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Synergistic study of corrosion inhibition of sulphadoxine and pyrimethamine on mild steel in acidic medium

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ABSTRACT

The synergistic effect of an antimalarial drug sold under the trade name "Antimal", a combination of sulphadoxine and pyrimethamine, which contains nitrogen, oxygen and sulphur atoms in their molecular structure, was studied as a low cost and ecofriendly corrosion inhibitor for mild steel in 0.1M HCl solution at room temperature by weight loss technique. The results obtained show that the drug has promising inhibitive properties at all concentrations considered in this study. The inhibition efficiency was also found to increase with increase in the concentration of the inhibitor. A mechanism for the inhibitive action of the drug as well as its kinetics has also been proposed.

KEYWORDS

Corrosion inhibition;
Sulphadoxine and pyrimethamine;
Mild steel;
Weight loss technique.

INTRODUCTION

Man has benefited immensely from the advent of metallic structures, whether in their pure form or alloyed. However, there has been serious threat to the durability of metallic structures; in one part due to the natural tendency for metals to return to their original forms –the ore– and in the other part due to adverse human activities in which metals are being exposed to aggressive environments.

The quest to reduce the extent to which corrosion destroys metallic structures has drawn the attention of many[1]. One of the most practical ways for monitoring corrodent behaviours as well as the protection of metals against corrosion is the application of chemical corrosion inhibitors[2,3]. Most of these corrosion inhibitors are synthetic chemicals, expensive and toxic[4]. Therefore, research activities in recent times have been geared towards developing cheap, non-toxic and environmentally friendly corrosion inhibitors[5]. These are mostly referred to as "green-inhibitors."

The attention drawn toward towards "green inhibitors" –originally, naturally occurring substances– has been extended to pharmaceuticals. This may be due to the knowledge that pharmaceuticals posses molecular structures with heteroatoms like S, P, N and π-bonds that are characteristics of established organic corrosion inhibitors[6,7]. This development may have been driven by the merits of pharmaceuticals over natural plant extracts whose complex compositions have to contain active corrosion inhibitors constituent(s) identified and isolated at additional expense before commercialization, whereas pharmaceutical chemicals are readily available with known composition thereby shortening the

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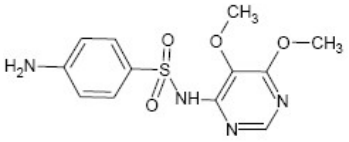
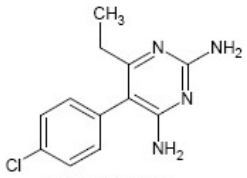
time that would be required for practical application studies[8].

A survey of available literature has shown a wide spectrum of drugs exhibiting corrosion inhibitive effect on metals in acidic media; amongst these are sulpha drugs[9], antibacterials[10], antibiotic[5], etc. As part of our contribution to the growing interest of exploring cost-effective "green corrosion inhibitors", the present work describes a study of corrosion protection action of an antimalarial drug with trade name "Antimal" on mild steel in HCl solution using the weight loss technique. Antimal is an antimalarial drug consisting of two compounds, sulphadoxine and pyrimethamine each constituting 500mg and 25mg of the drug respectively. Therefore, the combined molecular weight of a tablet is 558.5g/mol and their structures are shown below:



Sulphadoxine



Pyrimethamine

EXPERIMENTAL

Thus far, various techniques have been employed to monitor corrosion of metals, *viz*: weight loss method, gasometric methods, thermometric methods, electrochemical methods, etc. The experimental model developed for this study was implemented using the weight loss technique. The weight loss method of monitoring corrosion rate is useful because of its simple application and reliability[11].

Materials

Commercially available grade of mild steel sheets (purity 98%) of 0.10cm in thickness used in this study were identified and obtained locally. The sheets were mechanically pressed cut into 3cm by 3cm coupons with small hole of about 5mm diameter near the upper edge to help hold them with glass hooks. The coupons were polished to remove unwanted adhering impurities using emery papers, degreased with acetone, washed in double distilled water and dried in a desiccator before use[12]. The concentrations of the hydrochloric acid were prepared by dilution method[13].

Inhibitor

The antimalaria drug used in this study was purchased locally as "Antimal' tablets. Each tablet contains 500mg of N′ (5, 6-dimethoxy-4-pyrimethanyl) sulphanilamide (sulphadoxine) and 25mg of 2, 4-diamino-5-(*p*-chlorophenyl)-6-ethylpyrimidine (pyrimethamine). With this combination, each tablet of the drug has molecular weight of 558.5g/mol. With these characteristics, the drug was suspected to possess a good inhibitive effect. The drug was used without further purification. The concentrations of the drug ranged from 3.78×10^{-3}M to 15.13×10^{-3}M.

Weight loss measurements

In the weight loss experiment, five plastic containers were labelled A to E, each containing 500ml of HCl solution. The first beaker was reserved as blank while each of the four remaining beakers contain the drugs at different concentrations all placed at room temperature (about 30°C). The metal coupons were immersed in the experimental solutions with the help of glass hooks and monitored daily (after 24hours). The weights of the specimens were noted before immersion. After every immersion time of 24hours, the specimens were removed, polish with emery papers, washed in double distilled water, degreased with acetone, dried in warm air and re-weighed. From the initial and final weights of the specimens, the loss of weights was calculated and the corrosion rate (in mpy^{-1} –millimetre penetration per year) was computed from the equation below[14]:

$$Corrosion\ rate, CR = \frac{534W}{DAt} \quad (1)$$

where W is the weight loss (g), D is the density of the specimen (7.85g/cm^3), A is the surface area of specimen (cm^3) and t is the immersion time (days).

The efficiency of the inhibitor was computed using the equation below[15]:

$$Inhibition\ efficiency, \%IE = \frac{W_o - W_1}{W_o} \times 100 \quad (2)$$

where W_o is the weight loss without inhibitor and W_1 is the weight loss with inhibitor.

RESULTS AND DISCUSSION

Weight loss measurements

The effect of an antimalarial drug, "Antimal"

(sulphadoxine + pyrimethamine), was studied as a corrosion inhibitor for mild steel in 0.1M solution of HCl at room temperature using the weight loss technique. The results obtained show that the inhibitor inhibited acid corrosion of mild steel efficiently. The result on TABLE 1 shows that the inhibition efficiency increased as the concentration of the inhibitor increased. This indicates that more of the inhibitor molecules were needed to sufficiently cover a wider surface area thereby preventing attack by aggressive ions[16]. There is a remarkable inhibitive effect at 15.13×10^{-3}M of the inhibitor where the inhibition efficiencies are maintained high above 60% throughout the six days of studies without being replenished.

TABLE 1: Values of inhibition efficiencies for the corrosion inhibition of mild steel in 0.1M HCl by "Antimal" (sulphadoxine + pyrimethamine)

Inhibitor Concentration ($\times10^{-3}$M)	Inhibition Efficiency (%)					
	1day	2days	3days	4days	5days	6days
3.78	67.57	63.64	56.52	50.33	50.94	45.45
7.56	70.27	65.45	57.97	53.49	51.89	47.93
11.35	78.38	74.55	68.66	66.28	63.21	58.68
15.13	83.78	76.36	70.15	67.44	66.98	63.63

The corrosion behaviour of mild steel in a corrodent is symbolized by the degree to which it dissolves and this is measured as corrosion rate. Corrosion rate, is thus an important measurement in corrosion studies[14]. With the help of equation 1, we have computed the corrosion rate of mild steel in 0.1M solution of HCl with and without the inhibitor as shown in TABLE 2.

As observed from TABLE 2 the inhibitor (which constitute two compounds) was able to significantly and progressively reduce the corrosion rate through the control solution to the one with the highest concentration of the inhibitor. Also, a cursory observation of Figure 1, which shows the variation of weight loss over time, indicates that the extent to which the inhibitor molecules have been able to reduce the corrosiveness of the acid medium. However, as it is seen, the weight loss persistently increased with increase in time across all the concentrations of the inhibitor.

Kinetics of corrosion inhibition

Chemical kinetic treatment of the data was necessary in order to obtain information about the order of the reaction. If the concentration of the corroding metallic material is estimated in terms of weight loss per volume (g/l) of the corrodent, then, the kinetics of the system can be proposed. Following the work of Sharma and Sharma[17], we assume that if *a* g/l is the initial concentration of the mild steel (MS) and after time, *t*, *x* g/l of MS had decomposed into corrosion products. Therefore, the remaining concentration of MS at time, $t=(a–x)$g/l. If a plot of $\log(a-x)$ against *t* gives a straight line graph, then the reaction can be said to be a first order reaction. It was based on this that we calculated for the remaining concentration of MS and obtained a graph shown in Figure 3. The shape of the graph in Figure 3 shows that the system under consideration followed a first order kinetics.

TABLE 2 : Values of corrosion rate for the corrosion inhibition of mild steel in 0.1M HCl by "Antimal" (sulphadoxine + pyrimethamine)

Time (days)	Corrosion Rate, CR (mp/y)				
	Blank	3.78×10^{-3}M	7.5×10^{-3}M	11.40×10^{-3}M	15.13×10^{-3}M
1	0.1165	0.0378	0.0346	0.0346	0.0189
2	0.0866	0.0315	0.0299	0.0221	0.0205
3	0.0724	0.0315	0.0315	0.0221	0.0210
4	0.0677	0.0323	0.0323	0.0228	0.0220
5	0.0668	0.0323	0.0334	0.0246	0.0221
6	0.0635	0.0346	0.0346	0.0262	0.0231

Correlation of corrosion rate with time

The variation of corrosion rate was computed and presented as Figure 3. It is observed that the corrosion rate of the blank progresses faster than that estimated for the inhibited system. The gradual decrease in the corrosion rate is probably due to the passivity acquired by the metal specimen as a result of covering of a thin film of the inhibitor on the metal-corrodent interface.

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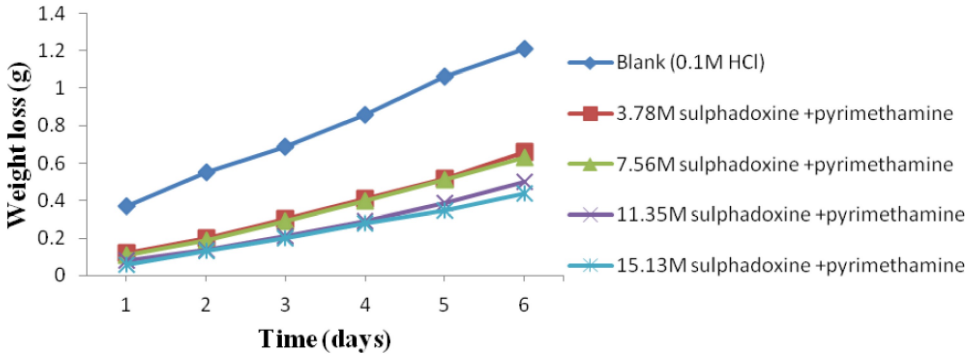

Figure 1 : Variation of weight loss with time for the corrosion of mild steel in 0.1M HCl and containing different inhibitor concentrations at 30°C

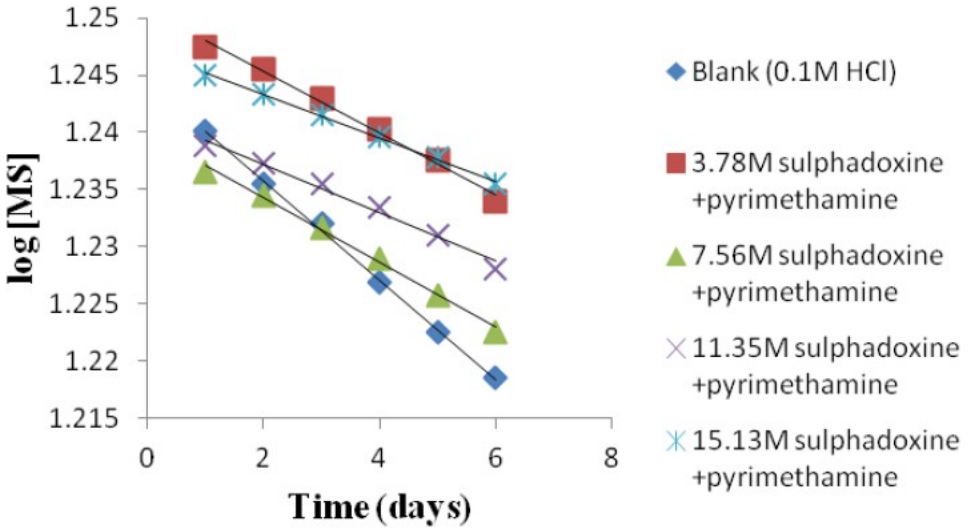

Figure 2 : Linear plots of log of concentration of mild steel against time

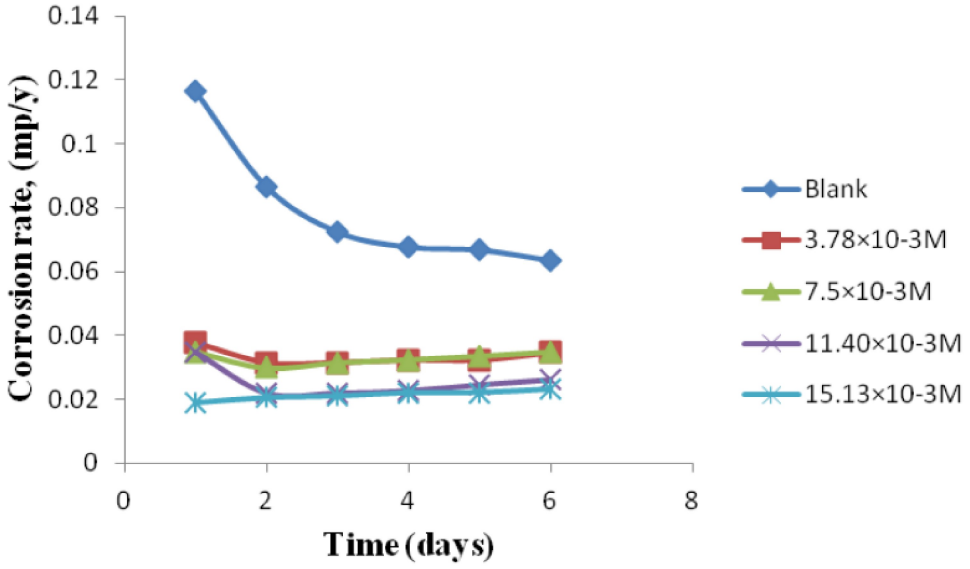

Figure 3 : Variation of corrosion rate (mp/y) with time in days for the corrosion of mild steel in 0.1M HCl with different concentration of the inhibitor

Mechanism of corrosion inhibition

The inhibition action of organic compounds as corrosion inhibitors may be related to the concept of molecular adsorption on the metal surface[18,19]. The

action of the inhibitor molecules may be due to the presence of N, S, O heteroatoms as well as the aromatic rings which contain π-electrons in their molecular structures. The collaborative action of the two molecular compounds leads to increase in the bulkiness of the inhibitor which in turn enhances the wider coverage on the metal surface. Furthermore, due to the presence of many heteroatoms (with lone pairs of electrons) as potential adsorption centres throughout the structure of the molecules, whatever orientation the molecules make towards the metal surface, it would result in coordination between the inhibitor-metal interfaces. This further enhances the degree of adsorption between the inhibitor molecules and the metal surfaces.

CONCLUSION

Sulphadoxine and pyrimethamine combination as "Antimal" significantly reduced the corrosion rate of mild steel in 0.1M solution of hydrochloric acid at all concentrations. The corrosiveness of the corrodent medium reduced as noted in the computed corrosion rates due to the action of the inhibitor molecules in protecting the metal surface. The behaviour of the inhibitors indicates the action of their molecular structure. It should be noted that, the synergistic study of the drug is preliminary as the authors will in due course investigate the inhibition actions of the molecules that make up the "Antimal" drug individually.

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