

Inhibition of Acid Corrosion of Mild Steel by Pyridoxal and Pyridoxol Hydrochlorides

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The action of pyridoxal hydrochloric (PXA) and pyridoxol hydrochloride (PXO) on the corrosion of mild steel in hydrochloric acid (HCl) solution was studied using the weight loss and gasometry methods. The percentage inhibition efficiencies increase with the concentration of the inhibitors and decrease with increase in temperature. The efficiencies increase in the order PXO > PXA. The kinetic treatment of the results gave first order kinetics. The relative inhibitive efficiency of these compounds has been explained on the basis of structure dependent – electron donor properties of the inhibitors.

Keywords: Mild steel, corrosion inhibitor, pyridoxol hydrochloride; pyridoxol

1. INTRODUCTION

The corrosion of metals remains a world-wide scientific problem as it affects the metallurgical, chemical and oil-industries. The increasing interest in the manufacture of hydrochloric acid has created the need for obtaining information on the corrosion resistance of mild steel to hydrochloric acid attack. Of particular importance also is the need to introduce certain organic compounds as inhibitors into the mild steel – corrodent system to prevent corrosion of the mild steel [1,2]. Mild steel corrosion in acid solution has been effectively controlled by the use of organic substances containing nitrogen, oxygen, or sulphur in the conjugated system as inhibitors [1-3].

The particular interest in the general field of organic inhibitors is the nature of the chemical bond at the metal surface and an explanation of why these substances often provide such excellent protection [4-6]. The objective of the present investigation is to explore the inhibitory properties of PXA and PXO on mild steel in hydrochloric acid solution.

2. EXPERIMENTAL

The material studied is a mild steel sheet 0.1cm in thickness provided by World Bank Engineering Workshop, University of Port Harcourt, Port Harcourt, Nigeria.. The chemical composition and preparation of mild steel coupons are described in detail in our previous report [7]. The additives (PXA and PXO) and HCl were of Analar grade and doubly distilled water was used for the preparation of all the solutions. Additives concentrations of 1.0×10^{-6} , 1.0×10^{-5} , 1.0×10^{-4} , 1.0×10^{-3} and 1.0×10^{-2} M were prepared in 2 M HCl solutions.

2.1 Weight loss determination

Rectangular specimens (5cm x 2cm x 0.1cm) of mild steel were used for the determination of the weight loss. The coupon were weighed and their initial weight recorded prior to immersion in 250ml beakers containing 200ml of 2 M HCl as corrodent and then with addition of different concentrations (1.0×10^{-6} , 1.0×10^{-5} , 1.0×10^{-4} , 1.0×10^{-3} and 1.0×10^{-2} M) of each of the additives to the corrodent at 30°C. The variation of weight loss was monitored at 24 h interval progressively for 168 h per coupon at 30°C. This experiment was repeated at 40 and 50°C. The procedure for weight loss determination was similar to that reported previously [7].

2.2 Hydrogen evolution measurements

For hydrogen evolution measurements, the test apparatus was set up as that reported previously [8]. A weighed mild steel coupon (2 x 2 x 0.1cm) was dropped into the reaction vessel containing 100ml of 2 M HCl at 30°C and the volume of hydrogen gas evolved was recorded as a function of time. The experiment was repeated in 2 M HCl containing different concentrations of the additives as in weight loss measurements.

3. RESULTS AND DISCUSSION

Figures 1 and 2 show the dependence of weight loss (g) of mild steel on the concentration of the additives (PXA and PXO) in the 2 M HCl solution at 30°C. Similar weight loss curves were obtained in 2 M HCl solution with various concentration of the additives at 40 and 50°C. The weight loss (g) of mild steel coupon in the acid decreases with increasing concentration of the additives in the acid, suggesting that the additives are corrosion inhibitor for mild steel in 2 M HCl solution.

The extent of the decrease in the weight loss (Figs. 1 and 2) was found to depend on the inhibitor and its concentration. The inhibition efficiency (%I) of each inhibitor on mild steel, at 30, 40 and 50°C, was calculated using the equation:

$$\%I = \frac{W_o - W_i}{W_o} \times 100 \quad (1)$$

where W_0 and W_i are the values of the weight loss (or volume of H_2 gas evolved) of mild steel without and with the inhibitor, respectively. The value of inhibition efficiency (%I) in the presence of different concentration of inhibitors used in 2 M HCl solution at 30, 40 and 50°C are listed in Table 1. In general, PXO inhibits corrosion processes more strongly than PXA (Table 1). It is clear from Table 1 that $PXO > PXA$ in their inhibitory action on mild steel surface. The inhibition efficiency increases with increasing concentration of the inhibitor and decreasing temperature of the HCl – inhibitor systems (Table 1) and reaches a maximum value which depends on the inhibitor. At the 1×10^{-2} M inhibitor concentration, values of 71.9% and 58.2% were obtained for PXO and PXA respectively.

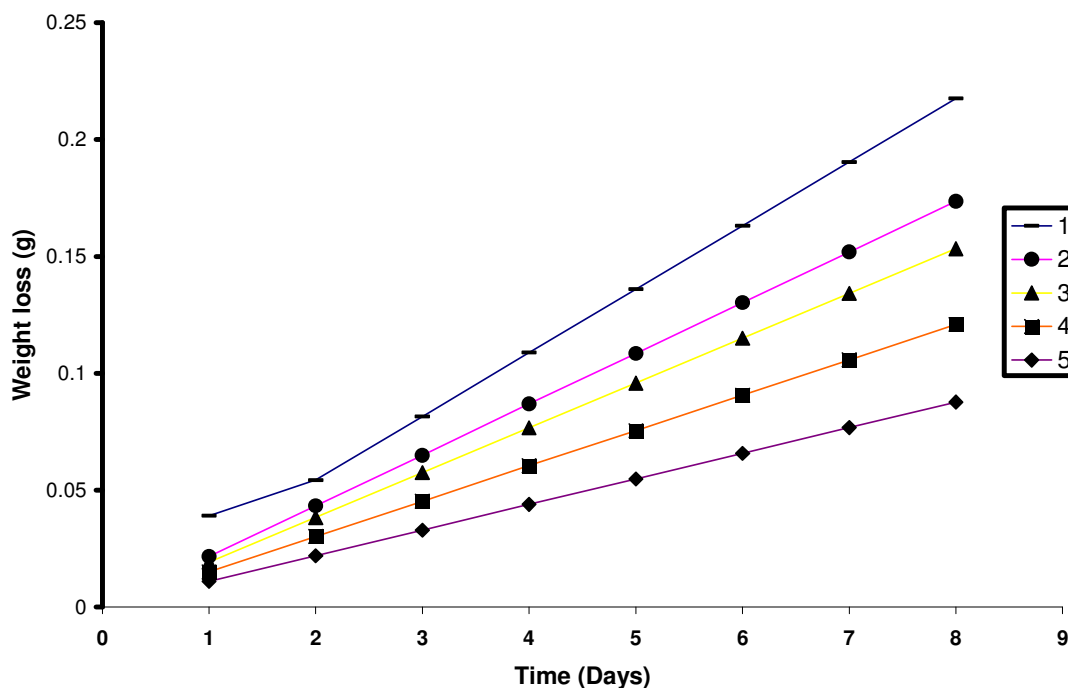


Figure 1. Variation of Weight Loss with time for mild steel coupons corrosion in 2 M HCl solution in the presence of PXA at 30°C: (1) 1×10^{-6} M; (2) 1×10^{-5} M; (3) 1×10^{-4} M; (4) 1×10^{-3} M; and (5) 1×10^{-3} M

The values of inhibition efficiency from hydrogen evolution measurements for the inhibitors are presented in Table 2. Table 2 also reveals that the order of the inhibitors to protect the mild steel surface in 2 M HCl solution is $PXO > PXA$. In comparison, the values of inhibition efficiency obtained from the hydrogen evolution measurements at 30°C are in agreement within the limit of experimental errors (± 10) with that of weight loss measurements.

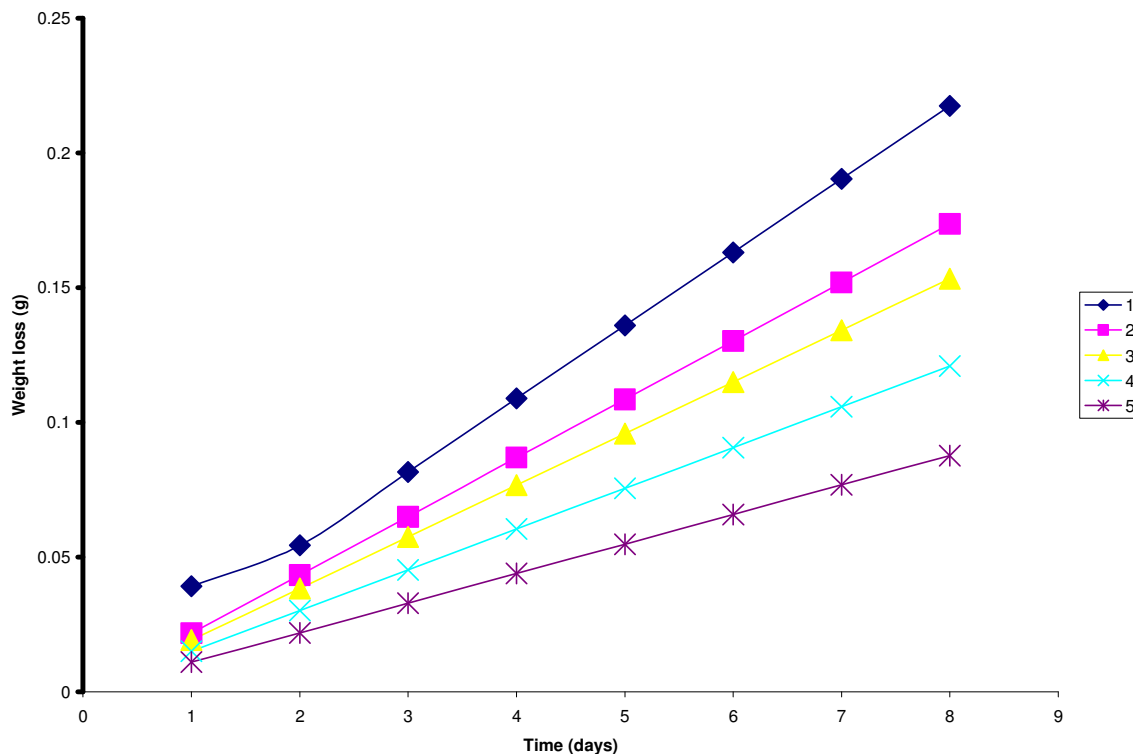


Figure 2. Variation of Weight Loss with time for mild steel coupons corrosion in 2 M HCl solution in the presence of PXO at 30°C: (1) 1 x 10⁻⁶M; (2) 1 x 10⁻⁵M; (3) 1 X 10⁻⁴M; (4) 1 x 10⁻³M; and (5) 1 x 10⁻³M

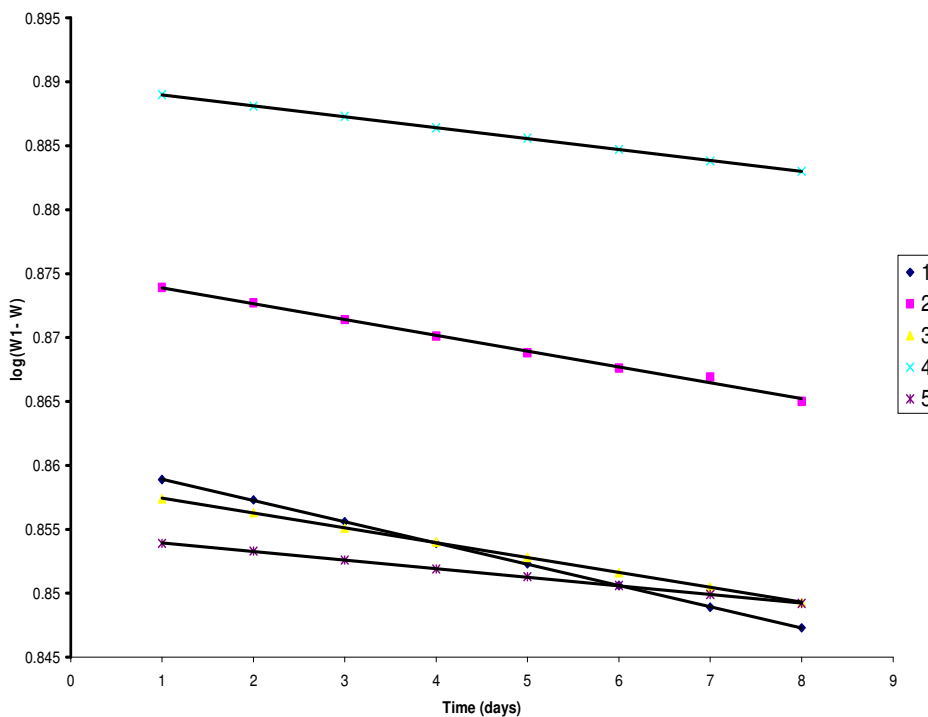
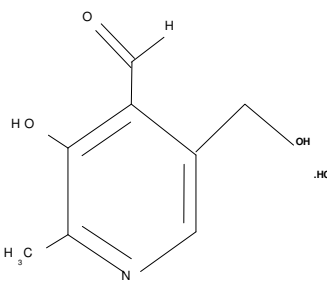
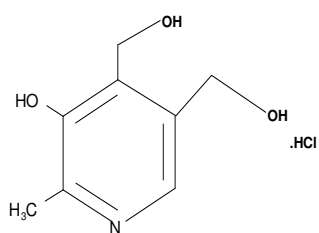


Figure 3. Variation of Log Wt for mild steel coupons corrosion in 2 M HCl solution in the presence of PXA at 30°C: (1) 1 x 10⁻⁶M; (2) 1 x 10⁻⁵M; (3) 1 X 10⁻⁴M; (4) 1 x 10⁻³M; and (5) 1 x 10⁻³M

3.1 Kinetics and mechanism of the corrosion inhibition of mild steel in HCl solution

The corrosion of mild steel in HCl solution is an heterogeneous one, comprising of anodic and cathodic reactions [9]. Based on this, the kinetic analyses of the data were considered necessary. In this study, W_i and ΔW represent the initial weight of mild steel coupon and weight loss of mild steel coupon at time t , respectively at constant temperature. When $\log(W_i - \Delta W)$ was plotted against time (days) for 2 M HCl solutions without and with PXO at 30°C (Fig. 3). A linear variation is observed which confirms a first order reaction kinetics with respect to mild steel in HCl solutions in the absence and presence of the inhibitors. Similar plot was observed for 2 M HCl solutions containing PXA. This observation was in agreement with earlier work [7,9] on the kinetics of acid corrosion of mild steel.

Table 1: Percentage inhibition in 2 M HCl solution containing inhibitors from weight loss measurements.

| Inhibitor | Concentration M | Inhibition efficiency % | | |
|--|----------------------|-------------------------|-------|-------|
| | | 30°C | 40°C | 50°C |
|  Pyridoxal hydrochloride | 0 | - | - | - |
| | 1.0×10^{-6} | 26.85 | 15.90 | 7.26 |
| | 1.0×10^{-5} | 38.46 | 17.19 | 12.82 |
| | 1.0×10^{-4} | 48.21 | 20.76 | 20.59 |
| | 1.0×10^{-3} | 51.02 | 28.46 | 25.26 |
| | 1.0×10^{-2} | 58.15 | 36.24 | 34.73 |
|  Pyridoxol hydrochloride | 0 | - | - | - |
| | 1.0×10^{-6} | 30.41 | 19.90 | 8.62 |
| | 1.0×10^{-5} | 44.49 | 20.33 | 14.10 |
| | 1.0×10^{-4} | 50.94 | 38.23 | 30.00 |
| | 1.0×10^{-3} | 61.34 | 43.83 | 40.01 |
| | 1.0×10^{-2} | 71.93 | 56.68 | 49.14 |

3.2 Comparison of the corrosion inhibition behaviour of pyridoxal and pyridoxol hydrochloride

The inhibitory action of PXA and PXO revealed that PXO exhibits a more effective corrosion inhibition tendency than PXA. The difference in the inhibitory properties of the inhibitors is closely related to the difference in the availability of electrons in the two molecules due to difference in their

molecular structures (Table 1) rather than different in molecular weights. The two structures are similar except that PXA carries the substituent $X = O$ while PXO carries $X = OH$. The carbonyl pull of the $X = O$ group of PXA pulls electrons away from the ring, and subsequently from the nitrogen which is the adsorption center. Whereas in PXO the lone pair of electrons on the oxygen bonded to the carbon is delocalised to the ring by a positive mesomeric effect. This makes electrons available to the ring and then to the nitrogen atom which is also the adsorption center for PXO. The nitrogen atom in PXO therefore undoubtedly has high electron density for adsorption on to the mild steel surface than PXA.

Table 2: Percentage inhibition in 2 M HCl solution containing inhibitors from hydrogen evolution measurements at 30°C.

| Concentration, M | Inhibition efficiency, % | |
|----------------------|--------------------------|-------------------------|
| | Pyridoxal hydrochloride | Pyridoxol hydrochloride |
| 1.0×10^{-6} | 22.20 | 25.00 |
| 1.0×10^{-5} | 33.00 | 37.50 |
| 1.0×10^{-4} | 44.31 | 50.00 |
| 1.0×10^{-3} | 56.10 | 62.66 |
| 1.0×10^{-2} | 66.70 | 75.12 |

4. CONCLUSION

The order of inhibition efficiency was pyridoxol hydrochloride - pyridoxal hydrochloride. The inhibition efficiency increases with increasing inhibitor concentration. A first order type of reaction is obtained from the kinetic treatment of the data. The difference in the inhibitory properties of the two inhibitors is closely related to the difference in the availability of electrons in the molecules of the inhibitors.

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