



## CORROSION INHIBITION OF MILD STEEL IN 0.1M HYDROCHLORIC ACID MEDIA BY CHLOROQUINE DIPHOSPHATE

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### ABSTRACT

The results of trials on Chloroquine diphosphate as eco-friendly corrosion inhibitor for mild steel in 0.1M HCl solutions using weight loss technique over a duration of 49 days (1176 hours) are reported. The results obtained indicated that Chloroquine phosphate had promising inhibitive effect at all concentrations used in the study, on the corrosion of mild steel in 0.1M HCl with the observed inhibitive effect reducing with time. The Langmuir adsorption isotherm is proposed for Chloroquine diphosphate adsorption on mild steel in HCl solution.

**Keywords:** corrosion, mild steel, inhibitor, chloroquine diphosphate, HCl, quinoline ring, inhibition efficiency, eco-friendly.

### 1. INTRODUCTION

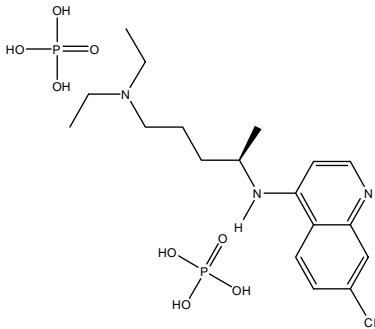
Corrosion inhibitors are of great practical importance, as they are extensively employed in reducing metallic waste in production, minimizing the risk of material failure and the consequent sudden shut-down in industrial processes that leads to added costs. [1] Most acid inhibitors are organic compounds containing nitrogen, oxygen, and sulphur, such as amines and heterocyclic compounds [2, 3]. The search for "green inhibitors" which has been focused on natural occurring substances [4-16], have expanded towards pharmaceuticals due to the observations that a lot of pharmaceuticals have molecular structures with heteroatoms such as S, P, N, and O, and  $\pi$ -bonds that are characteristic of established organic corrosion inhibitors. [17-25]. This trend is believed to be also propelled by the inherent advantages in pharmaceuticals, as natural plant extracts with their very complex compositions, need to have the particular inhibition active constituent identified and isolated at extra expense before commercialization, whereas pharmaceutical chemicals are readily available, have a known and usually mono composition which thus shortens the time and expense involved before practical use or commercialization. Different types of drugs have been reported in literature to exhibit inhibitive effect on a range of metals in acidic environments. These include sulphur drugs [17], antibacterials [26, 27], antifungals [28, 29], muscle relaxant [30], among others.

Chloroquine with IUPAC name N'-(7-chloroquinolin-4-yl)-N, N-diethyl-pentane-1, 4-diamine is a bitter, colourless, dimorphic powder soluble in water at pH 4.5, but less soluble at more neutral or alkaline pH. Chloroquine has a quinoline ring like that of quinine and a side chain identical to that of quinacrine (Figure-1), and had been the drug of choice for treatment of malaria [31]. This has the chemical formula  $C_{18}H_{26}ClN_3$  and molar mass

of 319.872g/mol and when associated with two phosphate moieties composed each of a central phosphorus atom coordinated by three OH groups in a single bond and an oxygen atom in a double bond, become Chloroquine diphosphate. Chloroquine is more readily available as Chloroquine diphosphate ( $C_{18}H_{26}ClN_3 \cdot 2H_3PO_4$ ) with IUPAC name 7-chloro-4-(4-diethylamino-1-methylbutylamino) quinoline diorthophosphate and molar mass of 515.86 g/mol. This is the form in which Chloroquine was used in this work. Chloroquine is a weak base and has been reported to be capable of accumulating to high concentrations on acidic surface [32].

With evidence of resistance by the malaria parasite to Chloroquine, there has been a lot of research on new potential applications for this cheap and widely available pharmaceutical compound [31, 33-36]. Whereas most of the research has been focused on alternative medical applications [31], the present effort is geared towards a possible usage of Chloroquine diphosphate as an active corrosion inhibitor for metallic materials.

Irvin and Irvin [37] reported that 4-aminoquinolines (Chloroquine diphosphate inclusive) are able to accept protons in aqueous acidic solutions in widely separated steps to become doubly protonated species. In dilute aqueous acidic solutions these are able to accept protons most probably through the ring nitrogen. In concentrated aqueous solutions of strong mineral acids a second proton is accepted by their aromatic nucleus most probably through reversible reaction with the 4-amino group. Chloroquine has been reported to exist a doubly protonated cation at physiological pH (i.e., pH  $\approx$  7.4) [37, 38]. The possibility of Chloroquine diphosphate and related compounds forming complexes with metals (Cobalt (II), Nickel (II) and Iron (III)) has been reported [39].



**Figure-1.** Structural representation of chloroquine diphosphate ( $C_{18}H_{26}ClN_3 \cdot 2H_3PO_4$ ).

## 2. MATERIALS AND METHODS

Test coupons of mild steel with 0.10% carbon content (Table-1) was cut from metal sheets to dimensions of (60 x 30 x 1.0) mm, with a 3mm diameter hole drilled towards one longitudinal end for suspension in the test media. The sharp edges arising from the cutting and drilling steps were smoothed with a hand file. Next the specimens were cleaned in acetone, dried, weighed with an analytical balance obtain the initial weights of the test coupons, labeled, and polypropylene strings attached for suspension in the media.

**Table-1.** Composition of the mild steel.

Element	C	S	P	Mn	Si	Cr	Ni	Mo	Fe
Content (%)	.10	.021	.022	.33	.011	.025	.032	.013	99.446

Concentrated HCl acid was diluted with distilled water to obtain the required quantities of 0.1M HCl. 1000ml of 0.1M solution was added to 0ml, 6ml, 12ml, 18ml, 24ml and 30ml of pharmaceutical grade Chloroquine phosphate syrup, respectively to obtain a concentration of Chloroquine base corresponding to 0mg/l, 60mg/l, 120mg/l, 180mg/l, 240mg/l and 300mg/l of Chloroquine base per litre of the dilute acids, respectively or molar concentrations of 0 M,  $1.16 \times 10^{-4}$  M,  $2.33 \times 10^{-4}$  M,  $3.49 \times 10^{-4}$  M,  $4.65 \times 10^{-4}$  M, and  $5.82 \times 10^{-4}$  M, respectively. The beakers were placed in a digitally controlled water bath maintained at 30°C, with a sample withdrawn from each beaker after every 7 days, washed in running distilled water with a rubber bung, washed in ethanol, then in acetone, dried and weighed to determine the final weight.

The weight loss per unit surface area in  $mg/cm^2$  was calculated and plotted against exposure time in hours (Figure-2) with the slopes corresponding to the corrosion rate in  $mg/cm^2/hr$ . Surface coverage ( $\theta$ ) and inhibition efficiency (%) are calculated from weight loss data after 1176 hours (49 days) of exposure using the formulas below:

$$\text{Inhibition Efficiency (IE) \%} = \frac{W_0 - W_x}{W_0} \times 100 \quad (1)$$

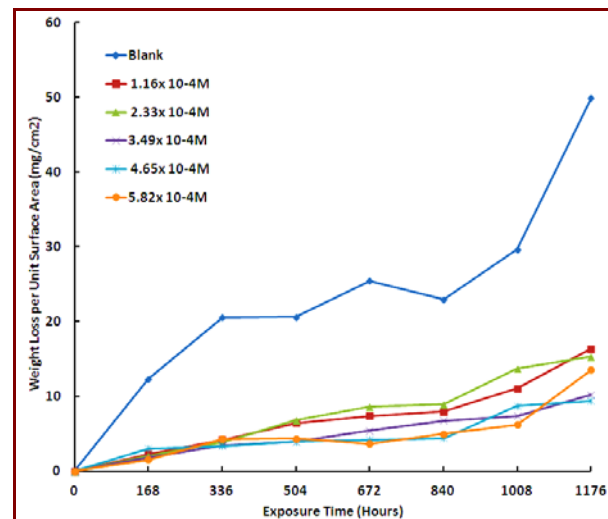
$$\theta = \frac{W_0 - W_x}{W_0} \quad (2)$$

Where

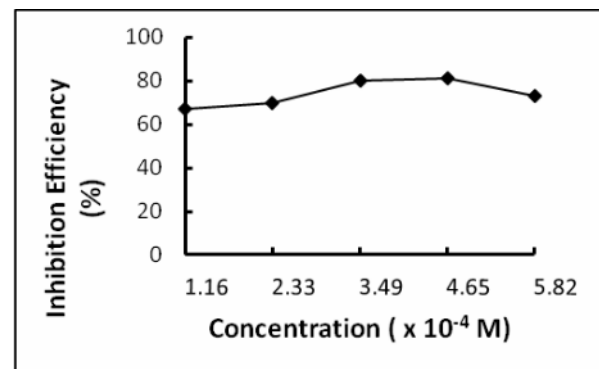
$W_0$  = weight loss in absence of inhibitor

$W_x$  = weight loss in the presence of inhibitor

The variation of inhibition efficiency with time after 1176 hours of exposure is illustrated in Figure-3.



**Figure-2.** Plot of weight loss per unit surface area ( $mg/cm^2$ ) Vs exposure time (hours) for different chloroquine phosphate concentrations in 0.1M HCl acid solution.



**Figure-3.** Variation of inhibition efficiency with concentration after 49 days (1176 hours).



### 3. RESULTS AND DISCUSSIONS

The results (Figure-2) show that Chloroquine Phosphate had significant inhibitive effect on the corrosion of mild steel in 0.1M HCl at all concentrations employed in the study. This is significant considering the duration of the test (in excess of 1000 hours). A gradual increase in inhibition efficiency with inhibitor concentration up to a concentration of  $4.65 \times 10^{-4}$  M per litre of acid was observed (Figure-3) after which a slight decrease in inhibition efficiency was observed.

Since organic inhibitors are known to function by adsorption, adsorption isotherms which relate the surface coverage ( $\theta$ ) to the inhibitor concentration ( $C$ ) are important for the understanding of the mechanism of (organic)/ adsorption inhibitors. From published literature the adsorption of most organic corrosion inhibitors seem to be best described by three adsorption isotherms namely, the Langmuir, Temkin, and Freundlich adsorption isotherms, out of the many adsorption isotherms.

The Langmuir adsorption isotherm which is hinged on three basic assumptions, (a) that the surface of the adsorbant (in this case the mild steel test coupon) is in contact with a solution containing an adsorbate that is strongly attracted to the surface (monolayer adsorption), (b) that the surface has a fixed number of possible adsorption sites where solute molecules can be adsorbed, which are equivalent, and (c) that the ability of a molecule to be adsorbed is independent of the occupation of neighbouring sites (no interactions between adsorbed molecules); can be expressed in the form below:

$$C/\theta = 1/K + C \quad (3)$$

Where

$C$  = concentration of the adsorbate in the bulk of the electrolyte

$\theta$  = degree of surface coverage

$K$  = equilibrium constant of the adsorption process.

A linear plot of  $C/\theta$  vs.  $C$  yielding a straight line of slope equal to unity indicates strict compliance to the Langmuir adsorption isotherm and its assumptions. Surface coverage data calculated from weight loss measurements was used to fit curves for different adsorption isotherms and the results indicate that the adsorption of Chloroquine diphosphate on mild steel at low pH is best described by the Langmuir adsorption isotherm. The  $R^2$  value, very close to unity (0.98) obtained in the linear plot of  $C/\theta$  vs.  $C$  (Figure-4), being indicative of a close adherence to Langmuir adsorption isotherm [40].

Based on this result it is inferred that Chloroquine diphosphate molecules adsorb to the surface of mild steel in dilute HCl by chemisorption. This position is supported by the observation (Figure-3.) that beyond a certain concentration ( $4.65 \times 10^{-4}$  M) of Chloroquine diphosphate, addition of more Chloroquine diphosphate did not lead to increase in inhibition efficiency, as once all the available adsorption sites are all occupied (in monolayer adsorption), adsorption becomes insensitive to adsorbate concentration in the bulk solution. It is believed that

higher inhibition efficiency in excess of the 80% obtained with  $4.65 \times 10^{-4}$  M of Chloroquine diphosphate per litre of 0.1M HCl acid might be possible with lower concentrations of the pure Chloroquine diphosphate powders, to be employed in planned follow-up studies. This is hinged on the thinking that the other components in the Chloroquine syrup may have probably been in competition with Chloroquine diphosphate molecules for adsorption sites on the mild steel, thus reducing surface coverage by Chloroquine diphosphate molecules and hence inhibition efficiency. Though the mechanism of adsorption to the metal surface is not yet established, it is believed that the quinoline ring is very probable to play a significant role due to the presence of  $\pi$ -electrons which might interact with the d-orbital of the metal.

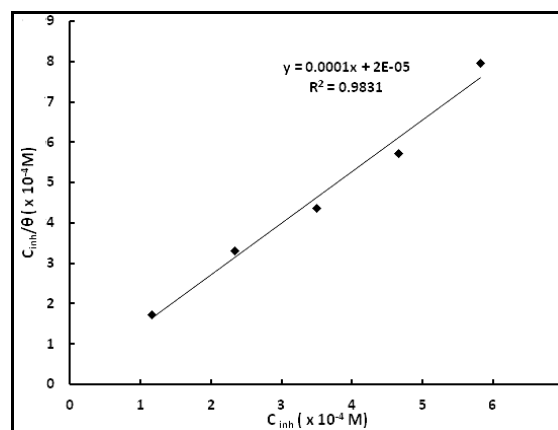


Figure-4. Langmuir adsorption plot for chloroquine diphosphate at 30°C.

### 4. CONCLUSIONS

From the results obtained and reported herein, it is concluded that Chloroquine phosphate (a cheap drug), which seems to be at the end of its service life as an anti-malarial due to reported drug resistance can be a viable candidate for an alternative use as an eco-friendly corrosion inhibitor for mild steel in dilute HCl acid solutions. The observed inhibition of mild steel corrosion in 0.1M HCl most probably occurs by a chemisorption process.

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