion inhibition by HPMP can be attributed to the adsorption of its molecules at the metal surface.

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