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Effect of 5, 5-Diphenylhydantoin on Corrosion of Mild Steel in 1M. Hydrochloric Acid Solution

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Abstract: Corrosion is a very natural a phenomenon and a serious problem in the global world, converts a refined metal to a more chemically-stable form, such as its oxide, hydroxide, or sulfide. Most prominent corrosion inhibitors are organic compounds containing nitrogen, Sulphur, oxygen, and phosphorus in their functional groups. The mechanism of these compounds has been proposed to be the adsorption, by means of lone pairs of electrons, of the organic functional groups on the metal surfaces. Hydrochloric acid is the most difficult of the common acids to handle from the stand's points of corrosion and materials of construction. The acid is very corrosive to most of common metals and alloys. In the experiment we have analyse 7 different PPM solution reacting for 24 hours such as from 10-500 PPM resulting in which as corrosion inhibition increases with increase in PPM i.e having high amount of 5,5-diphenylhydantoin.

Keywords: corrosion, 5,5-diphenylhydantoin, hydrochloric acid, mild steel, inhibitor.

I. INTRODUCTION

A refined metal is transformed naturally by corrosion into a more stable chemical form, such as its oxide, hydroxide, or sulphide. It is the progressive deterioration of materials (often metals) due to their environment's chemical and/or electrochemical reactions. The degradation of a material as a result of interaction with its environment is known as corrosion. Corrosion has an impact on the materials' microstructure, mechanical characteristics, and outward appearance. For instance, corrosion is defined as the deterioration of paint and rubber due to sunshine or chemicals, fluxing of the steel-making furnace's liner, and the attack of one solid metal by another molten metal. India's iconic Delhi pillar, which was created around 2000 years ago, is practically brand-new, it is about 32 feet high & 2 feet in diameter, It has been exposed mostly to a rid condition.

Researchers from numerous industrial sectors have been interested in studies on the prevention of steel corrosion in acidic environments and the troublesome chemical processes that result. Steel frequently experiences corrosion, which has a negative impact on both its price and safety. Rust, or the corrosion of iron, can modify the mechanical and chemical characteristics of plants, vessels, pipes, and other processing equipment and result in structural damage. These impacts show that corrosion would result in significant expenses if a workable solution was not found through study and research. In many different sectors, especially those that use steel for chemical and petrochemical processes, preventing steel corrosion has been crucial. Numerous investigations have been made on efficient corrosion prevention strategies. In industrial procedures like pickling, cleaning, descaling, etc., acids are frequently utilised. Metal dissolution rates can be effectively decreased by inhibitors. Adsorption onto the metal surface, which is typically devoid of oxides, is the first stage in the action of inhibitors in an acidic solution. The inhibitor that has been absorbed then slows the cathodic or anodic electrochemical corrosion reaction. Because the mechanism may alter depending on the experimental circumstances, it is frequently impossible to pinpoint a single general mechanism for an inhibitor. The concentration, pH, kind of acid anion, and type of metal are only a few examples of the variables that may affect an inhibitor's inhibitory mechanism. The methods of action of inhibitors with the same functional group may also differ depending on a number of variables, such as how the molecular structure affects the functional group's electron density and the size of the molecule's aromatic and aliphatic protons. Because they are widely used in decreasing metallic waste during production and reducing the danger of material failure (and the ensuing unexpected shutdown of industrial processes that results in additional expenses), corrosion inhibitors are of significant practical value. To avoid metal deterioration and reduce acid usage, corrosion inhibitors are crucial. Most often used acid inhibitors are organic substances with nitrogen, sulphur, and oxygen atoms in them. The adsorption interactions between the inhibitors and the metal surface are typically responsible for the inhibitory effect that organic compounds exert on the dissolution of metallic species. In this study, a novel coumarin derivative, PMBH, was created, and spectroscopic methods were used to clarify and confirm its chemical structure.

Using various electrochemical experiments, the inhibitory effect of PMBH on the corrosion of mild steel in 1.0 M HCl was examined. Scanning electronic microscopy was used to conduct surface studies on the corroded surfaces (SEM).

Due to its widespread use in industry, mild steel corrodes when subjected to different industrial settings and circumstances. One of the most practical methods for protecting metals against corrosion, especially in acidic conditions, has been reported to be the application of inhibitors. The chemical structure of the inhibiting molecules has a significant impact on an inhibitor's ability to inhibit other molecules. Organic chemicals with functional groups comprising nitrogen, sulphur, oxygen, and phosphorus are the most well-known corrosion inhibitors. The adsorption of the organic functional groups onto the metal surfaces via lone pairs of electrons has been hypothesised as the mechanism for these compounds. The adsorption of these substances is influenced by the electrochemical potential at the metal/solution interface, temperature, the electronic structure of the inhibiting molecules, the steric factor, the aromaticity and electron density at the donor site, the presence of functional groups, the molecular area, and the molecular weight of the molecule. Due to their seven-membered structure, 1,5-benzodiazepines meet these requirements, acting as corrosion inhibitors with a high degree of unsaturation. According to a survey of the literature, while there are many reports on the production and pharmacological effects of benzodiazepine derivatives, relatively few studies have been done on how to employ them as corrosion inhibitors. The mechanism of corrosion inhibition is explained using Monte Carlo simulations and quantum chemistry computations. The current investigation's goal is to create benzodiazepine derivatives and assess how well they inhibit carbon steel corrosion in 1 M hydrochloric acid. Techniques like electrochemical impedance spectroscopy and potentiodynamic polarisation were used. To supplement the experimental findings, Monte Carlo simulations and quantum chemical calculations for the benzodiazepine derivative were carried out. This approach saves money and uses the least amount of inhibitor, preventing wastage²⁸. However, the majority of them are poisonous, expensive, and non-biodegradable²⁹⁻³⁶.

Many inorganic and organic chemicals have good corrosion inhibition action. Researchers have concentrated on the creation of heterocyclic aromatic organic chemicals utilised as effective corrosion inhibitors because to cost, health concerns, and environmental regulation restrictions³⁹. The majority of organic inhibitors are adsorbed onto metal surfaces, where they create a dense barrier coating. As excellent corrosion inhibitors, organic compounds with heteroatoms like nitrogen, sulphur, oxygen, and phosphorus as well as aromatic rings, double bonds, and triple bonds are particularly useful in sulfuric acid media.

Alkenes, alkynes, and compounds with aromatic rings' heteroatom, lone pair, and p-electrons content all affect an inhibitor's effectiveness, according to studies. It has been discovered that heterocyclic organic molecules containing nitrogen work better as corrosion inhibitors. Recent investigations have shown that the availability of electronegative atoms in the molecules and the quantity of aromatic systems both boost the inhibitory efficacy of organic compounds containing heterocyclic nitrogen⁴⁷. Investigating the effectiveness of corrosion inhibition and the function of functional groups with various aromatic systems is therefore important. The goal of the current effort is to create, characterise, and employ 5, 5-Diphenylhydantoin (DPH) as mild steel corrosion inhibitors in a 1M hydrochloric acid solution. Weight loss method was used to study the corrosion behaviour of mild steel in the presence of this inhibitor. The generated Langmuir adsorption map is linear. This shows that a thin, consistent layer of DPH inhibitor has been produced on the surface of mild steel.

Researchers from several industrial sectors have been interested in studies on preventing the corrosion of steel in acidic conditions and the troublesome chemical processes that result. Steel frequently experiences corrosion, which has a negative impact on both its price and safety. Rust, or the corrosion of iron, can modify the mechanical and chemical characteristics of plants, vessels, pipes, and other processing equipment and result in structural damage.

II. EXPERIMENTAL PREPARATION

Mild steel coupons with dimensions of 3 cm x 1 cm x 0.3 cm were cut from commercial-grade sheets that were readily available on the market and had a composition of (wt%) C: 0.16 percent, Si: 0.10 percent, Mn: 0.40 percent, P: 0.013 percent, S: 0.02 and remainder as iron. These coupons served as the substrate for weight loss and polarisation techniques. Mild steel coupons of 3 cm by 1 m by 0.3 cm were sheared for EIS experiments. The specimens' surfaces were polished sequentially with 1/0, 2/0, 3/0, and 4/0 grade emery paper. The surface was initially polished with emery paper of a lower quality, and then it was polished with emery paper of a higher grade in a direction opposite to the first. The coupons were then degreased by washing in acetone after being washed in soapy water and rinsed with double-distilled water. The remaining surface was covered with enamel lacquer, including the side edges, with the exception of a 1 cm² working area on one side and a small section at the tip for electrical contact on the other. Finally, desiccators were used to dry and store these coupons.

Double-distilled water was used to create the potent 1M solution of AR grade sulfuric acid that was purchased from Merck Chemicals. Without further purification, market-purchased inhibitors were utilised as-is. As corrosion inhibitors, experiments were made in a solution of 1M sulfuric acid at various concentrations between 10 ppm and 500 ppm. Mild steel coupons that were 3 cm x 1 cm x 0.3 cm in size were sheared, abraded, washed, and prepared according to the aforementioned processes for Electrochemical Impedance Spectroscopy (EIS) experiments. The chemicals obtained from Merck, Aldrich (India), and Loba Chemicals (India) were of AR grade and used in the experiment as-is without additional purification. The recently created inhibitors were created and purified in a lab. TLC constantly examined the reaction's pace of completion. The Fourier Transmission Infra-Red (FTIR) spectroscopic method was used to describe the chemicals at ANA Laboratories, an ISO 17025 accredited laboratory located at 15-17, M. K. Bros. Industrial Estate, Jarimary, Andheri (E), Mumbai.

Solution Development

In the current study, the corrosion behaviour of mild steel in a 1M sulfuric acid solution was explored, and the inhibition effectiveness of several inhibitors at concentrations (10-500ppm) was assessed. The AR grade (98%) sulfuric acid from Merck Chemicals was diluted with double-distilled water to create the potent 1M sulfuric solution.

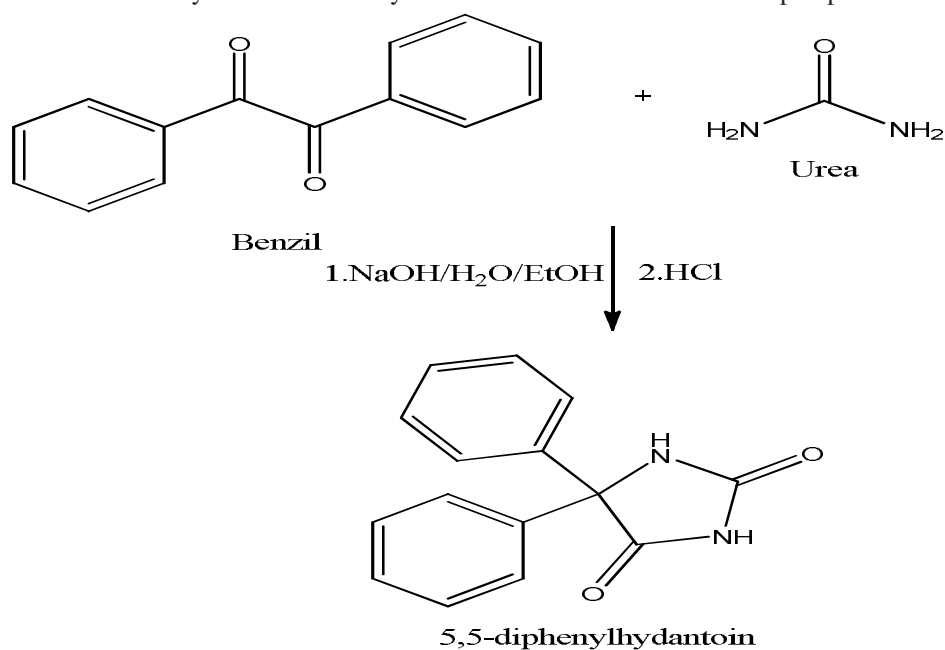
III. METHODS & SYNTHESIS

A. Approach

- 1) *Measurement of Weight Loss:* Test tubes containing 10 ml of test solutions with and without inhibitor solution were used for the triplicate measurements of weight loss in the range of 10-500 ppm. The coupons were immersed for 24 hours at 280°C, plus or minus 10°C, after which they were removed from the test tubes, rinsed with double-distilled water, cleaned with acetone, dried, and weighed. It was observed what the typical weight loss was.
- 2) *Synthesis of 5, 5-Diphenylhydantoin:* Aim-To Prepare 5,5-Diphenylhydantoin from Benzil and Urea

B. Procedure

- 1) In a 50 cm³ round bottom flask with a reflux condenser, combine 1 g of benzil, 0.56 g of urea, 2.9 cm³ of 30 percent aqueous NAOH solution, and 15 cm³ of ethyl alcohol.
- 2) On boiling of water bath, reflux the reaction mixture for about two hours.
- 3) After cooling, add 25 cm³ of distilled water to a 100 cm³ beaker, add the reaction mixture, and stir continuously for about five minutes.
- 4) To get rid of the insoluble by-product, filter it at the suction pump.
- 5) To precipitate the result and chill it, acidify the filtrate with concentrated HCL.
- 6) Dry the product once it has been crystallised from ethyl alcohol and filtered at the suction pump.



IV. RESULT & DISCUSSION

A. Finding and Analysis

How to Measure Weight Loss

Inhibition efficiency (IE percent), determined using the formula below, is displayed in Table-4.1 along with weight loss data for mild steel obtained with and without inhibitor.

$$IE \% = \frac{W_0 - W_i}{W_0} \times 100 \quad (1)$$

Where W_i and W_0 are the weights of mild steel in the presence and absence of inhibitor, respectively, IE percent is calculated as $(W_0 - W_i)/W_0 \times 100$. The outcome demonstrates that the effectiveness of the inhibition rises with inhibitor concentration. Nevertheless, a 300-ppm solution of DPH exhibits an anomaly of lower inhibition efficiency as compared to the typical tendency of higher efficiencies with increasing inhibitor concentration. Table 4.2 displays the inhibitors' adsorption properties.

Adsorption Isotherm 4.2

The adsorption isotherm can offer the fundamental details on how the inhibitor interacts with the metal surface. Different isotherms are investigated to evaluate the adsorption mode, but the Langmuir adsorption isotherm amazingly well fits the corrosion inhibition data provided by the weight loss method. The following equation can be used to determine the percentage of surface covered (%) per cm^2 area:

$$\theta = \frac{IE \%}{100} \quad (2)$$

where IE represents inhibitory effectiveness. A straight line with a slope of almost one is created for the inhibitor by graphing the graph of $\log C$ against $\log(1-\theta)$, as shown in Figure 4.2.1 as follows.

Table 4.1: Weight loss data of mild steel without and with different concentrations of DPH in 1M Hydrochloric acid solution.

Inhibitor	Conc. (ppm)	Weight Loss (mg)/24 hrs.	Inhibition Efficiency (IE) %
Control (i.e., 1M. Hydrochloric acid Solution)	-	0.367	-
5, 5-Diphenylhydantoin	10	0.073	80.10
	50	0.11	70.02
	100	0.044	88.01
	200	0.026	92.91
	300	0.132	64.03
	400	0.093	74.65
	500	0.009	97.54

Table 4.2: Adsorption isotherm data for mild steel without and with different concentrations of DPH in 1M Hydrochloric Acid solution.

Inhibitor	Conc. (C)	LogC	θ	(1- θ)	$\theta/(1-\theta)$	Log $\theta/(1-\theta)$
5, 5-Diphenylhydantoin						
	0.000010	-5.0000	0.8010	0.1990	4.0251	0.6047
	0.000050	-4.3010	0.7002	0.2998	2.3355	0.3682
	0.000100	-4.0000	0.8801	0.1199	7.3402	0.8657
	0.000200	-3.6989	0.9291	0.0709	13.1043	1.1174
	0.000300	-3.5228	0.6403	0.3597	1.7800	0.2504
	0.000400	-3.3979	0.7465	0.2535	2.9447	0.4690
	0.000500	-3.3010	0.9754	0.0246	39.6504	1.5982

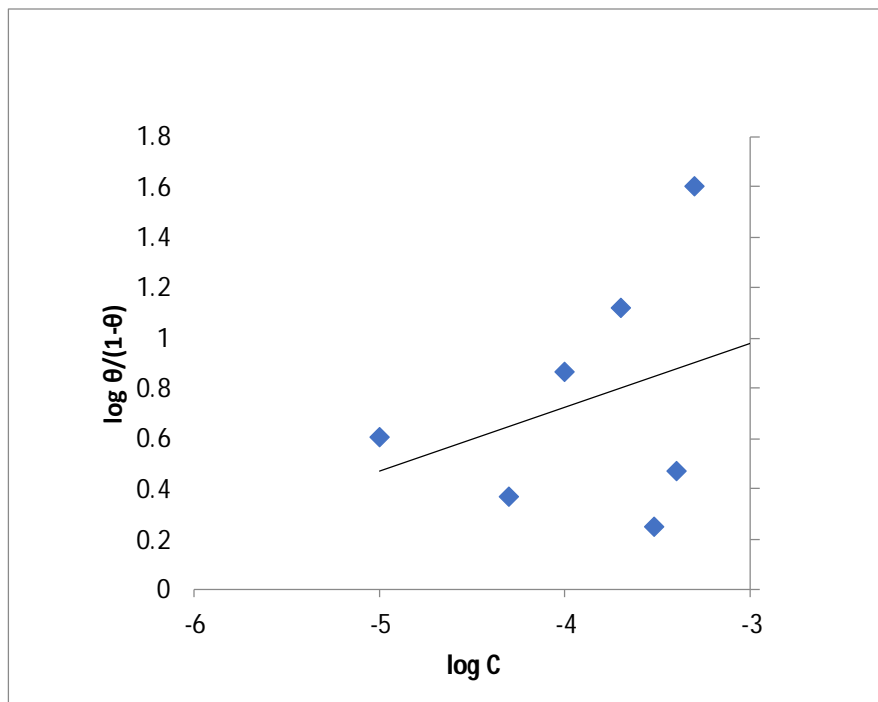


Figure: 4.2.1.

The Langmuir adsorption isotherm often fit corrosion inhibition data remarkably well. Plot of log C against log $\theta/(1-\theta)$ gave straight lines with the slope nearly one (as shown in Figure 4.2.1). This indicated the adsorption of these compounds on the mild steel surface obeys the Langmuir adsorption isotherm phenomenon. Adsorption parameters of inhibitors are given in Table 4.21.

V. MECHANISM

A weight loss technique has been used to study the effects of the corrosion inhibitor 5, 5-Diphenylhydantoin (DPH) on mild steel. Physisorption and chemisorption are two methods that can be used to control corrosion. The electrostatic force of attraction between protonated cations (DPH cationic molecules) in the acidic solution and the negatively charged iron surface caused by the chloride layer is what causes chemisorption. From experimental data obtained by above technique revealed that inhibition efficiency of DPH is maximum (98%) in 500 ppm solution by the formation of surface film with $\text{Fe}(\text{OH})_2$ and inhibitor-Fe mixed complex. Regardless, 300 ppm inhibitor solution shows anomalous behaviour of less efficiency than expected. At 300 ppm concentration, the solution may become more acidic due to the de-protonation of inhibitor molecules. At this concentration, all relatively large pores and cracks of the film are accessible to be filled up with inhibitor-Fe complex.

This complex might be formed due to the interaction between the dissolved irons with the inhibitor anion in the solution. Nevertheless, there are still numerous tiny film pores that can be penetrated by corrosive species but not by bigger inhibitor molecules. They can still act as active corrosion sites. Meanwhile, due to the acidification of the solution, the surface film becomes thinner. Iron will dissolve faster via the pores of this thinner coating. As a result, at 300 ppm of inhibitor solution, corrosion rate increases and inhibition efficiency declines. The rate of inhibition begins to increase again at greater concentrations, and at 500 ppm solution, because of a second acidification, formerly small pores become wider and are sealed by stable inhibitor-Fe complex molecules, which reduces mild steel corrosion.

VI. CONCLUSION

- 1) In a media containing 1M hydrochloric acid, DPH can effectively inhibit the corrosion of mild steel.
- 2) The inhibition efficiency increases with an increase in DPH concentration up to a solution concentration of 200 ppm, after which it increase in inhibitor concentration to 300 ppm. DPH performs best, with an inhibition efficacy of roughly 98 percent, at 500 ppm inhibitory concentration.
- 3) DPF chelates with Fe to form their complexes, which precipitate and mix with the $\text{Fe}(\text{OH})_2$ surface film to create a dense, protective surface coating that prevents mild steel from corroding.

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