

Inhibition of Acid Corrosion of Zinc using *Butryuspermuyum Parkii* Leaf Extract

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Abstract

A new corrosion inhibitor *Butryuspermumparkii* (BSP) leaf extract, was tested for zinc metal in 0.05M H₂SO₄, solution using weight loss techniques. The adsorption of BSP on the zinc surface in H₂SO₄ solution follows a Langmuir and Temkin's adsorption isotherms. The effect of temperature indicated that the corrosion rate and the inhibitor efficiency (%I) are temperature dependent in the range of 308K and 318K. Increase in temperature increased the corrosion rate but decreased the inhibitor efficiency (%I) in the absence and presence of the inhibitor. The kinetic data obtained indicates that the adsorption follows a first order type of reaction. Physisorption has been proposed for the inhibitor.

Key Words: Corrosion inhibitor, *Butryuspermumparkii*, Zinc metal, Langmuir isotherm, Temkin's model

Introduction

Corrosion inhibitors are chemical additives, which when added to a corrosive aqueous environment reduces the rate of metal wastage. They can also be referred to as substances that when added in small amounts to corrosiveness. Organic compounds containing hetero atom (N, S and O) have been proven to be very good inhibitors through adsorption on metallic surface by these atoms, lone pairs of electrons (Yadav, 1999, Ebenso *et al*, 1999, Onen, 2004).

The use of inorganic compounds and their derivatives as inhibitors for aqueous corrosion of metals have been reported by the various authors (Iboket *al*, 1995 and Ekpeet *al*, 1995). Reporting on the effect of molecular structure on the efficiency of amides and thiocarbonyl groups observed that their inhibitors efficiency are

compounds that do not contain them, N.S.O. surfactant have also been reported as a good corrosion inhibitors (Wang *et al*, 2005).

Dyes (azo, heterocyclic, xanthenes, cyanine and anthraquinoid) have been reported by several workers as corrosion inhibitors of aluminium and mild steel in acid corrodents (Ita and Edem 2000; Ebenso *et al*, 2004 and Onen, 2006) the structural features in dyes that impart colour are > C = C<, N=O, N = N, C = O, aromatic rings and NO₂. Most of the synthetic compounds (organic, inorganic etc.) used as inhibitors are very expensive and equally source of several health hazards. Their toxic characteristics limit the field of their application. It has become necessary therefore to find less expensive and non – hazardous inhibitors for the protection of materials/alloys against corrosion.

Zinc occurs in earth's crust to the extent of 132 ppm (part per million) by weight. It is the twenty fourth most abundant elements. It is found between group 2 and 3 in the periodic table and period 4 of the periodic table and are called 3d block metals because all the valence electrons are distributed in the 3d orbital (Lee, 1996, Ababio, 2001). Zinc is found in Canada, Australia China, former Soviet Union, Peru, U.S.A, Ogoja (Cross River State), Abakaliki (Ebonyi State) along Benue River in Adamawa State (Lee, 1996, Ababio, 2001). Zinc is used for galvanizing iron and steel to prevent rusting, in making alloys such as brass, in making dry cells and as anode in ordinary acidic dry cells and its alkaline version (Ababio, 2001). When metallic zinc is exposed to water, oxygen and other agents, metallic corrosion results loss of structural integrity or degradation in surface appearance is observed (Kristoff, 2009). It also leads to the reduction of the metal thickness, loss of mechanical strength and structural failure or break down.

Shea-butter (*Butryospermumparkii*) is called 'Kadanya' in Hausa and bears fruits by early November. The fruit, which is green in colour has a 41.3g/100g of carbohydrates 0.7 – 1.3g of proteins, 196.1mg/100g of ascorbic acid, 1.93g/ 100g of iron and 36.4 mg/100 of ascorbic acid, 1.93g/100g of calcium respectively (FAO, 1988). The fruit pulp is an available food source and it is also taken for its slightly laxative properties (Soladoyeet al, 1989).

From the availability literature, the use of *Butryospermumparkii*, BSP leaf extract has not been reported as a corrosion inhibitor. This study is therefore aimed at evaluating the inhibitory characteristics of the leaf extract of *Butryospermumparkii* on zinc corrosion in acidic solution using weight loss technique at 308K and 318K.

The choice of BSP is based on the fact that it is readily available all year round.

Materials And Method

Materials Preparation

The zinc sheets for this investigation were obtained from Mubi Market, Adamawa State. The zinc sheets were mechanically press cut into 5.0 x 4.0 cm and thickness of 6.0×10^{-3} cm. The sheets were used without further polishing. They were however, degreased in absolute ethanol, dried in propanone and stored in moisture free desiccators before corrosion studies commenced. The average mass of the coupons was 7.98 – 8.02 g and total surface area of the coupons exposed was 18.4cm^2 (Onen, 2006).

Shea butter (*butryospermumparkii*) leaves were obtained from Muva – village in Mubi – North Local Government Area of Adamawa State. The leaves were washed, dried at room temperature 25°C (298K) and pulverized. The leaves were pulverized and sieved. The fine particles of the leaves were extracted with methanol and water respectively. The leaf powder, extracted in a conical flask after 24 hours, gave a better yield in ethanol than in water. A concentration range of 1.0, 3.0, 5.0, 7.0 and 10.0mg/1000mL of the extracts in 30 mL methanol – 70 mL water mixture was prepared and used as inhibitors at 308K and 318K

Weight loss Measurements

Gravimetric measurements were carried out as earlier reported by Onen (2004). The tests were performed in triplicate to guarantee the reliability of the results and the mean value of weight loss is reported. The reproducibility of the experiment was higher than 94%.

Corrosion rates for zinc in 0.50M MH_2SO_4 and different concentrations of

BSP were determined for 168 hours immersion period from weight loss data using the formula

$$C R (mdd) = \Delta W / DAT \quad (1)$$

where ΔW is weight loss (g), D is the density of the metal, A is the area of zinc coupons and T is the time of exposure (hours) (Onen, 2004).

The percent inhibition efficiency (%I) was calculated using the expression

$$\%I = \frac{\rho_0 - \rho_1}{\rho_0} \times 100 \quad (2)$$

where ρ_0 and ρ_1 are the corrosion rates in uninhibited and inhibited in H_2SO_4 solutions respectively (Onen, 2004).

The surface coverage (θ) at each concentration of the inhibitor was determined using the relation

$$\theta = 1 - \frac{\rho_1}{\rho_0} \quad (3)$$

Where ρ_0 and ρ_1 are corrosion, rates, the absence and presence respectively of inhibitor in H_2SO_4 solutions at the same temperature (Onen, 2004).

Results and Discussion

Variation of Corrosion rates, Inhibition efficiency and surface coverage with Temperature and Concentration

The values of weight loss, corrosion rate (mdd), inhibition efficiency (%I) and the surface coverage (θ) for zinc in 0.05M H_2SO_4 with *Butryospermumparki* leaf extract and blank are presented in Table 1. Corrosion rate (mdd) was observed to be highest in the blank at 308K. Similar trend was observed at 318K but with higher values of corrosion rate. Plot of mean weight loss of zinc specimen against blank and inhibitor (BSP leaf extract) concentrations in 0.05M H_2SO_4 solution for 168 hours at 308K is shown in figure 1. A bar chart showing inhibition efficiency (%I) against inhibitor (BSP leaf extract) conc. In 0.05M H_2SO_4 solution for zinc at 308K and 318K is reflected in figure 2.

From Table 1 and Figure. 2, it is observed that the inhibition efficiency (%I) and surface coverage (θ) for zinc metal increase with increasing temperature.

Table 1: Corrosion Parameters for Zinc in 0.05M H_2SO_4 containing BSP Leaf Extract from Weight loss measurements

Inhibitor Conc. (mgdm ⁻³)	Weight loss (mg)		Corrosion rates (mgdm ⁻³ d ⁻¹) x 10 ⁻⁵		Inhibition efficiency (%I)		Surface coverage (θ)	
	308K	318K	308K	318K	308K	318K	308K	318K
BLANK	0.270	0.273	7.89	7.97	-	-	-	-
BSP								
1.0	0.139	0.145	4.06	4.24	48.52±1.00	46.89±0.23	0.49	0.47
3.0	0.129	0.136	3.77	3.97	52.22±0.35	50.18±0.42	0.52	0.50
5.0	0.116	0.126	3.39	3.68	57.04±1.20	53.85±0.80	0.57	0.54
7.0	0.112	0.117	3.27	3.42	58.52±0.90	57.14±0.62	0.59	0.57

10.0	0.106	0.111	3.10	3.24	60.74±2.15	59.34±1.00	0.61	0.59
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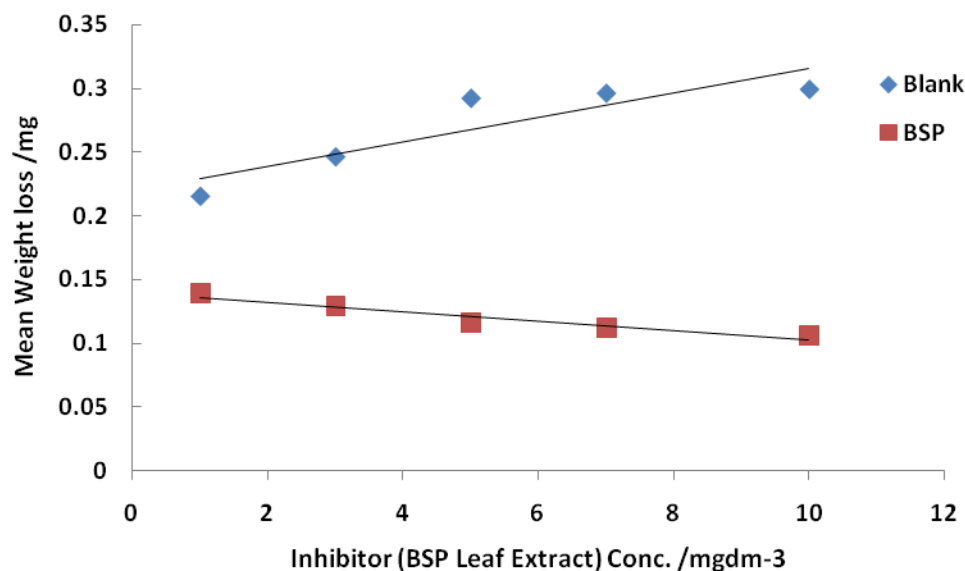


Figure 1: Plot of Mean Weight loss of Zinc specimen versus Blank and Inhibitor (BSP) Conc. in 0.05M H₂SO₄ Solution for 168 hours at 308K

These observations are in agreement with those made by several researchers (Ekpe et al 1997; Onen, 2004 and Onen, 2006) and may be attributed to an increase in the rate of ionization and diffusion of the active ions in the corrosion process the observed trend may also be due to the fact that rates of chemical reactions generally increase with acid concentration and temperature.

Table 1 and figure 2 reveal that the efficiencies were highest at 10.0mgdm⁻³ BSP (highest concentrations of BSP studied). Thus, efficiency increases with increasing BSP concentration and at low temperature indicating that BSP inhibited Zinc corrosion to an appreciable extent. The corrosion rate was highest in the blank at 308K. Similar trend was observed at 318K but with higher values of corrosion rate. With the addition of inhibitor (BSP) the

corrosion rate decreased with inhibition efficiency (%I) and surface coverage (Θ)

increased significantly with increasing concentration in the other:

1.0 mgdm⁻³ (48.52%I) and 4.06 x 10⁻⁵ mdd corrosion rate) < 3.0 mgdm⁻³ (52.22%I) and 3.77 x 10⁻⁵mdd corrosion rate) 5.0mgdm⁻³ (57.04%I ad 3.39 x 10⁻⁵mdd corrosion rate) < 7.0 mgdm⁻³ (58.32%I and 3.27 x 10⁻⁵mdd corrosion rate) < 10.0mgdm⁻³ (60.74%I_E and 3.10 X 10⁻⁵mdd corrosion rate for zinc of BSP inhibitor). However, inhibition efficiency (%I) and surface coverage decrease with increasing temperature (308K and 318K) with 60.74 and 59.34 at 308K and 318K for BSP inhibitor.

The decrease in inhibition efficiency with increasing temperature shows that the time for the weight loss on the introduction

of BSP as an inhibitor of metal zinc surface becomes shorter. This assertion agrees with the findings of Ebenso *et al* (1999) and Onen and Nwifo (2007). The effectiveness of BSP as a corrosion inhibitor is due to the presence of some phytochemicals- alkaloids, phenols, saponins, tannins etc which contains $-C=O$, $C=N$, $C=OH$, $Ph-OH$ e.t.c

functional groups (Rozenfield, 1981, Wallace-Bruce, 1995)). These groups adsorb on the zinc surface through their lone pairs of electrons. The lone pairs of electrons are delocalized and thus, produce resonance stabilization energies which stabilize the compounds. This assertion agrees with earlier report by El-Naggar (2007).

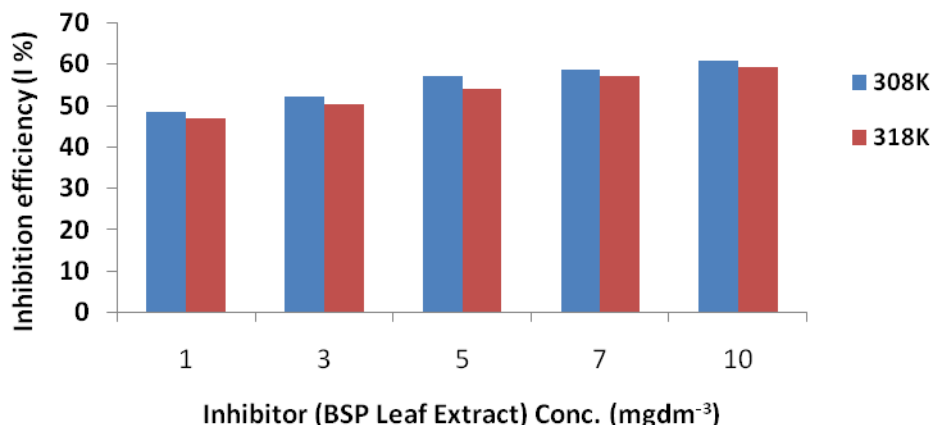


Figure 2: Plot of Inhibition efficiency (%I) against Inhibitor (BSP leaf extract) Conc. (mgdm⁻³) in 0.05M H₂SO₄ Solution for Zinc Corrosion at 308K and 318K.

Thermodynamic and Kinetic Analysis of the Results

The activation energy E_a recorded in Table 2 was calculated using the equation.

$$E_a = \left[2.303 R \frac{T_1 T_2}{T_2 - T_1} \right] \log \frac{\rho_2}{\rho_1} \quad (4)$$

where R is the gas constant, ρ_1 and ρ_2 are corrosion rates at T_1 and T_2 respectively (Akmetovet *al*, 1989). The values of rate constant k , also recorded in Table 2 were obtained from plots of $\log C$ against time, t (days). The half – life, $t_{1/2}$ value on Table 2 were computed from the expression.

$$t_{1/2} = 0.693/k \quad (5)$$

The values of heat of adsorption, Q_{ads} (Table 2) were obtained from the relation:

$$Q_{ads} = 19.147 \left[\log \frac{\theta_2}{1-\theta_2} - \log \frac{\theta_1}{1-\theta_1} \right] \left[\frac{T_1 T_2}{T_2 - T_1} \right] \quad (6)$$

where θ_1 and θ_2 are degree of surface coverage at 308K and 318K respectively (Yadav, 1999 and Onen, 2007). All the values of Q_{ads} are negative for zinc corrosion as shown in Table 2. This is an indication that the adsorption process is spontaneous. This implies also that the inhibition process is an exothermic in nature. More so, the inhibition efficiency decrease with increase in temperature which agrees with earlier findings by other authors (Ebenso *et al*, 1999 and Onen, 2006).

Table 2: Kinetic data for zinc corrosion in 0.05 MH₂SO₄ with inhibitor (BSP leaf extract) and blank at 308K and 318K

System/Conc. (mg/dm ⁻³)	Rate constant (k) (s ⁻¹) x 10 ⁻³		Half-life, t _{1/2} (secs.)		Activation energy of absorption, Ea kJmol ⁻¹		Heat of Adsorption Q _{ads} , (kJ mol ⁻¹)	
	308K	318K	308K	318K	308K	318K	308K	318K
Blank	4.96	5.50	1.40	1.26	0.82		-6.53	
BSP								
1.0	9.33	9.50	0.74	0.73	0.87		-6.52	
3.0	10.17	10.67	0.68	0.65	4.21		-9.90	
5.0	10.67	11.00	0.65	0.63	6.69		-6.69	
7.0	11.00	11.83	0.63	0.69	3.65		-6.79	
10.0	12.17	12.50	0.57	0.55	3.60		-7.29	
Mean					<u>3.80</u>		<u>-7.29</u>	

Adsorption Model(s)

It is evident from Table 1 and figure 2 that the inhibition efficiency (%I_E) and surface coverage (Θ) increased with inhibitor concentration and decreased with increasing temperature. This further confirms physical adsorption (physisorption) mechanism for the inhibition process. The high surface coverage's observed of high inhibitor course is due to very strong interaction between the adsorbed species. The surface coverage data implies that the adsorption of BSP and MFGD (inhibitors) at the zinc interface may

be due to electrostatic force between the atoms of metal surface and the adsorbate. This observation agrees with assertion earlier made (Ekpeet *al* 1995; Ekpeet *al* 1997, Onen, 2006 and Onen and Nwufo 2007).

The extent of adsorption of inhibitor molecules on the zinc metal surface was further establish by plotting log C/Θ against concentration, C at 308K and 318K (figure 3). Similarly, Temkin's isotherm was plotted as log C against the surface coverage (Θ) values at 308 and 318K (figure 4). The data obtained from this study between 308K and

318K, were found to fit Langmuir and Temkin's adsorption models. This is an indication that corrosion inhibition of zinc is due to the formation and maintenance of a

protective film on metal surface. This affirms the assertion made by Ebenso *et al* (2004) and enunciated in previous study by Onen (2007).

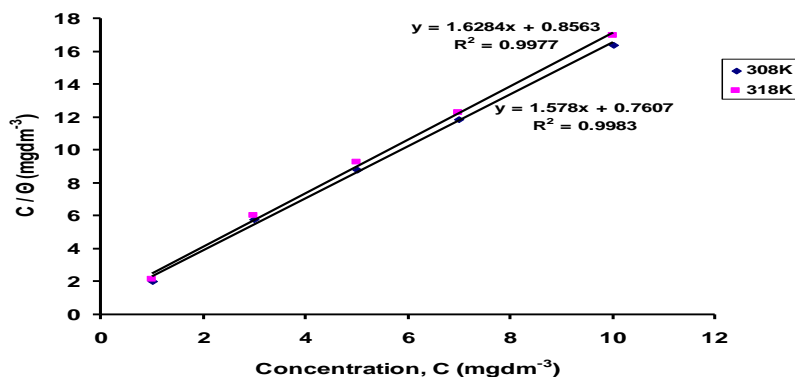


Figure 3: Langmuir Adsorption Isotherm on Zinc surface of BSP – leaf extract in 0.05M H₂SO₄ solution for 168 hours at 308K and 318K.

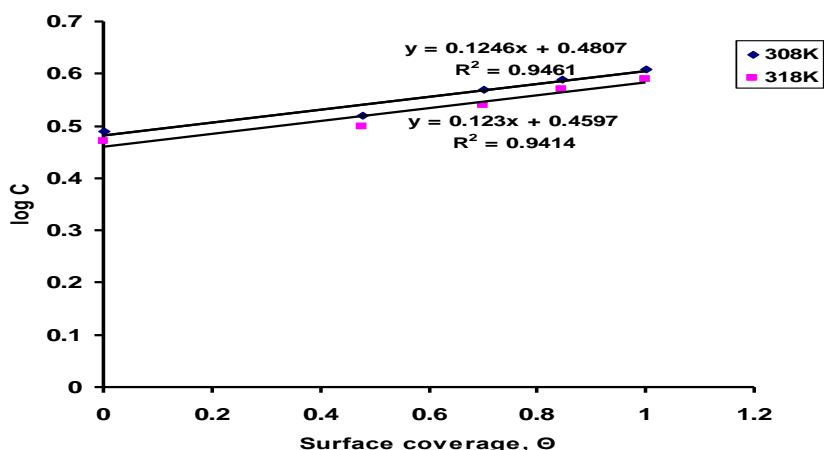


Figure 5: Temkin's Adsorption Model for zinc in 0.05M H₂SO₄ containing BSP at 308K and 318K.

Mechanism of Inhibition of Zinc corrosion

Table 2 shows the calculated values of rate constant (k), half-life, t_{1/2} and activation energy, Ea. The average value of the activation energy Ea of BSP is 3.80 kJmol⁻¹ for zinc corrosion which is lower than 40.0 kJmol⁻¹. This implies that, the inhibitor is physically adsorbed on zinc

surface. Physical adsorption requires that the average Ea to be ≥ 40.0 kJmol⁻¹ and the percentage inhibition efficient should increase at lower temperatures. This agrees with earlier report by Onen (2006). Figure 1 reflect the anodic reaction order with respect to zinc, i.e , the anodic reaction (equation 7).

$$\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^- \quad (7)$$

It could be said that the inhibition of zinc corrosion in H₂SO₄ solution by BSP influenced the anodic reaction order.

Conclusion

The extract of BSP inhibits the corrosion of zinc in 0.05M H₂SO₄ solutions, with inhibition efficiency of 60.74±2.15% at 10 mg extract concentration and the inhibition efficiency decreased with increase in temperature. The adsorption of the inhibitor molecules was consistent with Langmuir and Temkin's models and a first order kinetics was obtained from the kinetics consideration of the weight loss measurements.

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