International Journal of Scientific Engineering and Research (IJSER)
ISSN (Online): 2347-3878
Impact Factor (2018): 5.426

Thermodynamics Study of Inhibitory Action of Lignin Extract from *Gmelina arborea* on the Corrosion of Mild Steel in Dilute Hydrochloric Acid

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Abstract: ***Inhibitive effect of Lignin extract from Gmelina arborea bark on the corrosion of mild steel in 1M Hydrochloric Acid solution was studied by weight loss method with various periods of contact and temperature. The study revealed that the percentage inhibition efficiency increased with increase in inhibitor concentration. The temperature studies reflect that the adsorption of inhibitor on metal surface takes place via physisorption and through a spontaneous process. The inhibition at the metal surface was confirmed by X- ray diffraction examination.***

Keywords: Lignin extract, mild steel, corrosion inhibitor, thermodynamic studies, Gmelina arborea

1. Introduction

Metallic materials are still the most widely used group of materials particularly in both mechanical engineering and transportation industry. However, the usefulness of metals and its alloys are constrained by corrosion (Buchweishaija, 2009). Corrosion is an undesirable phenomenon that ought to be prevented using corrosion inhibitors. Corrosion inhibitors have continued to play a crucial role in the industry where metals are exposed to acid environment. Plant extracts have been receiving increasing attention as green corrosion inhibitors because of their richness in natural biodegradable chemicals that are environmentally friendly (Olusegun *et al*., 2011). This paper reports the inhibition of corrosion of mild steel in dilute HCl solution using lignin extracted from *Gmelina Arborea*.

2. Experiments

2.1 Extraction of Lignin

Gmelina arborea tree readily available in Federal Polytechnic Nekede, Owerri, Imo State Nigeria was utilized as the source of lignin. The *Gmelina arborea* bark were collected from the tree, cut into small pieces and were sun dried for one week. The dried samples were then pulverized into fine powder using an electric grinding machine. The wood sample was subjected to extraction with 15% (w/v) NaOH at 80^{o}C for 2 hours with continuous agitation. The ratio of wood sample to liquid in the extraction was 1:10. After 2 hours, the mixture was removed, allowed to cool for 12 hours after which it was filtered and the filtrate was acidified by drop-wise addition of 40% H_2SO_4 to a pH of 2.0. The lignin was isolated by precipitation and was filtered, washed with 70% ethanol and dried in an oven at 60^{o}C to obtain pure lignin extract of *Gmelina arborea* bark.

2.2 Solution Preparation

Solution of HCl was prepared by dilution of concentrated HCL 37% (w/v) from BDH using deionized water. All chemicals and solvents used were of analytical reagent grade. All solutions were prepared using deionized water.

2.3 Coupons Preparation

The metal coupon used in this study was mild steel. Rectangular coupons of mild steel were cut into 3.0mm x 3.0mm x 0.7mm dimensions. Pre-treatment of the surface of coupons was carried out by cleaning with emery paper, rinsed with deionized water, degreased with acetone, dried and stored in a dessicator prior to use.

2.4 Weight Loss Measurements

The polished and pre-weighed mild steel coupons were immersed in 100ml of 1M HCl solutions of the respective inhibitor/blank solutions maintained at 303, 313, 323, 333 and 343K in a thermostated bath for 2 hours with 1.0 % lignin extract. After which the coupons were removed washed, cleaned and weighed. Another set of experiment was carried out at room temperature for various concentrations of 0.5, 1.0, 1.5, 2.0 and 2.5% of lignin respectively in 1M HCl for 12 days. The coupons immersed in these solutions were weighed at two days intervals. Mass loss and corrosion rate measurements were deployed to evaluate the corrosion behavior of the test samples. The corrosion rate (g/cm^2/hr) and Inhibition efficiency (%) were calculated from the relationship:

$$\text{Corrosion Rate (CR)} = W/At \ (g/cm^2/hr) \quad (1)$$

Where, W = Weight loss of the mild steel after time t (grams), A = the area of the mild steel coupon (cm^2), t = the time of immersion (hours)

$$\text{Inhibition Efficiency IE (\%)} = 1 - W_1/W_2 \times 100 \quad (2)$$

2.5 FT – IR Analysis

The FT-IR analysis of the pure Lignin extract and Lignin extract after corrosion were studied using Fourier Transform Infrared Spectrophotometer (Happ-Genzel Model) to determine the functional groups present in the lignin and responsible for its inhibitive properties.

2.6 XRD Analysis

X-ray diffraction (XRD) analysis was carried out on the pure mild steel, mild steel with inhibition (inhibitor) and mild steel without inhibition (blank) for phase identification of the mild steel.

3. Results and Discussion

3.1 Effect of Concentration on Inhibition Efficiency and Corrosion Rate of Lignin Extract on Mild Steel

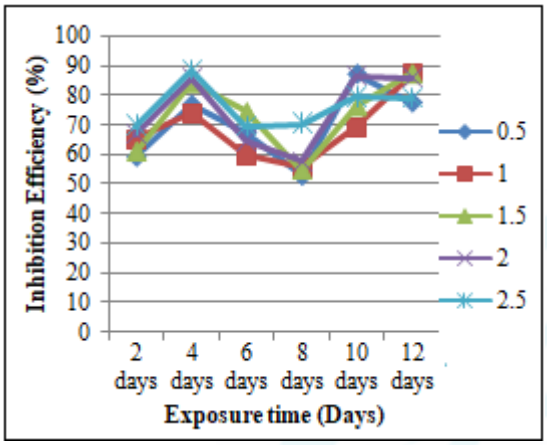

Figure 1: Variation of inhibition efficiency with exposure time for corrosion of mild steel in 1M HCl

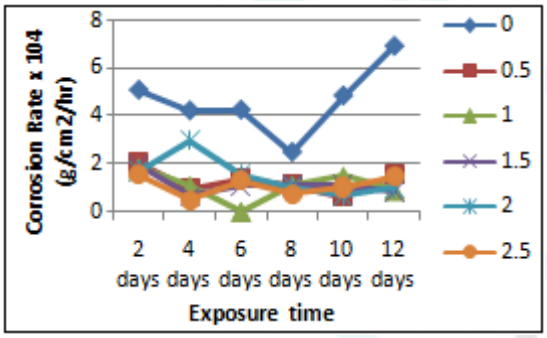

Figure 2: Variation of corrosion rate with exposure time for corrosion of mild steel in 1M HCl

The variation of inhibition efficiency and corrosion rate of mild steel in 1M HCl in the absence and presence of various concentrations of lignin extract of *Gmelina arborea* bark for 2days, 4days, 6days, 8days, 10days and 12days are shown in figure 1 and 2. The result showed that the corrosion rate of mild steel in 1M HCl decreases with increase in the concentration of the extract at all days, indicating that the lignin extract of *Gmelina arborea* bark inhibited the corrosion of mild steel in 1M HCl. Similar results have been obtained by other researchers using lignin extract (Alaneme and Olusegun, 2012) and (Altwaiq *et al.*, 2011). The inhibition efficiency of the lignin extracts on the mild steel increases with increase in concentration of the extract. The inhibitive effect of the lignin extract is attributed to the presence of some functional groups in the extract as revealed by the Infrared Spectrophotometer result as shown in Figure 5.

3.2 Effect of Temperature on Corrosion Rate

The stability and mechanism of adsorption of the lignin extract on the mild steel surface was studied by evaluating the variation of corrosion rate and inhibition efficiency with temperature (303- 343K) (Figure 3 and 4).

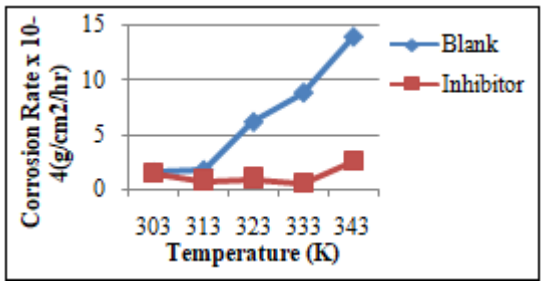

Figure 3: Variation of corrosion rate with temperature for corrosion of mild steel in 1M HCl

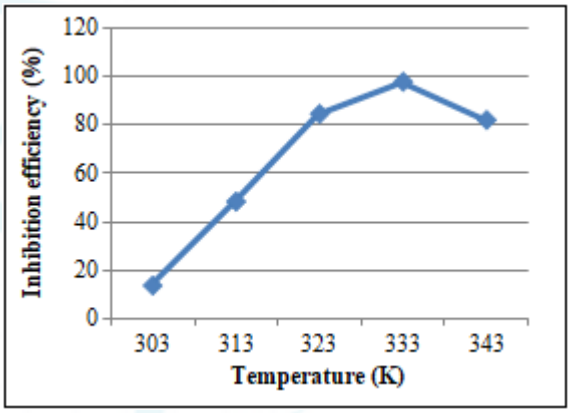

Figure 4: Variation of inhibition efficiency with temperature for corrosion of mild steel in 1M HCl

It is observed in figure 4 that the inhibition efficiency of lignin extracts reached equilibrium of 97.50% at 60^{o}C and decreased to 81.80% at 70^{o}C which shows the tendency for partial desorption of the inhibitor from metal surface. However, inhibition efficiency of the lignin extract ranged between 13.60% - 97.50% for the temperature range as shown in the diagram.

3.3 Analysis of FT-IR Spectra

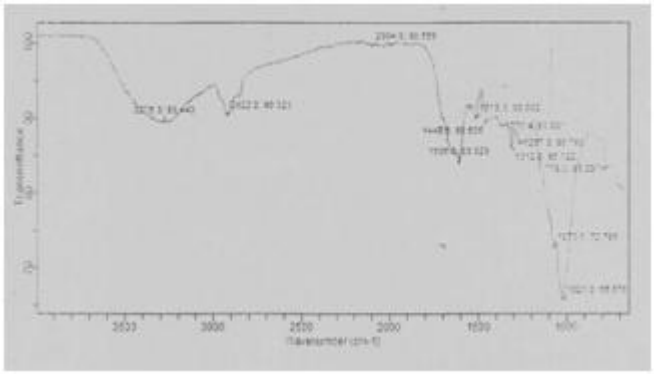

Figure 5: IR spectrum of pure lignin extract

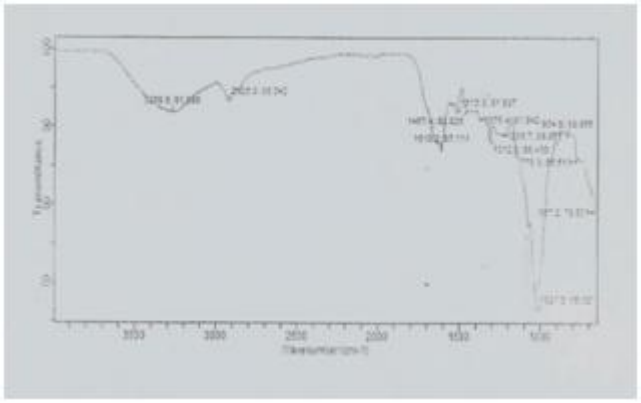

Figure 6: IR spectrum of lignin extract after corrosion

FT-IR spectra of pure lignin and lignin extract after corrosion is given in figure 5 and 6. The OH stretch of alcohol frequency decreased from 3376.3cm^{-1} to 3268.9cm^{-1}, frequency of C-O stretching of ester also decreased from 1267.3cm^{-1} to 1233.7cm^{-1}. C-H stretching frequency of methylene group increased from 2922cm^{-1} to 2926cm^{-1}, 1449.9cm^{-1} C-H stretch of CH_3 group increased to 1457.4cm^{-1} and N-H bending of primary amine increased from 1606.6cm^{-1} to 1610.2cm^{-1}.

The band due to conjugated triple bond of C≡C stretching at 2094cm^{-1} and C-O stretching of phenol at 1072.6cm^{-1} did not appear in IR spectrum of lignin after corrosion which may have been used in the formation of a metal-organic adsorption on the surface of the mild steel. These shifts in frequencies suggest that there is interaction between the metal and the inhibitor (Petchiammal *et al*., 2013). The changes in the FT-IR spectrum of the lignin extract after corrosion study are significant. The increase in frequencies after corrosion indicates formation of Fe^{2+} - lignin extract complex on the metal surface due to interaction of Fe^{2+} formed on the anodic sites of the metal surface (Sribharathy *et al*., 2013). The adsorption of the extract can also be attributed to displacement of water molecules on the surface of the metal.

3.4 X-ray Diffraction Analysis (XRD)

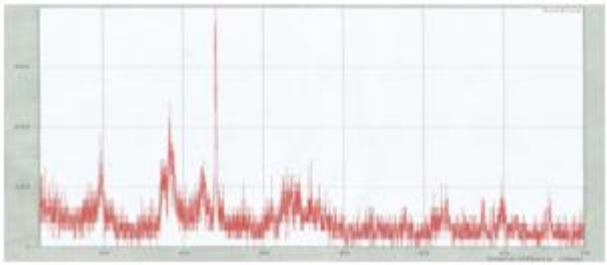

Figure 7: XRD of mild steel after corrosion without inhibitor

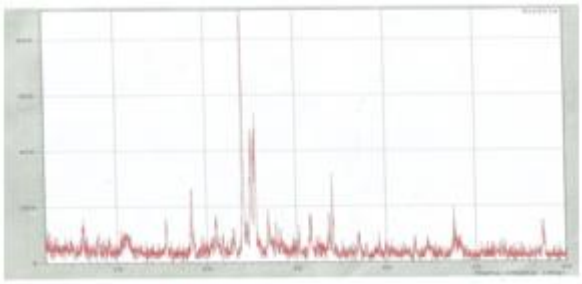

Figure 8: XRD of mild steel after corrosion with inhibitor

The XRD diffractogram of polished surface of mild steel exposed in 1M HCl solution in absence and presence of 1% lignin extract are shown in figure 7 and 8. In comparism of XRD diffractogram in the peak intensity of the polished mild steel obtained, the diffractogram exhibited high intensity interference on the mild steel in absence of inhibitor in 1M HCl. These explain the fact that the surface was already undergoing a localized attack, whereas there was low intensity interference on the surface of mild steel in the presence of inhibitor. This result confirms that lignin extract inhibited corrosion of mild steel through adsorption of the inhibition molecules on the metal surface.

3.5 Thermodynamic and Adsorption Studies

The adsorption characteristics of lignin extract were studied by fitting data obtained for the degree of surface coverage of the inhibitor into Langmuir adsorption isotherm. The test revealed that the adsorption characteristics of the inhibitor fitted Langmuir adsorption isotherm. Langmuir isotherm plot of log (C/θ) against log C was linear with the intercept equal to -logK_{ads} for the extract. The estimated values for K_{ads} and R^2 are 1.55 and 0.867 respectively. The high adsorption equilibrium constant K_{ads} and correlation coefficient R^2 show that the mechanism of corrosion inhibition is due to the formation and maintenance of a protective film on the metal surface and that the additive covers both the anodic and cathodic sites through uniform adsorption (Wabanne and Okafor, 2001).

The equilibrium adsorption constant of adsorption obtained from the intercept of the Langmuir adsorption isotherm is related to the standard free energy of adsorption according to the equation 3.

$$\Delta G^0_{ads} = -2.303RT \log (55.5\ K_{ads}) \quad (3)$$

Where R is the gas constant, T is the temperature and K is the equilibrium constant of adsorption.

Calculated values of the free energy are presented in Table. From the results obtained, the free energies are negative and less than the threshold value of - 40kJ/mol required for the mechanism of chemical adsorption. Generally, values of ΔG^0_{ads} between 0 and – 20kJ/mol are consistent with electrostatic interaction between charged molecules and charged metal which indicates, the adsorption of lignin extract on mild steel surface is spontaneous with a mechanism of physisorption (Olasehinde *et al*., 2012 and Siaka *et al*, 2012) and the adsorbed layer was stable (Petchiammal *et al*., 2013).

Table 1: The free energy, enthalpy and entropy of adsorptions

Temp (K)	$\Delta G°_{ads}$ (KJ/mol)	ΔH (kJ/mol)		ΔS (kJ/mol/K)	
303	-11.2237	Without inhibitor	With inhibitor	Without inhibitor	With inhibitor
313	-11.5941	32.11	14.84	220.77	64.85
323	-11.9645				
333	-12.3349				
343	-12.7053				

3.6 Enthalpy and Entropy

Thermodynamic parameters such as enthalpy (ΔH) and entropy (ΔS) of activation of corrosion process was evaluated from the effect of temperature. The enthalpy and entropy of activation of corrosion process was calculated from the equation 4:

$$\log CR/T = \log (R/nh) + \Delta s/2.303R - \Delta H/2.303RT \quad (4)$$

Where CR is the corrosion rate, T is the absolute temperature, R is the molar gas constant, 'n' is Avogadro's constant; 'h' is the Planck's constant. A graph of log CR/T against 1/T is a straight line graph with a slope (-ΔH/2.303RT) and an intercept (log (R/nh) + ΔH/2.303R). From the slope and intercept, ΔH and ΔS were calculated as reported by Abiola et al, 2007.

The results presented in Table 1 shows that the enthalpy of activation was positive which reflects the endothermic nature of the mild steel dissolution process. Also, the entropy of activation was positive indicating that the activation complex represents association steps and that the reaction was spontaneous and feasible

4. Conclusion

Lignin extract from Gmelina arborea bark was found to be an efficient inhibitor for corrosion of mild steel in 1M HCl. The corrosion rates were observed to decrease with increase in concentration of the lignin extract but increases with temperature. X-ray diffraction analysis shows high intensity interference on the mild steel in absence of inhibitor in 1m HCl. FT-IR analysis shows the changes in the FT-IR spectrum of the lignin extract after corrosion study are significant. Inhibition efficiency increases with inhibitor concentration and the maximum percentage inhibition of 87.75% was achieved at concentration of 1.5v/v.

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