



Corrosion Inhibition of Zinc on HCl using *Nypa fruticans Wurmb* Extract and 1,5 Diphenyl Carbazone

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ABSTRACT: The corrosion inhibition of zinc in hydrochloric acid by extract of *Nypa Fruticans Wurmb* was studied using weight loss techniques. Maximum inhibition efficiency (and surface coverage) was obtained at an optimum concentration. However increase in temperature decreased the inhibition efficiency at the temperature range studied. The inhibition action of *Nypa Fruticans Wurmb* extract compared closely to that of 1, 5 Diphenyl Carbazone (DPC). Optimum inhibition efficiency for zinc in the presence of *Nypa Fruticans Wurmb* extract was 36.43% and 40.70% with DPC. The phenomenon of physical adsorption has been proposed from the activation energy values (19.33 kJ mol⁻¹ and 21.11 kJ mol⁻¹) with *Nypa Fruticans Wurmb* extract and DPC respectively. A first order kinetics has been deduced from the kinetic treatment of the results. The heat of adsorption, Q_{ad} range from (-33.63 to - 58.52 kJ mo l⁻¹) for both additives studied. Mean ΔG°_{ads} values (-7.82 to 8.68 kJ mol⁻¹) are negative and suggestive of adsorption on metal surface. The data obtained from this study fits well into the Langmuir isotherm. Evidence is hereby provided to show that *Nypa Fruticans Wurmb* extract and DPC inhibits the corrosion of zinc comparatively @ JASEM

Naturally occurring substances as inhibition of acid cleaning process has continued to receive attention as replacement for synthesized organic inhibitors. Investigation into the corrosion inhibition effects of some local plants (Ekpe *et al* 1994 and Loto 1998) have proposed parts of economic plants as pickling inhibitors. Not much has actually been achieved using these local plants, compared to the extensive research on synthesized organic inhibitors especially N – and S – containing organic compounds (Monticelli *et al* 1993 Ita and Offong 2000).

This study assesses the corrosion inhibition effect of the leaves of *Nypa Fruticans Wurmb* on the corrosion of zinc in hydrochloric acid medium. *Nypa Fruticans Wurmb* is of the family Arecaceae, a native of Asia and planted in Nigeria during the colonial administration. It grows abundantly along the coastal Nigeria. *Nypa Fruticans Wurmb* is highly utilized in other countries. Products are obtained from the leaves, the sap, fruit and stalk. Young shoots, decayed wood and buried roots or leaves find use as medicine in various parts of south Asia for herpes, toothache and head ache .The sap is a source of sugar about 14-17% of sucrose and organic acids and it is used to produce vinegar and alcoholic beverages in the Phillipines and Malaysia (Halos 1981). *Nypa Fruticans Wurmb* has not been extensively exploited in Nigeria. It's fast growing tendency is a continual threat to the more useful mangrove forest; hence the call for its eradication in some quarters (Ukoima 2000). This research work illustrates the similarity of

the inhibition properties of *Nypa Fruticans Wurmb* to a synthesized organic inhibitor.

EXPERIMENTAL

Material Preparation: The zinc sheets used for this study 98% pure were mechanically press-cut into 5 x 4 cm coupons of 1cm thickness. The coupons were examined carefully to check for rough edges, which could influence the corrosion monitoring process. Surface treatment of the coupons was done by degreasing in absolute ethanol and drying in acetone. They were then stored in moisture free desiccators before use. Fresh leaves of *Nypa Fruticans Wurmb* were dried and ground into powder. 10g of which was weighed into 100ml of 90% methanol in a 200ml volumetric flask. The flask was properly corked and left to stand for 48 hours with occasional shaking. The resultant mixture was filtered and methanol evaporated to dryness at 65°C in a water bath. This left a dark brown sticky residue, 0.5g of which was weighed, dissolved in 100ml of ethanol and made up to 1000ml by 0.1M HCl solution. This represents the stock solution from which different concentrations of 0.024, 0.04, and 0.08, 0.16 and 0.32gdm⁻³ were prepared by dilution with the same acid solution. Similar concentrations of DPC were also prepared. All reagents were of analar grade and doubly distilled water was used for the preparation of all solutions.

Weight loss corrosion test method: In the weight loss experiment, five 250ml beakers (in two sets) were labeled A, B, C, D and E containing 0.1, 0.5, 2.0, 2.5

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and 3.0M HCl solutions were placed in a thermostated water bath maintained at 30 or 40 °C. The zinc coupons were suspended in the beakers with the aid of glass hooks. The coupons were retrieved from their corrodent solutions at one hour material for 7 hours due to the high reactivity of zinc in HCl medium. Further measurements were carried out after introduction of the additives (*Nypa Fruticans* or DPC) in the beakers maintained at 30 or 40 °C. They were retrieved from the medium at 1hr interval for 7 hours. Each set of coupons was dipped into saturated ammonium acetate solution at room temperature, to terminate the corrosion reaction. They were washed by scrubbing with a light brush and dried in acetone and finally in an oven maintained at 80 °C. The weight loss of zinc coupons was evaluated in grams as the difference in the weight of the coupons before and after the test,

$$W = (W_i - W_f) \text{ g}$$

[W = weight loss of coupon, W_i = Initial weight of zinc coupon, W_f = Final weight of zinc coupon. Each reading reported is an average of three experimental reading recorded to the nearest 0.0001g on a santorium 3105 electronic balance. The inhibition efficiency of *Nypa Fruticans wurmb* extract or DPC acting as inhibitor was calculated using the formula,

$$I.E\% = \left[1 - \frac{W_1}{W_2} \right] \times 100$$

(Ekpe *et al* 1994)

Where w_1 and w_2 are the weight losses (gms) for zinc in the presence and absence of additives respectively in HCl solution at the same temperature. The degree of surface coverage, θ is given by the equation, (Atkins 1980)

$$\theta = 1 - \frac{W_1}{W_2}$$

The corrosion rate of zinc in the different corrosion medium was determined for a 7 hours immersion period from weight loss using the formula (NACE 1984)

$$\text{Corrosion Rate (mdd)} = \frac{534w}{DAT}$$

Where w = weight loss (mg) D = density of specimen (g cm^3) A = area of specimen (cm^2) and T is exposure time (hrs).

RESULTS AND DISCUSSION

Corrosion of zinc in HCl solution: Figure 1 shows the corrosion of zinc in different concentration of HCl at 30°C without additives. The result obtained indicates that the weight loss of zinc in HCl increased with increasing acid concentration. Similar trend was observed at 40°C. This can be attributed to the fact that the rate of chemical reaction increases with increasing acid concentration and/or probably due to increase in the rate of diffusion and ionization of active species in the corrosion reaction. This conforms to reports by Omodudu and Oforika (1999).

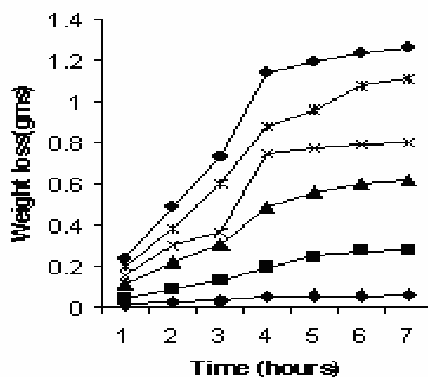


Fig.1 Variation of weight loss with time in different concentrations of HCl at 30 °C without additives.



Table 1. Calculated values of weight loss (gms), corrosion rate (mdd),% inhibition efficiency and surface coverage (Θ) for corrosion of zinc in HCl for the different systems at 30°C and 40°C.

Blank /gdm ⁻³	2.5x10 ⁻⁵	5.10 x10 ⁻⁴	0.0398	0.0499	-	-	-	-
0.32	6.11x10 ⁻⁴ (6.05x10 ⁻⁴)	7.64 x10 ⁻⁴ (7.80x10 ⁻⁴)	0.0295 (0.0291)	0.0431 (0.0428)	25.87 (26.88)	13.28 (14.22)	0.25 (0.27)	0.13 (0.14)
0.16	5.98x10 ⁻⁴ (4.86x10 ⁻⁴)	7.12 x10 ⁻⁴ (9.58x10 ⁻⁴)	0.0289 (0.0284)	0.0414 (0.0401)	27.38 (28.64)	7.03 (19.63)	0.27 (0.28)	0.17 (0.19)
0.08	5.23x10 ⁻⁴ (4.90x10 ⁻⁴)	7.54 x10 ⁻⁴ (9.68x10 ⁻⁴)	0.0253 (0.0236)	0.0464 (0.0456)	36.43 (40.70)	7.07 (8.61)	0.36 (0.40)	0.07 (0.86)
0.04	5.50x10 ⁻⁴ (5.15x10 ⁻⁴)	8.04 x10 ⁻⁴ (9.81x10 ⁻⁴)	0.0266 (0.0258)	0.0478 (0.0472)	33.16 (35.17)	4.20 (5.47)	0.33 (0.35)	0.04 (0.54)
0.024	7.68 x10 ⁻⁴ (6.17x10 ⁻⁴)	9.58 x10 ⁻⁴ (1.01x10 ⁻⁴)	0.0370 (0.0347)	0.0482 (0.0482)	7.03 (12.11)	3.40 (3.64)	0.07 (0.12)	0.034 (0.36)

Effect of the Temperature on Corrosion of Zinc in HCl Solution: Figure 2 reveals that at constant concentration of HCl, (0.1M), weight loss increases with increase in temperature. Similar plots were obtained for 0.5, 1.5, 2.0, 2.5 and 3.0M HCl

solutions. This observation implies that temperature favours the reactivity of the active constituents of the corrosion medium. It is of general knowledge that temperature increases the rate of most chemical reactions.

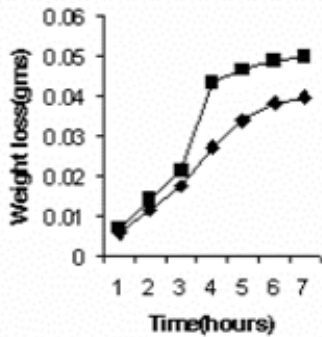


Fig 2. Variation of weight loss with time in 0.1M HCl at different temperatures .

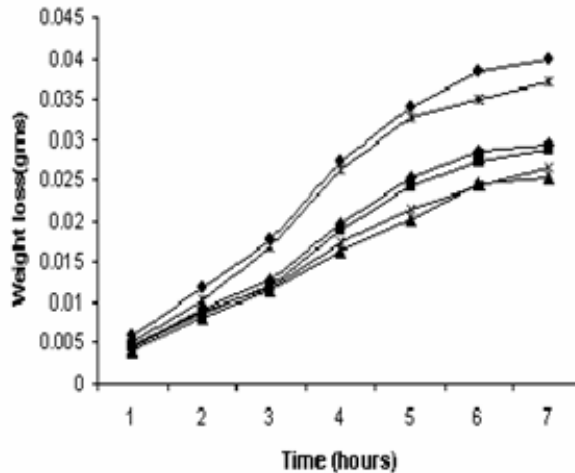
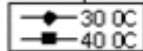
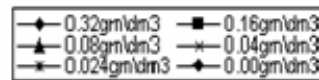


Fig 3 Variation of weight loss with time in 0.1 M HCl with various concentrations of *Nypa fruticans* leaves extract at 30°C



Effect of Additives on Corrosion of zinc: Figures 3 – 6 reveal that *Nypa Fruticans Wurmb* leaves extract and DPC inhibit the corrosion of zinc in HCl solution since there was a general decrease in weight loss with

either additive. However, inhibition though low, was maximum at lower additives concentration of 0.08gdm⁻³ and temperature of 30°C.

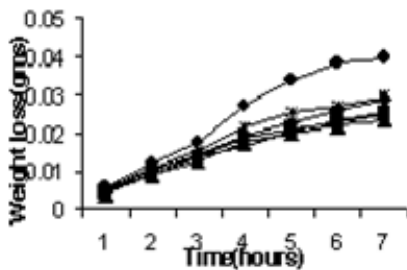


Fig 4 Variation of weight loss with time in 0.1M HCl with various concentrations of DPC at 30°C

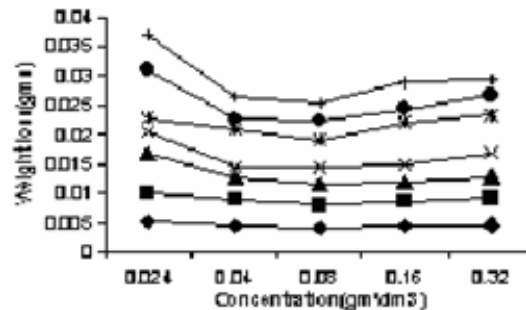
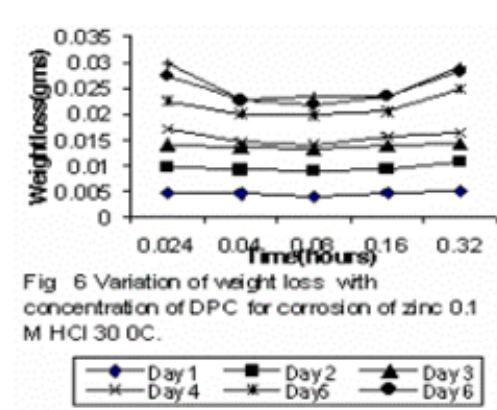


Fig 5 Variation of weight loss with various concentration of *Nypa fruticans* leaves extract for corrosion of zinc in 0.1 M HCl 30°C

Table 2. Calculated values of activation energy E_a (kJmol^{-1}) Heat of Adsorption, Q_{ad} (kJmol^{-1}) Rate constant, k (hours^{-1}) Half life (hours) for zinc at 30 and 40°C.

System	Activation energy E_a	Heat of adsorption Q_{ad}	Rate constant, k		Half life, $t_{1/2}$		Average ΔG_{ad}°
0.32	21.40 (26.52)	-32.33 (-53.69)	0.00125 (0.00135)	0.00164 (0.00189)	554.5 (513.2)	422.6 (366.7)	
0.16	8.04 (11.28)	-4.14 (-10.25)	0.00121 (0.00130)	0.00134 (0.00150)	572.8 (533.1)	517.2 (462.0)	
0.08	24.64 (29.03)	-48.97 (-54.43)	0.00109 (0.00139)	0.00149 (0.00172)	635.9 (493.4)	465.2 (402.9)	
0.04	18.96 (22.22)	-60.71 (-66.22)	0.00114 (0.00132)	0.00145 (0.00175)	608.0 (525.1)	478.0 (396.0)	
0.024	6.04 (16.50)	-52.11 (-58.92)	0.00138 (0.00146)	0.00149 (0.00180)	502.2 (497.0)	465.1 (385.1)	
Average E_a	19.33 (21.11)						

Values in parenthesis are for DPC



Hence at the end of the 7th hour in 0.1M HCl, with *Nypa Fruticans Wurbmb* extract concentration of 0.32gdm^{-3} weight loss of 0.0295g per hour was obtained while for 0.08gdm^{-3} weights loss of 0.0253g per hour was observed at 30°C. Under similar conditions weight loss observed for 0.32gdm^{-3} of DPC was 0.0291g and 0.0236g for 0.08gdm^{-3} . Values of corrosion rates, inhibition efficiency follow similar trend (table 1). Percentage inhibition efficiency was higher at additives concentration of 0.08gdm^{-1} than at 0.32gdm^{-3} for both additives. This minimum corrosion rate at specific concentration may probably be due to the formation of a soluble complex on metal surface as in the case of polyphosphates or as a result of protonation of additive molecules and subsequent acceleration of the hydrogen evolution process (Moore 1994). At higher temperature of 40°C maximum inhibition efficiency was obtained at additives concentration of 0.16gdm^{-3} . This shift may be due to the adsorption of more inhibitor molecules on the metal surface.

However inhibition decreases with increase in temperature. The maximum inhibition efficiency is lower at 40 °C than at 30 °C. This is in agreement with what is known about the dependence of adsorption on temperature that as temperature rises, the quantity adsorbed decreases and as a result, the isotherm of higher temperatures are below the isotherm of lower ones. It is of generally view that inhibition of metals in acidic solution results from the adsorption of molecules or ions of the inhibitor on the metal surface. The action of organic inhibitors depends on the type of interaction between the substance and the metallic surface. This could cause a change either in the electrochemical process mechanism or on the surface available to the process. The decrease in inhibition efficiency with increasing temperature, suggest weak adsorption interaction between zinc surface and the additives, which is physical in nature (Talati and Modi 1998).

In order to further support the assertion that physical adsorption is proposed, the values of

activation energy (E_a) were calculated using the integrated form of the Arrhenius equation.

$$\log \frac{K_2}{K_1} = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

Where K_1 and K_2 are rate constants at T_1 and T_2 respectively. The values are presented in Table 2. The low values recorded suggest physical adsorption (Barrow, 1993).

From the corrosion rates or surface coverage (θ) for different inhibitor concentrations the respective adsorption isotherms can be obtained.

The surface coverage data (table 1) fits into the Langmuir isotherm given as,

$$\frac{C}{\theta} = \frac{1}{b} + xC$$

Where C is concentration of additives. With either additive, it was shown (figure not given) that corrosion inhibition of zinc obeys the Langmuir isotherm. Hence the mechanism of inhibition may be due to the formation and maintenance of a protective film on the metal surface. The plots further suggest that both additives (*Nypa Fruticans wurmb* extract and DPC) cover both the anodic and cathodic regions through general adsorption following Langmuir isotherm.

Kinetic/Thermodynamic Treatment of weight loss results

Corrosion reaction is an overall reaction in which both solid and liquid phases are consumed. It is therefore difficult to apply most of the principles of chemical kinetics to corrosion reaction. Plots of $\log w_f$ against time in hours at 30°C in HCl for the different systems studied reveal linear plots signifying first- order kinetics. The values of rate constant (k) in table 2 were obtained from this plot. Similar plots were obtained at 40°C. This conforms to observations (Ibok *et al* 1994 and Ekpe *et al* 1994).

The values of heat of adsorption Q_{ad} were calculated using the following equation ,

$$Q_{ad} = 2.303R \log \left[\frac{\theta_2}{1-\theta_2} \right] - \log \left[\frac{\theta_1}{1-\theta_1} \right] x \frac{T_1 T_2}{T_2 - T_1} kJmol^{-1}$$

Where θ_1 and θ_2 are degrees of surface coverage at temperature T_1 and T_2 by the different additives. From Table 2 it is evident that in all the cases, the Q_{ad} values are negative and range from -4.14 kJmol^{-1} to $-60.71 \text{ kJmol}^{-1}$ with *Nypa Fruticans* extract and 10.25 kJmol^{-1} and $-66.22 \text{ kJmol}^{-1}$ for DPC as inhibitor. The negative Q_{ad} values also show that the adsorption and the inhibition efficiency decrease with temperature. ΔG_{ads}^0 values were obtained with the help of the equation,

$$\text{Log} C = \log \left[\frac{\theta_1}{1-\theta_1} \right] - \log B$$

Where $\text{Log} B = -1.74 - (\Delta G_{ads}^0 / 2.303RT)$ and C = additives concentrate

The values are presented in table 2. The negative values suggest strong adsorption on zinc's surface. As temperature increases the value of ΔG_{ads}^0 increases while percentage inhibition efficiency decreases. It is of note that ΔG_{ads}^0 up to -20 kJmol^{-1} are consistent with electrostatic interaction between charged molecules and the charged metal (physical adsorption) while ΔG_{ads}^0 values more negative than -40 kJmol^{-1} involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate bond (chemisorption).

The half life ($t_{1/2}$) values were calculated using the equation (Atkins 1980)

$$t_{1/2} = \frac{0.693}{k}$$

Half-life increases with increase in concentration of *Nypa Fruticans wurmb* extract or DPC, while the rate constant K, decreases with increase in concentration.

Comparative study of inhibition efficiencies of *Nypa Fruticans wurmb* and DPC show that they exhibit similar inhibition properties. From the result of weight loss against time, corrosion rate, half-life for both additives metal dissolution was inhibited to a comparative degree. The inhibition action of leaves, fruits, bark of trees and plant has been attributed to tannins (Loto 1998) and nitrogenous compounds in the extracts. The molecular structure of DPC reveals an amine type organic compound with nitrogen and phenyl groups. Both group have been found effective for corrosion inhibition and inhibitors of high molecular weight (carbon atom 12 and above) are better inhibitors than the methyl derivative (Finley and Hackerman 1960).

It may be reasonable to suggest that corrosion inhibition by both additives may be due to bulky nitrogenous organic compound or tannins, which contain polar groups. For *Nypa fruticans* extract, these may have effected inhibition through nitrogen bond on metal surface with the formation of *Nypa* - Zn^{2+} complex on the surface of the metal. Nitrogen atoms adsorbed on the metal surface through an unshared pair of electron may be responsible for film formation in DPC.

Conclusion

Nypa Fruticans Wurmb leaves extract and DPC inhibit the corrosion of zinc comparatively. Inhibition though generally low was maximum at an optimum concentration and low temperature. This may be due to protonation of the hydrogen evolution process or

the formation of a soluble complex on zinc surface by molecules of *Nypa Fruticans* Wurmb or DPC.

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