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ORGINAL ARTICLE

Comparative Studies on the Inhibitive Effect of Pyridoxal Hydrochloride, Pyridoxol Hydrochloride and 2-Benzoyl Pyridine on the Corrosion of Mild Steel in Hydrochloric Acid Medium.

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ABSTRACT
Weight loss and gasometric measurements have been used to study the inhibition of mild steel corrosion in hydrochloric acid solutions by three compounds; Pyridoxal hydrochloride (PXA), Pyridoxol hydrochloride (PXO) and 2-Benzoyl Pyridine (2BP) at 303K, 313K and 323K. The compounds inhibit the corrosion of mild steel in hydrochloric acid to a remarkable extent. 2-Benzoyl Pyridine (2BP) exhibited higher maximum inhibition efficiency than PXO and PXA at all the temperatures studied. Generally, inhibition was found to increase with increasing inhibitor concentration and decreasing temperature. A first – order type of mechanism has been deduced from the kinetic treatment of the results, and the process of inhibition was attributed to physiosorption. The difference in the inhibition behaviour of the three compounds is explained in terms of the difference in their molecular structures.
KEYWORDS: *Corrosion; Mild steel; Inhibition efficiency; Physiosorption; Kinetic treatment.*

INTRODUCTION

The corrosion of mild steel in hydrochloric acid is causing a lot of concern now than ever, due to the overwhelming use of mild steel in science and engineering [1]. It has been shown that organic compounds containing heteroatoms with high electronic density such as nitrogen, sulphur and oxygen, or those containing multiple bonds which are considered as adsorption centres, are effective acid corrosion inhibitors. The inhibitive action of these compounds is related to the presence of more than one atom with unshared electron pairs [2].

The aim of the present work was to investigate and compare the inhibitive effect of Pyridoxal hydrochloride (PXA), Pyridoxol hydrochloride (PXO) and 2-Benzoyl Pyridine (2BP) on the corrosion of mild steel in 2M HCl solution. The study was conducted using weight loss and gasometry.

The inhibition efficiencies, (%E) were calculated from the equation 1 below:

$$\%\,E = \frac{\Delta W_B - \Delta W_i}{\Delta W_B} \quad x\ \frac{100}{1} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

Where ΔW_B and ΔW_i are the weight loss (or hydrogen gas evolution) data of metal coupons in the absence and presence of the inhibitors respectively. This study is a continuation of our extensive studies on the efficiency of Pyridoxal hydrochloride and Pyridoxol hydrochloride as potential corrosion inhibitor for mild steel in hydrochloric acid solution [3].

MATERIALS AND METHODS

Material preparation

The sheets of mild steel obtained locally and of thickness 0.1cm, purity 98.76% were mechanically press-cut into 5cm X 2cm coupons in World Bank Engineering Workshop, University of Port Harcourt, and Port Harcourt, Nigeria. Material preparation is as reported in our former work [4].

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 303K. The variation of weight loss was monitored at 24 h interval progressively for 168 h per coupon at 303K. This experiment was repeated at 313K and 323K. The procedure for weight loss determination was similar to that reported previously [4].

Hydrogen evolution measurements

For hydrogen evolution measurements, the test apparatus was set up as that reported previously [5]. A weighed mild steel coupon (2 x 2 x 0.1cm) was dropped into the reaction vessel containing 100ml of 2 M HCl at 303K 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.

RESULTS AND DISCUSSION

Effect of corrodent concentration and temperature on mild steel corrosion.

The influence of corrodent concentration and temperature on mild steel corrosion has already been explained in our earlier works [3,4].

Similar observation and appropriate explanation for it was also given by earlier researchers [6-9].

Effect of additives on the corrosion of mild steel

Figs. 1 -3 reveal that the compounds 2BP, PXO and PXA actually inhibit the corrosion of mild steel in HCl solutions to a remarkable extent.

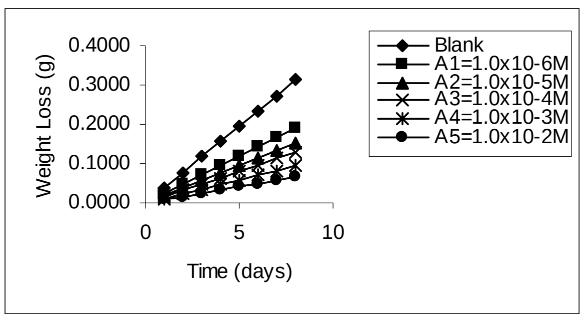


Fig. 1: Variation of weight loss (g) with time (days) for mild steel coupons in 2M HCl solutions containing 2-Benzoyl Pyridine at 303K.

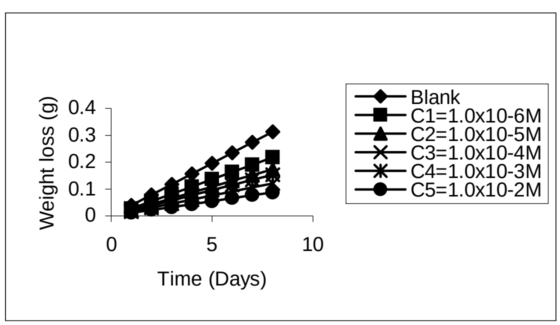


Fig. 2: Variation of weight loss (g) with time (days) for mild steel coupons in 2M HCl solution containing different concentrations of pyridoxol hydrochloride at 303K.

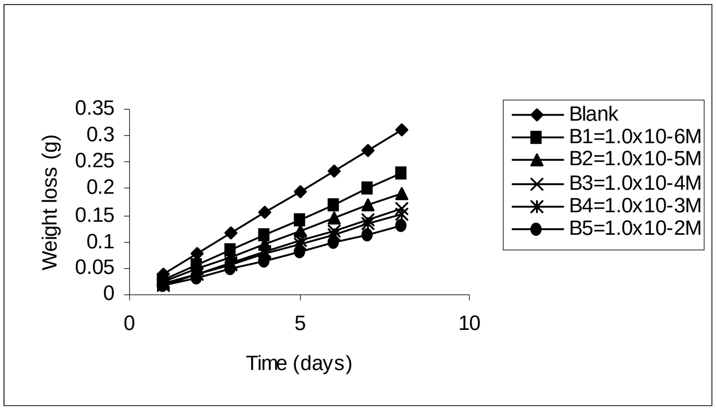


Fig. 3: **-** Variation of weight loss (g) with time (days) for mild steel coupons in 2M HCl solution containing pyridoxal hydrochloride at 303K.

The corrosion rate of the metal decreases with increase in the concentration of the additives.

Hydrogen evolution results via the gasometric assembly

The general decrease in hydrogen gas evolution with time as concentration of additives increased from 0.00001M to 0.01M (Figs. 4-6) confirm the inhibitory properties of the additives and also that the inhibition efficiency increases with concentration of the additives. Similar observation has been reported [7,10].

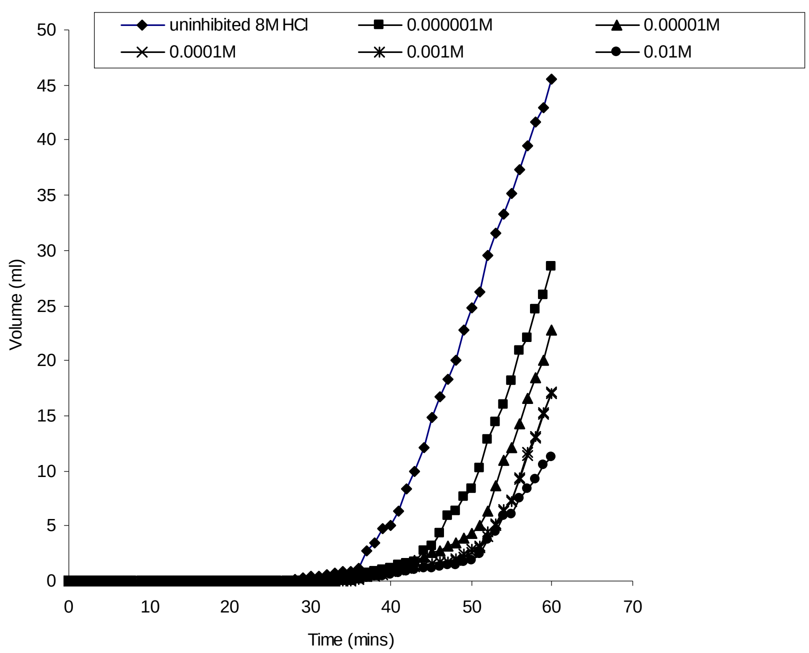


Fig. 4: Variation of Volume of Hydrogen gas evolved with time (minutes) for the inhibition of mild steel in 8M HCl solutions by 2-Benzoyl Pyridine at 303K

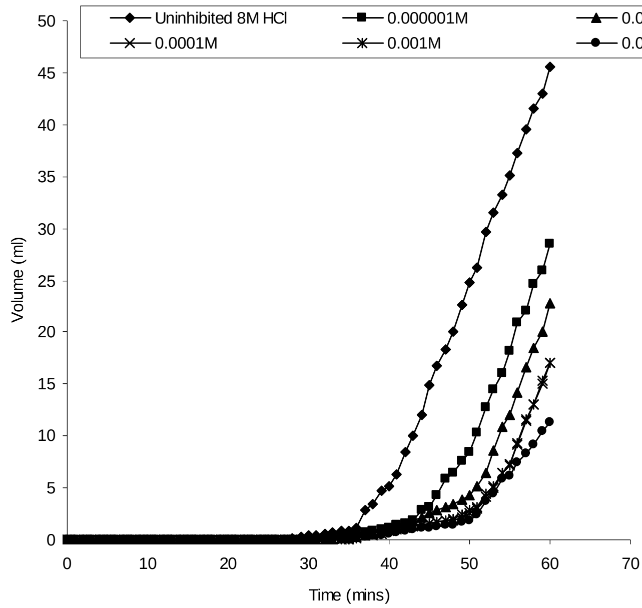


Fig. 5: Variation of Volume of Hydrogen gas evolved with time (minutes) for the inhibition of mild steel in 8M HCl solutions by Pyridoxol Hydrochloride at 303K

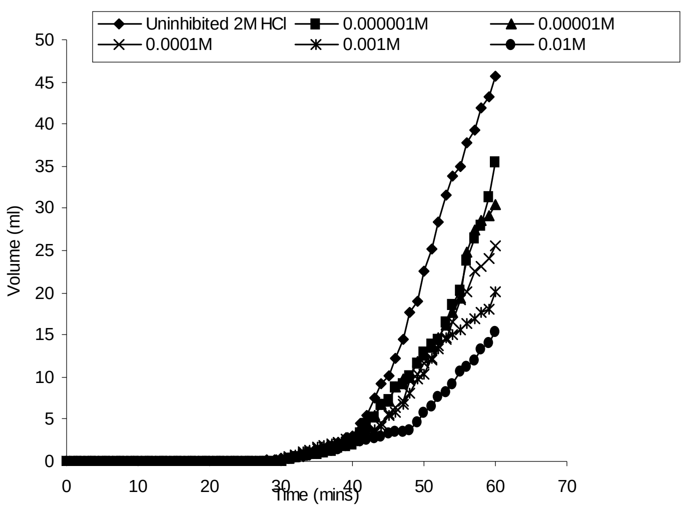


Fig. 6: Variation of Volume of Hydrogen gas evolved with time (minutes) for the inhibition of mild steel in 2M HCl solutions by Pyridoxal Hydrochloride at 303K.

Kinetic treatment of weight loss results

In this present study, the initial weight of mild steel coupon at time, t is designated Wi, the weight loss is ΔW and the weight change at time t, (Wi - ΔW). The plots of log (Wi - ΔW) against time (mins) at 303K and other temperatures studied, showed a linear variation which confirms a first order reaction kinetics with respect to the corrosion of mild steel in HCl solutions at 303K without inhibitor. The rate constant, half life and activation energies were calculated with first order equations (Tableb1-3).

Table 1: Kinetic data for mild steel in 2M HCl containing 2-Benzoyl Pyridine from weight loss measurement.

Inhibitor Concentration (M)	Rate Constant, K (day^{-1}) X 10^{-3}			Half-Life, $t_{1/2}$ (days) X 10^2			Activation Energy KJmo1^{-1}		Average Activation Energy KJmo1^{-1}	
	303K	313K	323K	303K	313K	323K	303K – 313K	313K-323K	303K-313K	313K-323K
1.0 X 10^{-6}	3.11	4.37	6.96	2.23	1.59	1.00	26.82	39.13		
1.0 X 10^{-5}	2.54	4.31	6.30	2.73	1.61	1.10	41.70	31.91		
1.0 X 10^{-4}	2.09	3.54	5.75	3.32	1.96	1.21	41.56	40.78	44.08	36.85
1.0 X 10^{-3}	1.55	3.03	4.62	4.47	2.29	1.50	52.86	35.46		
1.0 X 10^{-2}	1.10	2.28	3.54	6.30	3.04	1.96	57.48	36.99		

Table 2: The kinetic data for Mild steel in 2M HCl solution containing Pyridoxol hydrochloride at different temperatures.

Inhibitor Concentration (M)	Rate Constant, K (day^{-1}) X 10^{-3}			Half-Life, $t_{1/2}$ (days) X 10^2			Activation Energy KJmo1^{-1}		Average Activation Energy KJmo1^{-1}	
	303K	313K	323K	303K	313K	323K	303K – 313K	313K-323K	303K-313K	313K-323K
1.0 X 10^{-6}	3.78	6.09	8.41	1.83	1.14	0.82	37.61	27.15		
1.0 X 10^{-5}	2.91	5.81	7.83	2.38	1.19	0.89	54.53	25.08		
1.0 X 10^{-4}	2.67	4.44	5.85	2.60	1.56	1.18	40.11	23.19	50.04	23.89
1.0 X 10^{-3}	1.96	4.17	5.24	3.54	1.66	1.32	59.54	19.20		
1.0 X 10^{-2}	1.54	3.23	4.34	4.50	2.15	1.60	58.41	24.83		

Table 3: The kinetic data for Mild steel in 2M HCl solution containing Pyridoxal hydrochloride at different temperatures.

Inhibitor Concentration (M)	Rate Constant, K (day^{-1}) X 10^{-3}			Half-Life, $t_{1/2}$ (days) X 10^2			Activation Energy Kjmo1^{-1}		Average Activation Energy KJm01^{-1}	
	303K	313K	323K	303K	313K	323K	303K – 313K	313K-323K	303K-313K	313K-323K
1.0 X 10^{-6}	3.71	5.80	7.69	1.87	1.19	0.90	35.24	23.76		
1.0 X 10^{-5}	3.50	5.71	7.24	1.98	1.21	0.96	38.60	19.96		
1.0 X 10^{-4}	2.66	5.44	7.18	2.61	1.27	0.97	56.42	23.33	49.70	21.90
1.0 X 10^{-3}	2.50	5.24	7.56	2.77	1.32	1.06	58.36	18.89		
1.0 X 10^{-2}	2.12	4.53	6.00	3.27	1.53	1.16	59.88	23.63		

There is a general decrease in the rate constants from 303K - 323K with increasing concentrations of the additives (Tabs. 1-3). The increase in half-life ($t_{1/2}$) shown when the additives are present further supports the inhibition of mild steel in 2M HCl by the additives. The increase in half life indicates more protection of the metals by the additives. The average activation energies of 44.08 kJ mol^{-1}, 50.04 kJmol^{-1} and 49.70 kJmol^{-1} were obtained in the HCl – 2BP, HCl – PXO and HCl – PXA systems respectively at 303 - 313K. On the basis of these experimentally determined activation energy values, the additives are physically adsorbed on the coupons. Therefore, it is probable that a multilayer protective coverage on the entire mild steel surface was obtained.

Comparison of the corrosion inhibition behaviour of the inhibitors studied.

Table 4: The Inhibition Efficiency (%) for Mild steel corrosion in 2M HCl solution by 2-Benzoyl Pyridine, Pyridoxol hydrochloride and Pyridoxal hydrochloride at different temperatures.

Inhibitor Concentration (M)	**Inhibition Efficiency (%)**								
	2-Benzoyl Pyridine			Pyridoxol hydrochloride			Pyridoxal hydrochloride		
	303K	313K	323K	303K	313K	323K	303K	313K	323K
1.0 X 10^{-6}	38.82	30.60	20.22	30.41	19.90	7.26	26.85	15.90	8.62
1.0 X 10^{-5}	51.27	35.63	28.58	44.49	20.33	12.82	38.46	17.19	14.10
1.0 X 10^{-4}	58.95	48.22	36.93	50.94	38.23	30.08	48.21	20.76	20.59
1.0 X 10^{-3}	69.77	55.33	45.15	61.34	43.83	40.01	51.02	28.46	25.26
1.0 X 10^{-2}	89.41	67.55	58.13	84.77	56.62	49.14	72.86	36.24	34.73

The additives are found to be more effective at 303K (lower temperature) than 313K and 323K (higher temperatures), signifying that the compounds are physically adsorbed on the mild steel coupons.

The inhibitive effect of the inhibitors may be explained by considering the adsorption of the molecules through the heterocyclic nitrogen of the pyridine, available electron rich oxygen and complex formation (surface chelation) on the corroding metal surface. It is evident that the inhibition efficiency of 2BP, PXO and 2BP depends mainly on the molecular size of the compounds, the charge density on the adsorption sites, electron clouds, mode of interaction with the metal surface and formation of metallic complexes. Adsorption is expected to take place primarily through a functional groups of essentially C_6H_5N, OH and C=O and would depend on its charge density. Considering the structures of the compounds (figs.7-9), PXA, PXO and 2BP are polar molecules having a heterocyclic electron-rich nitrogen atom embedded in a benzene ring with a permanent negative charge.

On this basis, the adsorption of these compounds molecules may be through the nitrogen atom centers. For figure 9, there are two adsorption centers, the heterocyclic nitrogen atom, and the carbonyl oxygen atom that is also electron-rich having a permanent negative charge. Electrons are pulled from the benzene ring on the oxygen atom of the benzoyl group giving it higher electron density than others. Thus, 2-Benzoyl Pyridine is the most effective inhibitor with a maximum efficiency of 89.41% than PXO with a maximum efficiency of 84.77% and then PXA with 72.86%.

2BP could also been inhibiting best due to the presence of the two benzoyl groups which increase the molecular size of 2BP leading to a larger surface coverage. The effectiveness of 2BP also appears to depend on the high charged density on the adsorption N and O – sites. This may be due to the availability of the Π-electron clouds from the two benzene rings contained in the molecule (fig. 9). However, PXO (fig. 8) with almost the same molecule size with PXA (fig. 7), exhibits higher inhibition efficiency than PXA. The difference in inhibition efficiency of PXO and PXA could be explained in terms of the availability of electrons on the N – adsorption sites (since this is the only adsorption site they have). The carbonyl group of the aldehyde PXA pulls electrons away from the ring to the O –atom which is in para- position to the N –adsorption sites. Thus, reducing the electron clouds available on the nitrogen of PXA and giving it the lowest inhibition efficiency.

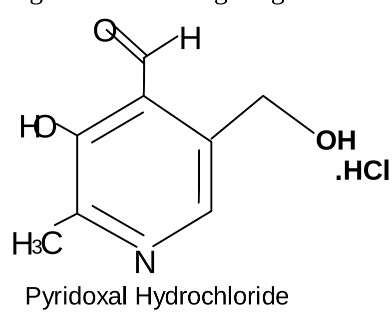


Fig.7: - Structure of Pyridoxal hydrochloride

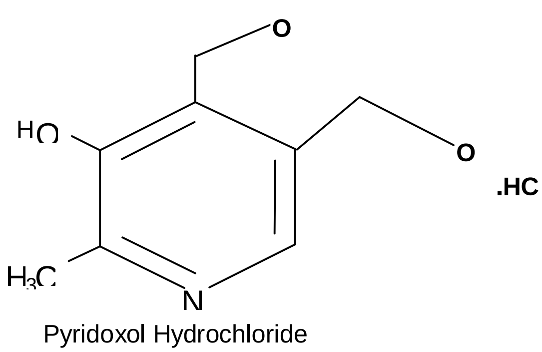
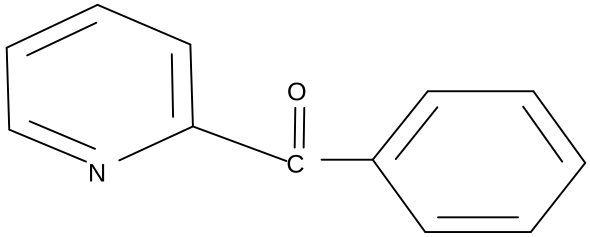


Fig. 8: - Structure of Pyridoxol hydrochloride



2- Benzoyl Pyridine

Fig. 9. Stucture of 2-Benzoyl Pyridine

CONCLUSION

The present study shows that 2BP, PXO and PXA inhibit the corrosion of mild steel in 2M hydrochloric solution to a remarkable degree, with the former being a better inhibitor than the other two. On the basis of activation energy and the experimentally observed increase in inhibition at low temperatures, a physiosorption process is proposed for the inhibitor action of the three compounds.

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