JCSE The Journal of Corrosion Science and Engineering

ISSN 1466-8858 Volume 7 Preprint 21 31 January 2005

INHIBITION OF THE CORROSION OF ALUMINIUM IN HYDROCHLORIC ACID SOLUTIONS BY PYRIDOXAL HYDROCHLORIDE.

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Abstract

The Inhibition of the corrosion of aluminum in hydrochloric acid solutions by pyridoxal hydrochloride has been studied using using weight loss and hydrogen gas evolution technique. Inhibition was found to increase with increasing inhibitor concentration and decreasing temperature. A first order mechanism has been deduced from the kinetic treatment of the weight loss results and the process of inhibition was attributed to physiosorption. The results obtained show that pyridoxal hydrochloride could serve as an effective inhibitor of the corrosion of aluminum in hydrochloric acid media.

Keywords: Corrosion inhibition; pyridoxal hydrochloride; kinetic treatment; physiosorption; weight loss

1. INTRODUCTION

Most metals are inherently unstable and have the natural tendency to react with their environments to attain lower energy by forming a chemical compound, in a more stable state. Since corrosion is always a function of the environmental conditions, control in some cases may be more concerned with preventing contact of the surroundings with the metal. This led to the usage of inhibitors in the control of corrosion [2]. Because of their lightweight and mechanical strength, aluminum and its alloys are very attractive materials for engineering application [1]. Corrosion inhibition of aluminum and its alloys was the subject of numerous studies [3-5].

Pyridoxal is available in a variety of forms including tablets, softgels, powders, and lozenges. It has been used for so many medications [6], but in this present study, pyridoxal hydrochloride is being investigated as inhibitor in the corrosion of aluminum in hydrochloric acid using weight loss and hydrogen gas evolution technique.

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2. Experimental

2.1 Material Preparation

First Aluminum Plc, Port Harcourt, supplied aluminum (3SR) sheets used in the present work. Every sheet was 0.53mm in thickness and 98.5% in purity. The aluminum sheets were cut into 5cm by 2cm for weight loss determination and a hole of 2mm were drilled on the center of one end of all the coupons for suspension inside the corrodent solution.

The coupons were used as supplied without further polishing but were degreased in absolute ethanol and dried in acetone. Prior to the experimental work, these already prepared coupons were stored in a moisture free desiccator to prevent contamination.

The inhibitors used and all other reagents were of Analar grade and doubly distilled water was used for the preparation of all solutions.

Inhibitor concentrations of 1.0×10^{-6}M, 1.0×10^{-5}, 1.0×10^{-4}, 1.0×10^{-3}M and 1.0×10^{-2}M were prepared in 2M HCl solutions. The prepared inhibitor solutions were used for all measurements.

2.2 Weight Loss Determination

Aluminum coupon of 5.0cm by 2.0cm and 0.053cm thickness were used for weight loss measurement. The total geometric surface area of coupon exposed is $20cm^2$. The coupons were suspended through a hole of 0.2cm diameter. Five different concentrations of pyridoxal hydrochloride 1.0×10^{-6}M, 1.0×10^{-5}M, 1.0×10^{-4}M, 1.0×10^{-3}M, 1.0×10^{-2}M and 2M HCl solution without inhibitor were maintained at 303K, 313K, and 323K. Previously weighed coupons were placed in the corrodent – inhibitor systems. Each coupon was removed from its solution at 30 minutes interval for 4 hours. The difference in the weight of the coupons was taken as the weight loss and recorded. The percentage inhibitor efficiency was calculated as

$$\% I = \frac{W_B - W_{in}}{W_B} \times 100$$

Where W_B and W_{in} are the weight loss of aluminum specimens without and with inhibitor, respectively.

Again five 250ml beakers which separately contained 0.5M, 1.0M, 1.5M, 2.0M and 2.5M HCl solutions were maintained at 303K, 313K, and 323K while previously weighed aluminum coupons were each suspended in each beaker for corrosion rate determinations. The coupons were always rinsed in distilled water and absolute ethanol, dried and re-weighed after removal from the corrodent concentrations. The weight loss was calculated in grams as the difference between the initial weight prior to immersion and weight after removal from the corrodent and recorded every 30 minutes for 240 minutes.

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2.3 Hydrogen gas evolution Technique

In the gas evolution measurement, the corrosion rates of aluminum were investigated by the hydrogen evolution rate at corrodent concentration 2M HCl with and without pyridoxal hydrochloride.
Variation in the volume of hydrogen evolved with time was recorded every 1 minute for 30 minutes. Aluminum coupons of dimension 1.0cm by 0.5cm were used. Each experiment was conducted on a fresh specimen of aluminum.
The hydrogen evolved is a function of the corrosion reaction and it displaces the fluid in the gasometric set-up, which is read directly. Experiments performed without inhibitors recorded the highest volume of hydrogen gas evolved. The percentage efficiency was calculated as:

$$\% \text{ Efficiency } = \frac{V_B - V_{in}}{V_B} \text{ X } 100\%$$

Where V_B and V_{in} are the volumes of hydrogen evolved without and with inhibitor respectively at 30 minutes

3.0 RESULTS AND DISCUSSION

3.1 EFFECT OF CORRODENT CONCENTRATION

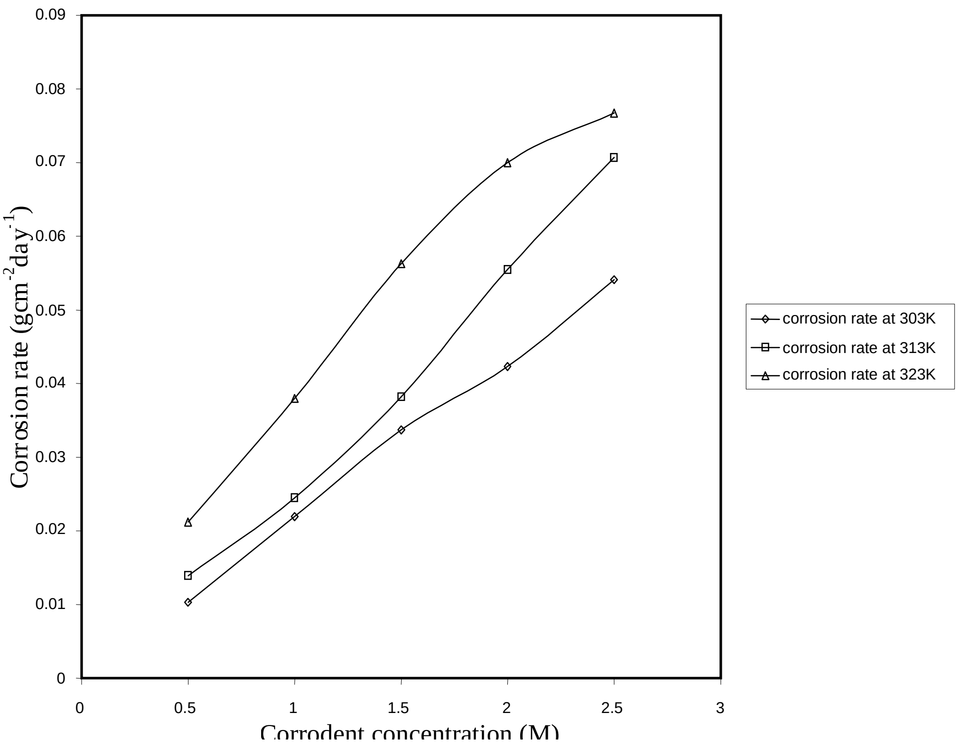

Figure 1: Variation of corrosion rate (gcm^{-2}day^{-1}) with corrodent concentration (M) for aluminium coupons in HCl solutions at different temperatures without inhibitor.

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Figure 1 shows that aluminum corrodes in different concentration of HCl solutions. There is an increase in the corrosion rate ($gcm^{-2}day^{-1}$) as the concentration of the acid increases, showing that corrosion of aluminum in HCl is a function of the concentration of the acid and follows the order, 2.5M >2.0M> 1.5M> 1.0M> 0.5M at 303K. Similar results were obtained at 313K and 323K. This observation agrees with the fact that the rate of a chemical reaction increases with increasing concentration.

Increase in temperature was also observed to increase the corrosion rate as shown in figure 1.This is probably due to increase in the rate of diffusion and ionisation of active species in the corrosion reaction. [2]

The corrosion is attributed to the presence of water, air and H^+ that accelerate the corrosion process. [8]

3.2 Effect of Temperature on aluminum

The effect of temperature is shown on the corrosion rate of aluminum as seen in figure 1and on the dissolution of aluminum in HCl in figure 2.

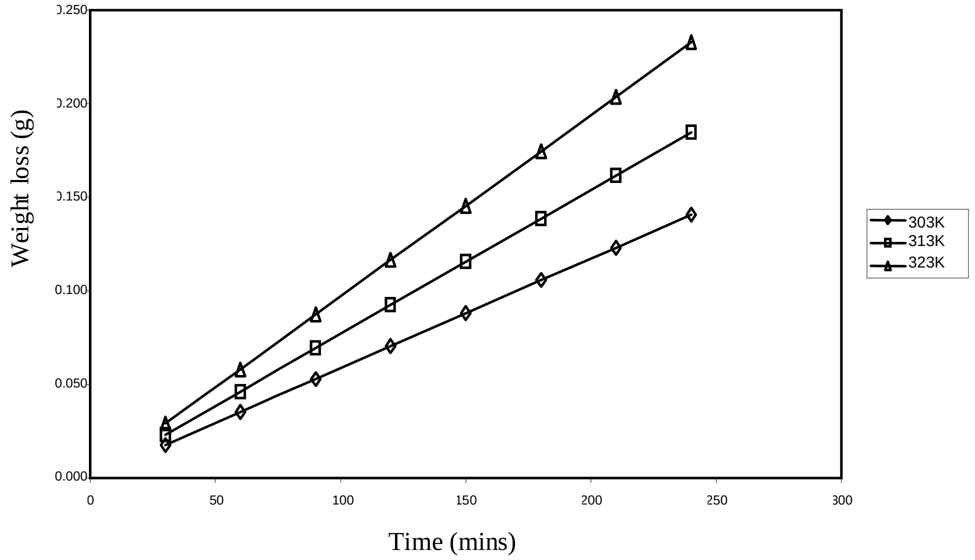

Figure 2: Variation of weight loss (g) with time (mins) for aluminium coupons in 2M HCl without inhibitor at different temperatures.

Figure 2 indicates that there is a general increase in weight loss as the temperature is increased from 303K to 313K and then to 323K. This is in accordance with the general rule guiding the rate of chemical reactions, which says that chemical reactions increase with increasing temperature.

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3.3 Inhibition action of pyridoxal hydrochloride on the corrosion of aluminum.

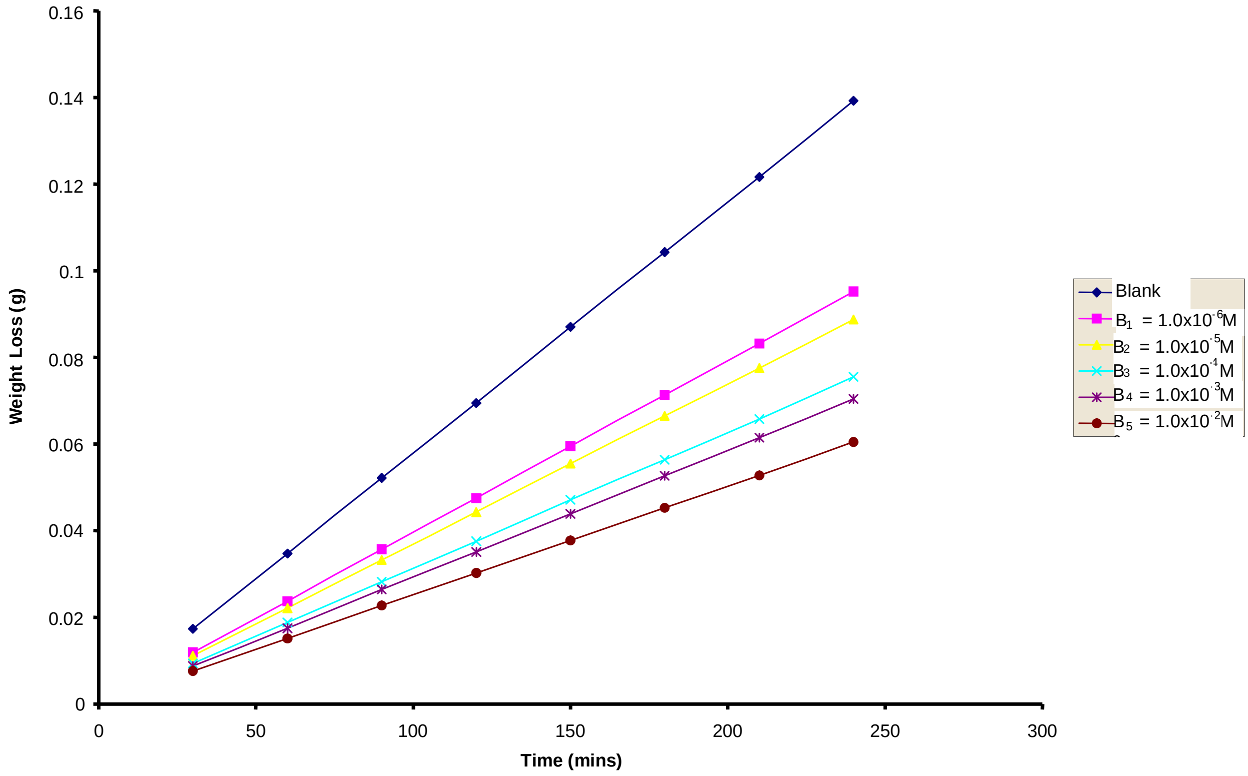

Figure 3: Variation of weight loss (g) with time (mins) for aluminium coupons in 2.0M HCl solution containing different concentrations of pyridoxal hydrochloride at 303K.

Figure 3 shows that pyridoxal hydrochloride used as inhibitor actually inhibits the acid corrosion of aluminum to a remarkable extent in 2M HCl solution because there is a general decrease in weight loss as the inhibitor concentration increases. This also shows that increase in concentration of inhibitor increases the inhibitor efficiency. Comparing the variation of the weight loss with time of exposure of aluminum in 2M HCl solution without additives at 303K (blank) with the ones containing the additives, there is a remarkable decrease in weight loss signifying corrosion inhibition. Similar trend was observed at 313K and 323K.

3.4 Effect of temperature on the inhibition efficiency of pyridoxal hydrochloride.

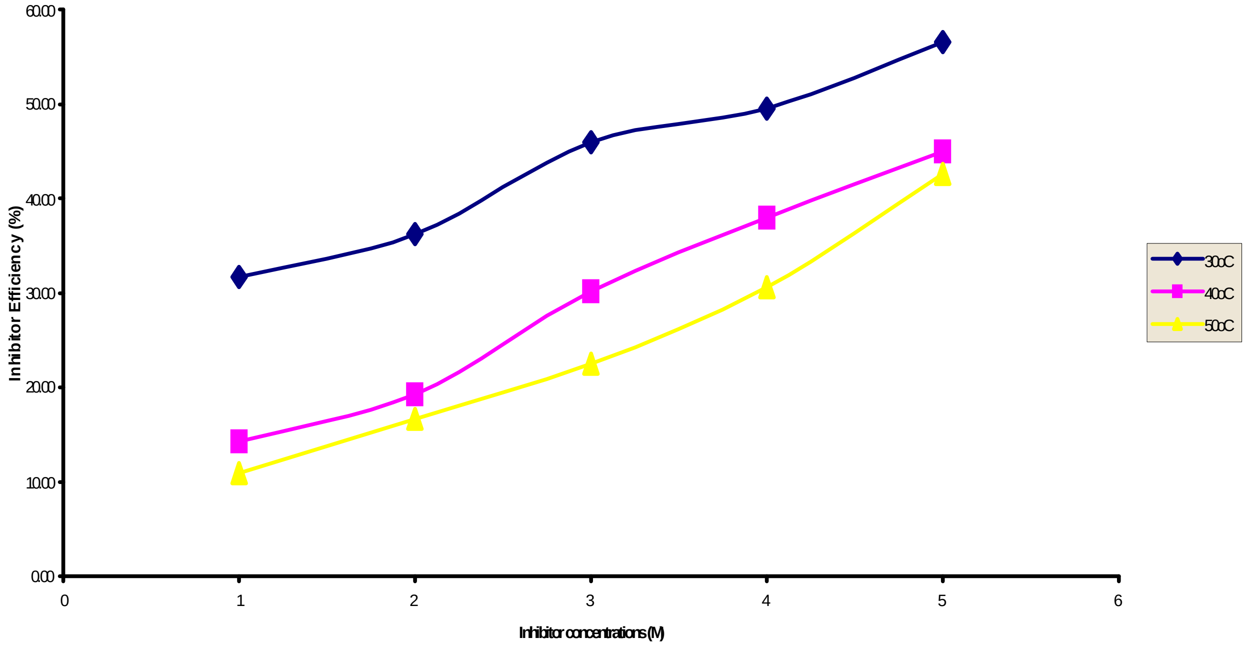

Figure 4: Variation of inhibitor efficiency with inhibitor concentration (M) for aluminium coupons in 2.0M HCl solution containing pyridoxal hydrochloride at different temperatures.

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Figure 4 shows the effect of varying the temperature and inhibitor concentration on the inhibition efficiency.
From this plot, it was observed that with increase in temperature from 303K to 313K and then to 323K, there is a marked decrease in the inhibition efficiencies. However, inhibition power of the additives increased as the concentration of the additives increased and as the temperature of the system decreased.

Table 1: Percentage Inhibition of Al in 2M HCl containing pyridoxal hydrochloride from hydrogen gas evolution technique

Percentage Inhibition (%)	Pyridoxal Hydrochloride Concentrations (M)				
	$1.0x10^{-6}$	$1.0x10^{-5}$	$1.0x10^{-4}$	$1x10^{-3}$	$1.0x10^{-2}$
	31.03	38.19	45.31	49.78	54.02

Table 1 shows the percentage Inhibition efficiency of pyridoxal hydrochloride on Al in 2M HCl from gasometric method of corrosion measurement. Since two methods, weight loss and hydrogen gas evolutions were used for the corrosion measurement during the experimental, it is important to show and compare the results of the methods to prove the autencity and the reproducibility of the result.

Table 2: Comparison of percentage inhibitor efficiency of weight loss and hydrogen gas evolution technique at 303K

Inhibitor Concentration (M)	Percentage Inhibitor Efficiency (%)	
	Weight loss	Hydrogen Evolution method
$1.0x10^{-6}$	31.64	31.03
$1.0x10^{-5}$	36.24	38.19
$1.0x10^{-4}$	45.90	45.31
$1.0x10^{-3}$	49.48	49.78
$1.0x10^{-2}$	56.52	54.02

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Hence table 2 shows that the percentage inhibitor efficiency of weight loss method and hydrogen gas evolution method are highly comparable having very close values. This invariably confirms the accuracy of the inhibitor efficiency's values.

Kinetics and mechanism of the corrosion inhibition of aluminum in HCl.
The corrosion of aluminum in HCl is a heterogeneous one, comprising of anoidic and cathodic reactions. Based on this, the kinetic analysis of the data was considered necessary. In the study, Wi represents the initial weight of aluminum coupon while ΔW represents the weight loss with time.

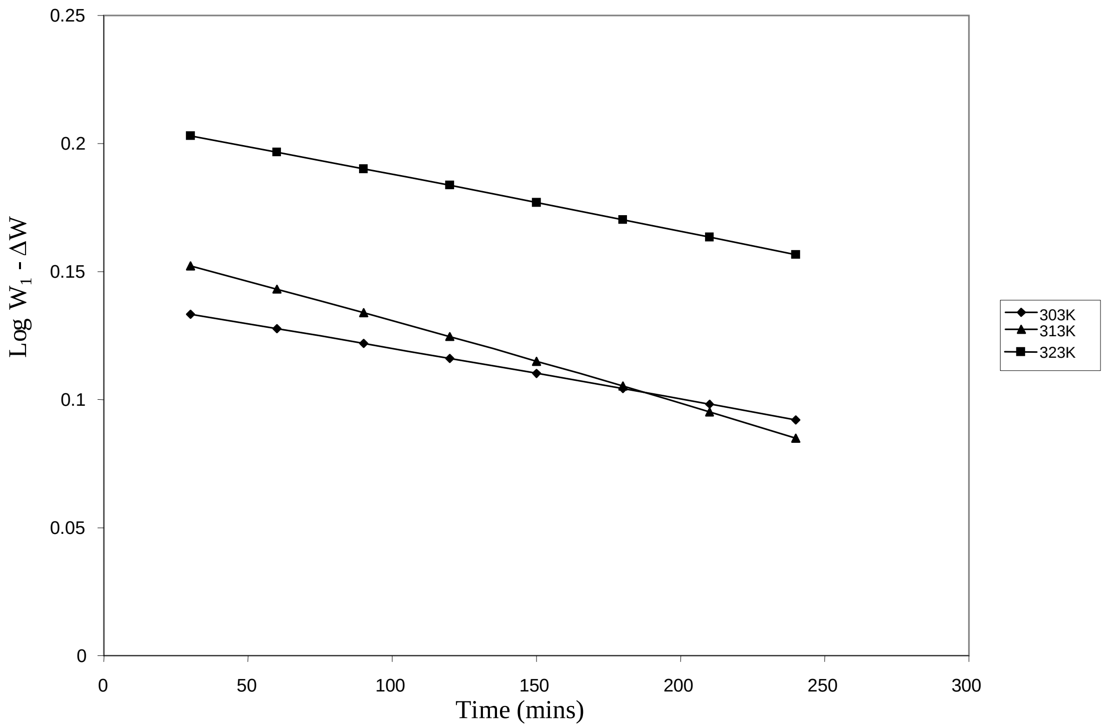

Figure 5: Variation of Log(wi - Δw) with time (mins) for aluminum coupons in 2.0M HCl at different temperatures without inhibitors.

When log (wi - Δw) was plotted against time (mins.) as shown in figure 5 at temperature of 303K to 323K, a linear variation is observed which confirms a first order mechanism with respect to aluminum corrosion in HCl solution (in the absence of additives). The rate constants were calculated from first order rate equation as:

$$K = \frac{1}{t} \ln \frac{w_i}{w_f}$$

Wi = Initial weight of the coupon, Wf = Final Weight and t = time in minutes.

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The half-life time, $t^1/_2$ was also calculated from the first order half-life equation:

$$t^1/_2 = \frac{0.693}{K}$$

Table 1: Kinetic data for aluminium in different concentrations of hydrochloric acid solution without additives.

Hydrochloric acid concentration (M)	Rate Constant, K $(min^{-1}) \times 10^{-4}$			Half life, $t^1/_2$ (mins) $\times 10^3$			Average activation energy $KJmol^{-1}$
	303K	313K	323K	303K	313K	323K	
0.5	1.08	1.19	2.01	6.42	5.82	3.45	32.58
1.0	2.19	2.29	3.74	3.16	3.03	1.85	
1.5	3.22	3.59	5.43	2.15	1.93	1.28	
2.0	4.29	4.79	6.76	1.62	1.45	1.03	
2.5	5.35	6.77	7.98	1.30	1.02	0.87	

Table 3 gives the kinetic data of the corrosion of aluminum in the corrodent at different temperatures without additives. It shows the rate constants at 303K, 313K and 323K and the half-life time $t^1/_2$ of the corrosion of aluminum in 2.0M HCl in the absence of the additives.
The Activation energy was calculated using the integrated form of the Arrhenius equation below:

$$\text{Log}\ \frac{k_2}{k_1} = \frac{Ea}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

Where Ea = Activation energy in Kjmol-1.
K = The rate constants.
T = Temperatures in Kelvin

$32.58kJmol^{-1}$ was obtained as the average activation energy of the metal-corrodent system without inhibitor.

Again when Log(Wi-ΔW) was plotted against time(mins) for the dissolution of aluminum coupon in 2M HCl solution containing different concentration of pyridoxal hydrochloride at 303K, a linear variation was also obtained as seen in figure 6.

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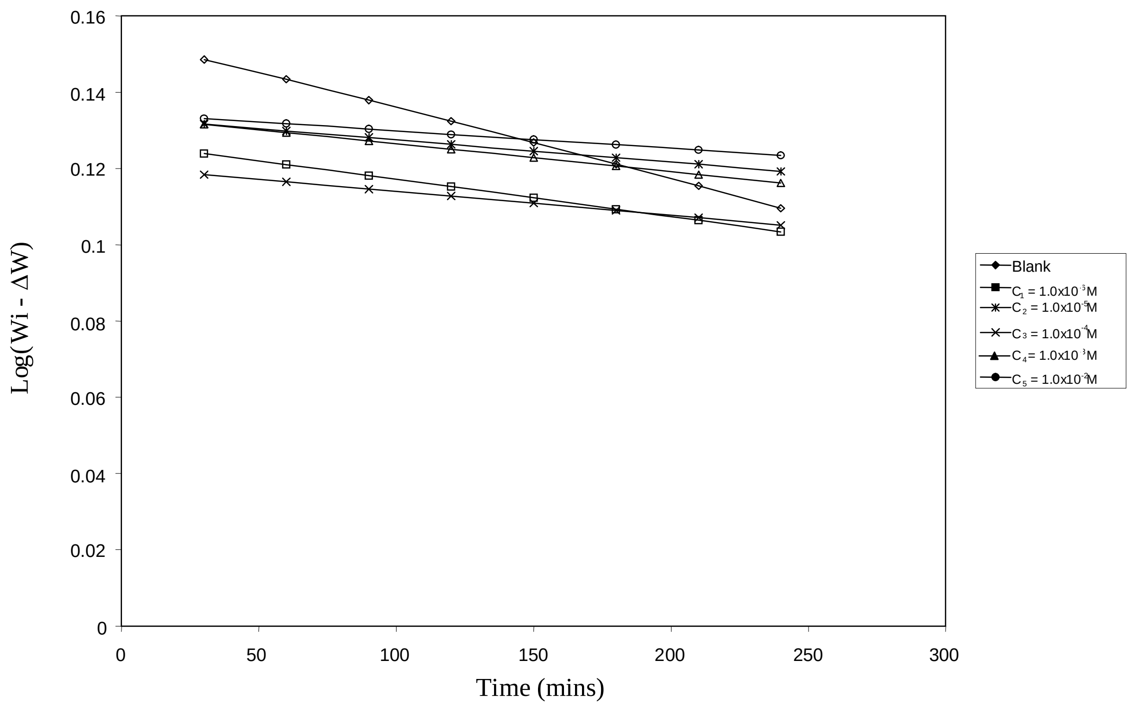

Figure 6: Variation of Log(wi - Δw) with time (mins) for dissolution of aluminium coupons in 2.0M HCl solution containing different concentration of pyridoxal hydrochloride at 303K.

This invariably confirms a first order mechanism for the inhibition reaction. The rate constants, half-life and activation energy were again calculated and the kinetic data obtained in the presence of pyridoxal hydrochloride using weight loss measurements is shown in table 4.

Table 4: Kinetic data for aluminium in 2M HCl containing pyridoxal hydrochloride from weight loss measurement.

Inhibitor concentration (M)	% Inhibition Efficiency			Rate Constant, K (min^{-1}) x 10^{-4}			Half-life, $t^1/_2$ (mins)x 10^3			Activation energy $kJmol^{-1}$	Average activation energy $kJmol^{-1}$
	303K	313K	323K	303K	313K	323K	303K	313K	323K		
$1.0x10^{-6}$	49.60	15.43	13.38	2.21	4.54	5.46	3.14	1.53	1.27	18.09	26.58
$1.0x10^{-5}$	61.45	37.15	32.49	1.66	3.59	4.58	4.18	1.93	1.51	20.47	
$1.0X10^{-4}$	67.65	46.65	42.69	1.43	2.87	4.03	4.85	2.42	1.72	28.54	
$1.0X10^{-3}$	68.91	50.95	49.24	1.34	2.59	3.23	5.17	2.68	2.15	18.56	
$1.0X10^{-2}$	75.41	67.26	54.38	1.05	1.75	3.07	6.60	3.96	2.26	47.25	

The rate constants generally decrease with increased inhibitor concentration at a particular temperature but increased as the temperature increases. Also as the inhibitor concentration increases, the percentage inhibitor efficiencies and the half-life time, $t_{1/2}$ increases for Pyridoxal at a particular temperature but decreases as the temperature increases.

The average activation energy value of 26.58kJmol-l which is lower than 80 kJmol-l confirms the physical adsorption mechanism proposed for the inhibition reaction. The increase in the half-life time, $t_{1/2}$ when the inhibitor is present as seen in table4 shows that pyridoxal hydrochloride inhibits the corrosion of aluminum in HCL solution but as the temperature increases, the half-life, $t_{1/2}$ decreases confirming that pyridoxal hydrochloride inhibits best at lower temperatures.

Similar trend in kinetic data has been reported by several investigators [3,4,5,7] and indicates that a good inhibitor is one that is able to increase the time of conversion of metals to corrosion products. [3,4]

The inhibition property of pyridoxal is due to the organic Nitrogen, it contains. This Nitrogen heteroatom is very rich in electrons and can donate its lone pair of electron into the empty orbital of the metals making the metal ion unavailable to Corroding agents. The molecular structure of pyridoxal revealed a pyridine type organic compound with Nitrogen and phenyl groups. Both groups have been found effective for corrosion inhibition.

Figure 7 shows the molecular structure of Pyridoxal hydrochloride.

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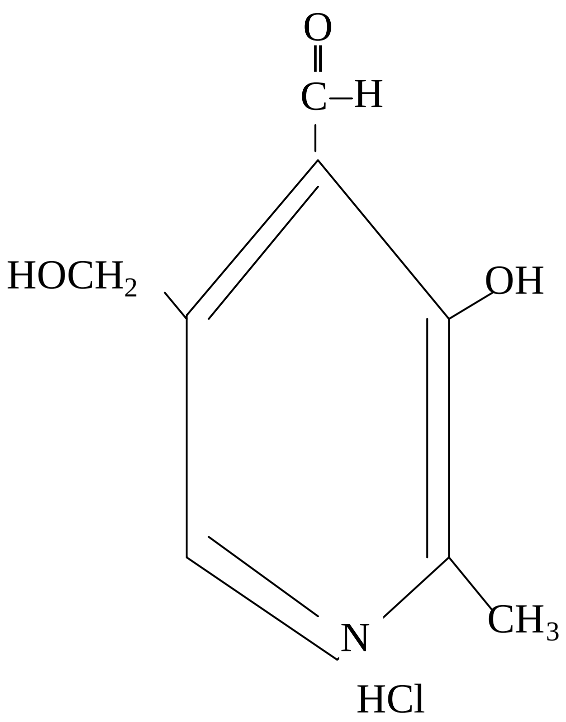
Figure 7: The structure of Pyridoxal hydrochloride



<u>IUPAC name: [3-hydroxyl-5-(hydroxyl methyl)-2-methyl-4-pyridine carboxaldehyde].</u>

Conclusion

This study shows that Pyridoxal inhibits the corrosion of aluminum in HCl solution to a remarkable extent. On the basis of the activation energy experimentally observed, physiosorption mechanism has been proposed for the inhibition action of the additives. The corrosion of aluminum in HCl solution in both inhibited and uninhibited reactions confirms a first-order type of mechanism. Inhibition is higher at low temperatures showing that Pyridoxal could serve as effective inhibitor of the corrosion of aluminum in hydrochloric acid media.

REFERENCES

(1) A.K. Maacyta Jour. Corr. Sci. Eng. 3,25, (2002). http://www2.umist.ac.uk/corrosion/JCSE/Volume3/paper25/v3p25html..

(2) D.U. Omo-odudu, and N.C. Oforka, Nig. Jour. of physics vol.11, (1999).

(3) O.K. Abiola, N.C. Oforka JCSE, J. corros. Sci. Eng. 3, 21,(2002). http://www2.umist.ac.uk/corrosion/JCSE/Volume3/paper21/v3p21.htm .

(4) E.E. Ebenso Jour. Nig. Corr. 1, (1), (1998).

(5). U.J. Ekpe, U.J. Ibok, B.I. Ita, O.E. Offiong, E.E. Ebenso Mater. Chem. Phy. 40,87, (1995).

(6) K.M. Wyatt, P.W. Dimock, P.W. Jones, P.M. SHAUGHN O' Bruen Jour of Biomedical Sc. 318, 7195, (1999

(7) E.E. Ebenso, P.C. Okafor, O.E. Offiong, B.I. Ita, U.J. Ibok, U.J. Ekpe Bull. Electrochem. 17,259, (2001).

(8) K.O. Orubite, N.C. Oforka Materials letters 58 (2004), 1768-1772.