Adsorption and Inhibitive properties of Ficus sycomorus gum on the corrosion of aluminium in HCl

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Abstract- *Ficus sycomorus* gum was tapped, collected and purified. The adsorption properties and inhibition potentials of the gum on aluminium in HCl was studied at different temperature of 303K and 333K using gravimetric method. The inhibition efficiencies of the gum increase with increase in concentration and decrease with increase in temperature and period of immersion. Values of activation energy of the inhibited corrosion reaction of aluminium were greater than the value obtained for the blank. Thermodynamic consideration revealed that adsorption of the inhibitor on aluminium surface was first order, exothermic, spontaneous and was through the mechanism of physical adsorption. The adsorption characteristic of the inhibitor was best described by the Langmuir adsorption isotherm.

Index Terms- *Ficus sycomorus,* adsorption, inhibition, aluminium.

I. Introduction

Gums are defined as molecular structures, tending to high molecular mass, usually with colloidal properties, such that, in an appropriate solvent, they produce gels or suspensions of high viscosity or solutions of low matter content that can absorb water at ten times their weight [1]. Generally, they contain carbon, hydrogen, oxygen, calcium, magnesium and potassium in the form of metallic salts which occur in various organic compounds. However it has been established that gums contain polysaccharides and some of their constituents.

It is very evident that gums have very vast application in pharmaceutical, food industries and recently as corrosion inhibitors. Green corrosion inhibitors are biodegradable and do not contain heavy metals or other toxic compounds. Some research groups have reported the successful use of naturally occurring substances to inhibit the corrosion of metals in acidic and alkaline environment. Green inhibitors are products of living organisms and are preferred because they are cheap, biodegradable and comply with required environmental standards that vitiated the abolition of chromates and other non-eco-friendly inhibitors. Available literature have also indicated that a wide range of natural polymers have been investigated as possible corrosion inhibitors. The role of inhibitors is to form a barrier of one or several molecular layers against acid attack [2]. This protective action is often associated with chemical and/or physical adsorption involving a variation in the charge of the adsorbed substance and transfer of charge from one phase to the other. Sulphur and/or nitrogen-containing heterocyclic compounds with various substituents are considered to be effective corrosion inhibitors [3].

The consequences of corrosion are many and varied and the effects of these on the safe, reliable and efficient operation of equipment or structures are often more serious than simple loss of a mass of a metal. Failures of various kinds and the need for expensive replacements may occur even though the amount of metal destroyed is quite small [4]. The corrosion of metals is one of the most significant problems faced by advanced industrial societies. It has been estimated that in the United States alone, the losses of corrosion annually amounts to tens of billions of dollars [5]. Therefore, there is a need to protect metals against corrosion. The use of inhibitors has been found to be one of the best options available for the protection of metals against corrosion [6]. Corrosion can be controlled by the addition of chemical substances called inhibitors into acid media. By definition, an inhibitor is a chemical compound which when added in a small amount to the corrosive environment alters the cathodic and or anodic reaction and subsequently reduces the corrosion rate [7]. Interaction between valuable metals (such as Al) and aggressive media (such as acid, base or salt) is a serious impediment that may risk cost benefit analysis in the operation of some industries. This is because, corrosion of these materials, if not reduced can induce damages to industrial installations [8].

Plant gum exudates from *Commiphora pedunculata* (CP) [2], *Raphia hookeri* (RH) [4], gum arabic [3], guar gum [9], *Anogessus leocarpus* (AL) [11] *and Ficus glumosa* (FG) have been reported as good corrosion inhibitors. The inhibitive effect of *Ficus glumosa* gum (FG) in the corrosion of mild steel in H2SO4 medium has been studied using the weight loss, gasometric, thermometric and scanning electron microscopy (SEM) techniques. They found that FG gum is a good adsorption inhibitor. An investigation into the mode of adsorption of the gum revealed that the adsorption is exothermic, spontaneous and fitted the mechanism of physical adsorption. Chemical constituents and corrosion inhibition potential of *Daniella olliverri* (DO) gum exudates were investigated [6] using weight loss and FTIR methods and the results obtained showed that the gum is acidic, brownish in colour, ionic and highly soluble in water but insoluble in acetone, chloroform and ethanol. GCMS spectrum of the gum indicated the presence of sucrose, dihex-5-en-2-yl phthalate, stearic acid, 2,6-dimethyl-4-nitrophenol and (E)-hexadec-9-enoic acid.

Therefore there is a need to study the adsorption properties of Ficus sycomorus (Baure in Local Hausa dialect) gum and the potential of the gum as corrosion inhibitor for aluminium in HCl. The present paper aims at studying the potentials of *Ficus sycomorus* gum exudate as corrosion inhibitor by weight loss method. The effects of temperature on corrosion and inhibition processes were discussed and thermodynamic parameters governing the adsorption process were also calculated.

II. MATERIALS AND METHODS

Materials

Materials used for the study were aluminium sheets of composition (determined by x-ray diffraction technique); Al (99.94), Cu (0.01), Mg (0.02), Si (0.03), Mn (0.02) and Zn (0.01). The aluminium sheets were mechanically press-cut into different coupons each of dimension, 5×4×0.05 cm. Each coupon used was degreased by washing with ethanol, cleaned with acetone and allowed to dry in air before preservation in a desiccator. All reagents used for the study were of analar grade and double distilled water was used for their preparation.

Tapping and collection of the gum

The crude *Ficus sycomorus* gum was obtained from Uran village in Gezawa Local Government Area of Kano State, Nigeria. The gum was collected from the tree by tapping [12] around mid-December during the day time.

Purification of the gum

The procedure adopted for the purification of the gum was similar to that used by [13] but with some modifications. The gum was dried in an oven at 40^{o}C for 2 hours. The sizes were reduced by blending. It was hydrated in double strength chloroform water for five days with intermittent stirring to ensure complete dissolution of the gum and strained through a 75μm sieve to obtain particulate free slurry which was allowed to sediment. The gum sediment was precipitated from the slurry using absolute ethanol, filtered and defatted with diethyl ether. The precipitate was again dried in the oven at 40^{o}C for 48 hours. The dried flakes were pulverized using a blender and stored in an air tight container.

Gravimetric method

In the gravimetric experiment [14], a previously weighed metal (aluminium) coupon was completely immersed in 250 cm^{3}of the test solution in an open beaker. The beaker was covered with aluminium foil and inserted into a water bath maintained at 303 K. After every 24 hours, the corrosion product was removed by washing each coupon (withdrawn from the test solution) in a solution containing 50% NaOH and 100 gl^{-1}of zinc dust. The washed coupon was rinsed in acetone and dried in the air before re-weighing. The experiment was repeated at 333 K. In each case, the difference in weight for a period of 168 hours was taken as the total weight loss. From the average weight loss (mean of three replicate analysis) results, the inhibition efficiency (%I) of the inhibitor, the degree of surface coverage (θ) and the corrosion rate of aluminium (CR) were calculated using equations 1.0, 2.0 and 3.0 respectively;

$$\%I = 1 - \left(\frac{W_1}{W_2}\right) \times 100 \qquad 1.0$$

$$\theta = 1 - \frac{W_1}{W_2} \qquad 2.0$$

$$CR = \frac{W_2 - W_1}{At} \qquad 3.0$$

where W1 and W2 are the weight losses (g) for aluminium in the presence and absence of the inhibitor, θ is the degree of surface coverage of the inhibitor, A is the area of the surface of aluminium coupon (in cm^2), t is the period of immersion (in hours) and ΔW is the weight loss of aluminium after time, t.

III. RESULTS AND DISCUSSIONS

Effect of concentration of the gum on the corrosion of Aluminium

Figures 1.0 shows the variation of weight loss with time for the corrosion of aluminium in 0.1 M HCl containing various concentrations of FS gum inhibitor at 303 and 333 K. From the figure, it is evident that the weight losses of aluminium increases with increase in the period of contact and with increasing temperature indicating that the rate of corrosion of aluminium in solution of HCl increases with increase in the period of contact and with increase in temperature. It is also obvious from the figure that the weight losses of aluminium in the presence of various concentrations of the inhibitor are lower than the corresponding weight loss obtained for the blank indicating that the gum studied inhibited the corrosion of aluminium in solution of HCl**.** Also, the weight loss of aluminium was found to decrease with increase in the concentration of the inhibitor indicating that the inhibition efficiency of the gum increase with increasing concentration and decrease with increase in temperature. The inhibition efficiencies of *Ficus sycomorus* gum under different temperatures calculated using equation 1.0 are presented in Table 1.0. The results obtained indicated that the inhibition

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efficiency of the gum increase with increase in concentration but decrease with increasing temperature hence, the gum is a good adsorption inhibitor and the adsorption on the surface of aluminium favours the mechanism of physical adsorption.

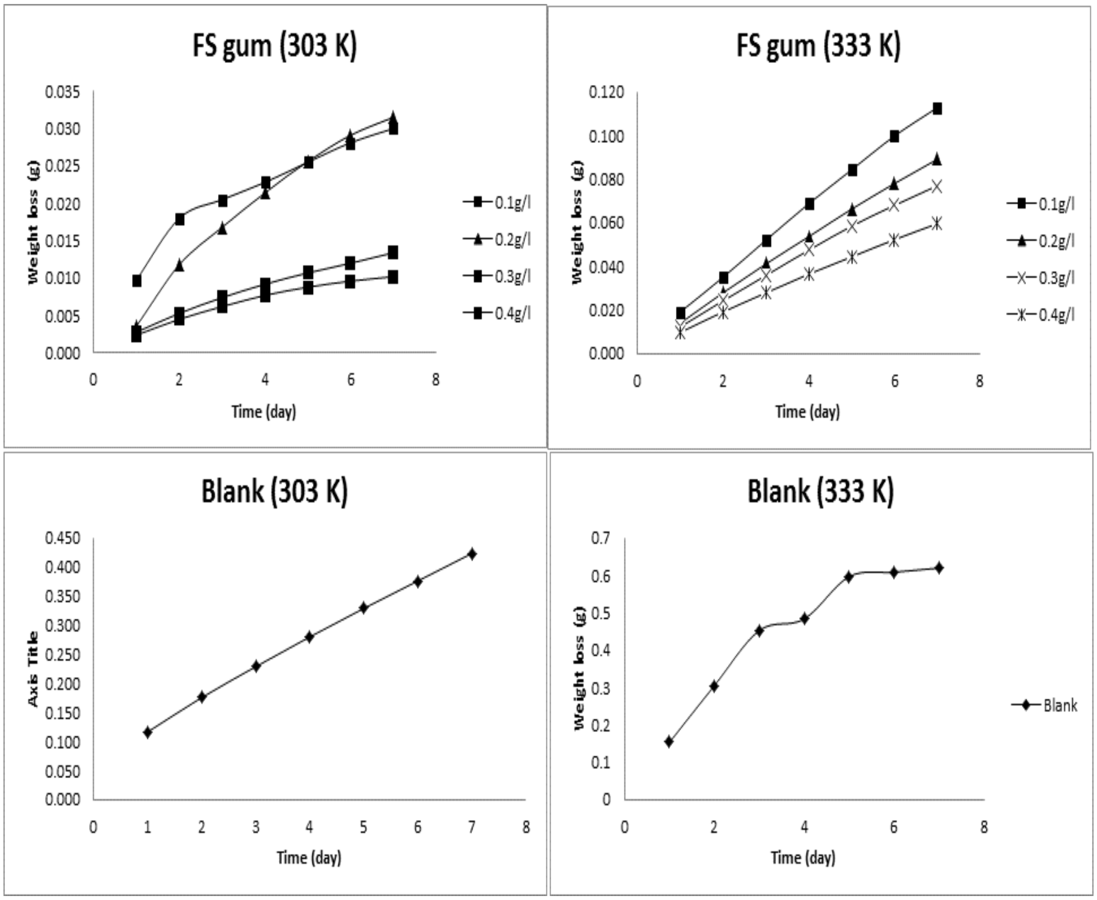

Figure 1.0: Variation of weight loss with time for the corrosion of aluminium in 0.1M HCl containing various concentrations of FS gum

Effect of temperature

The effect of temperature on the corrosion of aluminium in the absence and presence of various concentrations of *Ficus sycomorus* gum was studied using the logarithm form of the Arrhenius equation, which can be written as equation 4.0

$$\frac{CR_2}{CR_1} = \frac{E_a}{2.303RT}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad 4.0$$

where CR_1 and CR_2 are the corrosion rates of aluminium at temperatures, T_1 and T_2 respectively ($T_1 < T_2$), E_a is the activation energy and R is the universal gas constant. Calculated values of E_a are recorded in Table 1.0. E_a values ranged from 29.17 to 49.61 kJ/mol for different concentrations of *Ficus sycomorus* gum. These values are less than the threshold values expected for the mechanism of chemical adsorption (80kJ/mol) hence the adsorption on aluminium surface is consistent with the mechanism of physical adsorption. The activation energy was also found to increase with increase in the concentration of the inhibitor indicating increasing strength of retardation of the corrosion of aluminium with increase in the concentration of the gum. The activation energy for the blank was significantly lower than those obtained for systems containing the inhibitor, which also indicates that the corrosion of aluminium is retarded by the presence of the inhibitor.

Table 1.0: Corrosion rates of aluminium, inhibition efficiencies of the gum, activation energy and heat of absorption for the inhibition of the corrosion of aluminium by *Ficus sycomorus* gum exudate

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System	CR (303 K)	CR (333 K)	% I (303 K)	% I (333 K)	E_a (kJ/mol)	Q_{abs}(kJ/mol)
Blank	0.00013	0.000123	-	-	1.55	
0.1 g/l FS gum	8.9E-06	3.36E-05	91.15	72.69	37.20	-28.38
0.2 g/l FS gum	9.35E-06	2.65E-05	90.71	78.43	29.17	-20.72
0.3 g/l FS gum	3.96E-06	2.29E-05	96.06	81.36	49.13	-36.08
0.4 g/l FS gum	3.01E-06	1.77E-05	97.01	85.57	49.60	-35.65

Thermodynamic/adsorption considerations

The heat of adsorption of the inhibitor on the surface of aluminium was estimated using equation 5.0.

$$Q_{ads} = 2.303R\left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)\right]x\left(\frac{T_{1X}T_2}{T_2 - T_1}\right)kJmol^{-1} \quad 5.0$$

where Q_{ads} is the heat of adsorption, R is the gas constant and θ_1 and θ_2 are the degrees of absorption of the inhibitor at temperatures, T_1 and T_2 respectively. Calculated values of Q_{ads} are also presented in Table 1.0. From the results obtained, the values are negative indicating that the inhibition of the corrosion of aluminium in solution of HCl by *Ficus sycomorus* gum is exothermic.

The adsorption characteristics of the inhibitor was studied by fitting data obtained for the degree of surface coverage into different adsorption isotherms including Langmuir, Freundlich, Temkin, El awardy, Flory Huggins and Brokris Swinkel adsorption isotherms. The tests revealed that the adsorption of *Ficus sycomorus* gum best fitted the Langmuir adsorption isotherm, which can be expressed as equations 6.0 and 7.0.

$$\frac{C}{\theta} = C + \frac{1}{b_{ads}} \quad 6.0$$

$$log\left(\frac{C}{\theta}\right) = logC - logb_{ads} \quad 7.0$$

where C is the concentration of the inhibitor in the bulk electrolyte, b is the adsorption equilibrium constant and θ is the degree of surface coverage of the inhibitor. Figure2.0 shows the Langmuir plot for the adsorption of *Ficus sycomorus* gum on aluminium surface. Adsorption parameters deduced from the plots are presented in Table 2.0. From the results obtained, calculated R^2 values and the slopes of the plots were very close to unity indicating the fitness of the data to the Langmuir adsorption model. Therefore, there is no interaction between the adsorbed molecules.

The equilibrium constant of adsorption obtained from the Langmuir adsorption plot is related to the free energy of adsorption according to equation 8.0.

$$logb_{ads} = -\frac{1}{1.744}\left(\frac{\Delta G^0_{ads}}{2.303RT}\right) \quad 8.0$$

Values of ΔG^0_{ads} calculated from equation 8.0are also presented in Table 8.0 The free energies are negative and are within the range of values expected for the mechanism of physical adsorption hence the adsorption of *Ficus sycomorus* gum on aluminium surface is spontaneous and supports the mechanism of physical adsorption.

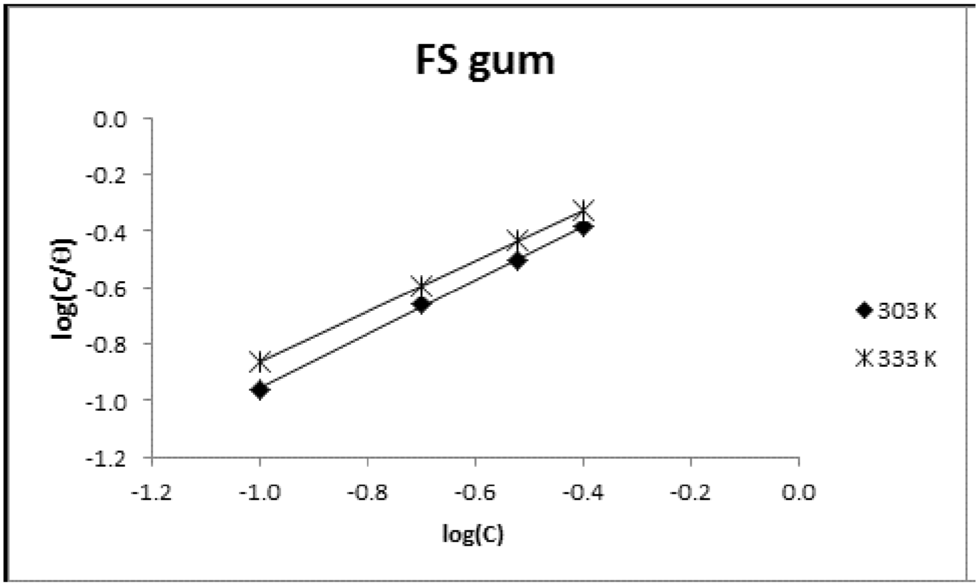

Figure 2.0: Langmuir isotherm for the adsorption of *Ficus sycomorus* gum exudate on aluminium surface

Table 2.0: Langmuir adsorption parameters for the adsorption of *Ficus sycomorus* gum on aluminium surface

Inhibitor	T (K)	Slope	$log b_{ads}$	ΔG^0_{ads} (kJ/mol)	R^2
Ficus Sycomorus	**303 K**	0.9508	-0.0039	-10.10	0.9999
	333 K	0.8865	0.0260	-10.27	0.9998

IV. CONCLUSION

Ficus sycomorus gum exudate is a good adsorption inhibitor for the corrosion of aluminium. The inhibition process was found to be first order, exothermic and spontaneous. The adsorption characteristics of the inhibitor favours physical adsorption and are consistent with Langmuir adsorption model. The gum is adsorbed on the surface of aluminium through some functional groups via the formation of multiple adsorption layers.

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