Adsorption and Chemical Studies on the Inhibition of the Corrosion of Aluminium in Hydrochloric Acid by *Commiphora africana* Gum

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Abstract

The inhibition and adsorption properties of *Commiphora africana* gum for the corrosion of aluminium in hydrochloric acid (HCl) medium was investigated. Results obtained from GCMS analysis of the *Commiphora africana* gum indicated the presence of oleic acid (35.19%), hexadecanoic acid (16.09%), dihex-5-en-2-ylphalate, stearic acid (12.63%), (9Z,12E) –tetradeca-9, 12-dien-1-ol (6.73%) and 2-(hydroxymethyl)-2-nitropropane-1, 3-diol (26.53%). The gum was found to be a good adsorption inhibitor for the corrosion of aluminium in HCl solution. The adsorption of the inhibitor was spontaneous, exothermic and best fitted the Langmuir adsorption model. From the pattern of the variation of inhibition efficiency with temperature, values of the activation and free energies were lower than their respective threshold values, obedient of the mechanism of physical adsorption was upheld for the inhibitor. Results obtained from the quantum chemical study and from the FTIR analysis of the corrosion products revealed that the corrosion active constituents of the gums are dihex-5-en-2-yl phthalate and 2-(hydroxymethyl)-2-nitropropane-1,3-diol.

1. Introduction

Industrial development is vital in the history of any developed country. Most industries use various types of metals including their alloy for the construction of their plants and other installations. In most cases, contact between the metal and aggressive medium (such as acid, base and salt) is unavoidable [1]. Hence, the metal is subjected to corrosion attack. Corrosion is an electrochemical process that tends to returns the metal to its original state [2].

In view of the above, industrial facilities exposed to corrosion are often protected by adopting several options including painting, oiling, cathodic and anodic protections, etc. However, the use of inhibitors has been found to be one of the best options available for the protection of metals against corrosion. Inhibitors are compounds that tend to retards the rate of corrosion of metals through the mechanism of adsorption, which can be through the transfer of charge from charge inhibitor molecule to charged metal surface (physical adsorption) or by electron transfer from the inhibitor's molecule to a vacant orbital (mostly d-orbital) of the metal [3].

Most corrosion inhibitors are organic compounds characterize by the presence of hetero atom (s) (such as N, O, P and S), suitable functional groups or aromatic centre [4-5]. In spite of the numerous inhibitors that have been investigated and reported, the search for corrosion inhibitors that are less expensive, biodegradable and environmental friendly (i.e. green corrosion inhibitor) is on the increase. The present study is aimed at investigating the corrosion inhibition potential of *Commiphora africana* (*CA*) gum for aluminium in hydrochloric acid (HCl) medium.

2. Materials and Methods

2.1. Collection of Gum Sample

Samples of *CA* gum were collected from matured stem of the plant during dry season. The gum was collected by tapping. A small axe was used to break the outer bark. Tapping was carried out by driving an area underneath the bark and was extended until the bark broke horizontally to give two broken edges. Gums formed were slowly collected along the length of the wounded trunk.

2.2. Purification of Gum

The gum was dissolved in cold distilled water and the clear solution was strained through muslin cloth before centrifugation, which yielded dense gel. The clear straw-coloured supernatant liquor was separated and acidified to acidic pH with dilute HCl. 80% of ethyl alcohol was slowly added and the gum precipitated was removed by centrifugation, washed with alcohol followed by ether and then dried.

2.3. Physicochemical Analysis

In order to obtain the percentage yield of the gum, dried, precipitated and purified samples of the gum were obtained and weighed. The percentage yield was estimated with reference to the weight of the crude gum.

The solubility of the gums was determined in cold water, hot water, acetone, chloroform and ethanol. 1.0 g of the gum was added to 50 mL of the respective solvents and left overnight. 25 mL of the clear supernatants were taken in small pre- weighed evaporating dishes and heated to dryness over a digital thermostatic water bath. The weight of the residue with reference to the volume of the solutions were determined using a digital top loading balance (Model XP-3000) and expressed as the percentage solubility of the gums in the solvents. The pH of the gum was determined by shaking 1% w/v dispersion of each of the sample in water for 5 min and the pH was measured using a pre-calibrated Oaklon pH meter (Model 1100). The electrode of the pH meter was immersed into the gum and the pH value was read directly through the meter's read out system.

2.4. Corrosion Studies

The aluminium sheet employed for the study was mechanically pressed cut into different coupons each of dimension 5 x 4 cm. Each coupon was degreased by washing with ethanol, cleaned with acetone and allowed to dry in the air before preservation in a desiccator. All reagents used for the study were Analar grade and double distilled water was used for their preparation.

2.5. Thermometric Method

In order to determine the corrosion rate in the different reagents, a three-neck flask with provisions for the introduction of chemicals and for insertion of thermometer was used for thermometric study. For each study, the aluminium coupon was introduced into the flask. Enough quantities of each solution were in turn transferred into the flask until the aluminium coupon was completely immersed. Once this was done, the temperature of the reacting solution was read at one-minute interval until a constant temperature was obtained. The reaction number (RN) of each system was calculated by dividing the difference between the highest and lowest temperature attained by the time interval. From the reaction number, the inhibition efficiency (% I) of the inhibitor was calculated using Equation 1.

$$\%I = \frac{RN_{aq} - RN_{wi}}{RN} X100 \qquad\qquad 1$$

where RN_{aq} is the reaction number in the absence of inhibitors (blank solution) and RN_{wi} is the reaction number of 2 M HCl containing the studied inhibitor.

2.6. Gravimetric Method

In the gravimetric experiment, a previously weighed coupon was completely immersed in 250 mL 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 24 hr, the corrosion product was removed by washing each coupon (withdrawn from the test solution) in a solution containing 70% nitric acid. The washed coupon was rinsed in acetone and dried in the air before reweighing. In each case, the difference in weight for a period of 168 hr was taken as the total weight loss. From the average weight loss (mean of three replicate analyses) 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 2-4 [6].

$$\% I = \left(1 - \frac{W_1}{W_2}\right) \times 100 \qquad\qquad 2$$

$$\theta = \left(1 - \frac{W_1}{W_2}\right) \qquad\qquad 3$$

$$CR = \frac{\Delta W}{At} \qquad\qquad 4$$

where *CR* is the corrosion rate of aluminium in g/cm^2/h, W_1 and W_2 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 aluminium coupon (in cm^2), *t* is the period of immersion (in hr) and *ΔW* is the weight loss of aluminium after time, *t*.

2.7. Chemical analysis of samples

2.7.1. FTIR analysis

FTIR analyses of *CA* gum and that of the corrosion products (in the absence and presence of *CA* gum) were carried out using Scimadzu FTIR-8400S Fourier transform infra-red spectrophotometer The sample was prepared using KBr and the analysis was done by scanning the sample through a wavenumber range of 400 to 4000 cm^{-1}.

2.7.2. GC-MS analysis

GC-MS analysis was carried out on a GC clarus 500 Perkin Elmer system comprising a AOC-20i autosampler and gas chromatograph interfaced to a mass spectrometer (GC-MS) employing the following conditions: column Elite-1 fused silica capillary column (30 x 0.25 mm ID x 1µM df, composed of 100% Dimethyl poly diloxane), operating in electron impact mode at 70 eV; helium (99.999%) was used as carrier gas at a constant flow of 1 mL/min and an injection volume of 0.5 µL was employed (split ratio of 10:1) injector temperature 250ºC; ion-source temperature 280 ºC. The oven temperature was programmed from 110 ºC (isothermal for 2 min), with an increase of 10 ºC/min, to 200 ºC, then 5 ºC/min to 280 ºC, ending with a 9 min isothermal at 280 ºC. Mass spectra were taken at 70 eV; a scan interval of 0.5 seconds and fragments from 40 to 450 Da. The total GC running time was 36min.

3. Results and Discussions

3.1. Physicochemical properties of *Commiphora africana* gum

Table 1 presents the physicochemical parameters (pH, taste, odour, percentage yield and solubility) of *CA* gum. From the results, it can be seen that the *CA* gum is acidic (pH = 4.2), yellowish brown in colour (Figure 1) and has an odour of honey. From the recorded values of solubility, it is evident that the solubility of the gum in water decreases with increase in temperature suggesting that at higher temperature, the degree of solvent-molecule interaction is reduced. However, the gum is insoluble in acetone and chloroform and sparingly soluble in ethanol (0.02%). The measured solubility of the gum in various solvents can be explained as follow. As a rule, polar compounds are soluble in polar solvents while non-polar compounds are soluble in non-polar solvents. Although, water is a universal solvent, its ability to dissolve polar compounds has been strongly established and is attributed to its high dielectric constant. Ethanol, acetone and chloroform are organic solvent. However, ethanol can ionize to produce hydroxyl ion (OH⁻). Consequently, the dielectric constant of ethanol is relatively higher than those of the other organic compounds. Therefore, to some extent, ethanol is able to dissolve *CA* gum.

Table 1. Physicochemical properties of *Commiphora africana* gum

Properties	
Colour	Yellowish-brown
Odour	Honey smell
Taste	-
pH(28°c)	4.2
Percentage yield (%w/w)	68
Solubility (%w/v)	
a. Cold water	9.50
b. Hot water	9.46
c. Acetone	0.00
d. chloroform	0.00
e. ethanol	0.02

Figure 1. Photograph of dried and hardened gum from *Commiphora africana*

3.2. GC-MS Study

Six prominent peaks were obtained from the GC-MS spectrum of *CA* gum. Values of retention time, mass peak, area under the curve and concentrations of likely chemical compounds (obtained through area and height normalizations) in each peak are presented in Table 2. In Figure 2, the chemical structures of the suggested chemical compounds are also presented [7].

In line 1, the major compound separated under a retention time of 24.467 min was dihex-5-en-2-yl phthalate (2.08%). The separated compound (molar mass = 330 g/mol) is characterized with 9 fragmentation peaks and a mass peak value of 29. In line 2, the most abundant fragmentation ion was 43 (i.e base peak), while the mass peak value was 59. The separated peak indicated the presence of 16.09% of hexadecanoic acid. This compound is an organic acid (molar mass = 256 g/mol) and is characterized with a retention time of 27.942 min. In line 3, the base and mass peak values were 67.05 (100%) and 35, respectively. Under a retention time of 29.058 min, the spectrum indicated the presence of 6.73% of (9Z,12E)-tetradeca-9,12-dien-1-ol (molar mass = 210 g/mol).

In line 4, characteristics base and mass peaks values of 55.05 and 72 were observed under a retention time of 29.108 min. The suggested compound, oleic acid is the most abundant (35.19%) constituents in *CA* gum, indicating that the gum may be a rich source of oleic acid. In line 5, GC-MS separation yielded base and mass peak values of 43 and 60, respectively. Consequently, under a retention time of 29.250 min, 12.69% of stearic acid (molecular mass = 284 g/mol) was identified. In line 6, the base and mass peak values obtained from the GC-MS analysis were 57.05 and 20, respectively. The most likely compound under a retention time of 14.725 min is nitroisobutyl glycerol (2-(hydroxymethyl)-2-nitropropane-1,3-diol) (molar mass = 151 g/mol). From the calculated concentration of glycerol (26.55%), it is evident that nitroisobutyl glycerol is the second most abundant constituents in the *CA* gum.

3.3. Corrosion inhibition study

Figure 3 shows the variation of weight loss with time for the corrosion of aluminium in solutions of HCl containing various concentrations of *CA* gum (as an inhibitor) at 303 K. From the plots, it can be seen that the weight loss of aluminium for the blank exceeded those obtained for the inhibited systems indicating that *CA* gum retarded the corrosion of aluminium in solution of HCl. It is also evident from Figure 4 that the weight loss of aluminium decreases with increase in the

concentration of *CA* gum suggesting that the gum is an adsorption inhibitor for the corrosion of aluminium in solution of HCl [8].

Table 2: Characteristics of suggested compounds identified from GC-MS of *Commiphora africana* gum

| Line No	IUPAC Name	Molecular formula	Molar mass (g/mol)	Retention time (s)	Mass peak	% Conc.	Fragmentation peak
1	Dihex-5-en-2-yl phthalate	$C_{20}H_{26}O_4$	330	24.467	29	2.80	42(10%),50(28%),65(48%), 76(50%), 93(38%) , 105(40%), 121(31%), 149(100%) , 177(50%)
2	hexadecanoic acid	$C_{16}H_{32}O_2$	256	27.941	59	16.09	41(79%), 43(100%), 60(70%),73(80%),85(25%),98(10%),115(10%),129(11%), 143(5%),157(7%), 171(7%),185(10%),199(6%), 213(20%), 227(8%), 256(20%)
3	(9Z,12E)-tetradeca-9,12-dien-1-ol	$C_{14}H_{26}O$	210	29.058	35	6.73	41(46%),54(38%),67(100%), 81(90%), 95(60%), 109(21%), 121(20%)
4	Oleic acid	$C_{18}H_{34}O_2$	282	29.108	72	35.19	41(90%), 559100%), 69(70%), 83(52%), 97(40%), 98(22%) 112(18%), 127(5%), 264(18%)
5	Stearic acid	$C_{18}H_{36}O_2$	284	29.250	60	12.63	41(72%), 43(100%), 57(69%), 73(72%), 85(30%), 98(20%), 116(10%), 129(18%), 171(8%), 185(12%), 199(10%), 213(6%), 227(100%), 241(20%), 284(29%)
6	2-(hydroxymethyl)-2-nitropropane-1,3-diol	$C_4H_9NO_5$	151	14.725	20	26.55	40(10%) , 42(20%) , 43(40%) , 57(100%) , 73(42%) , 86(12%)
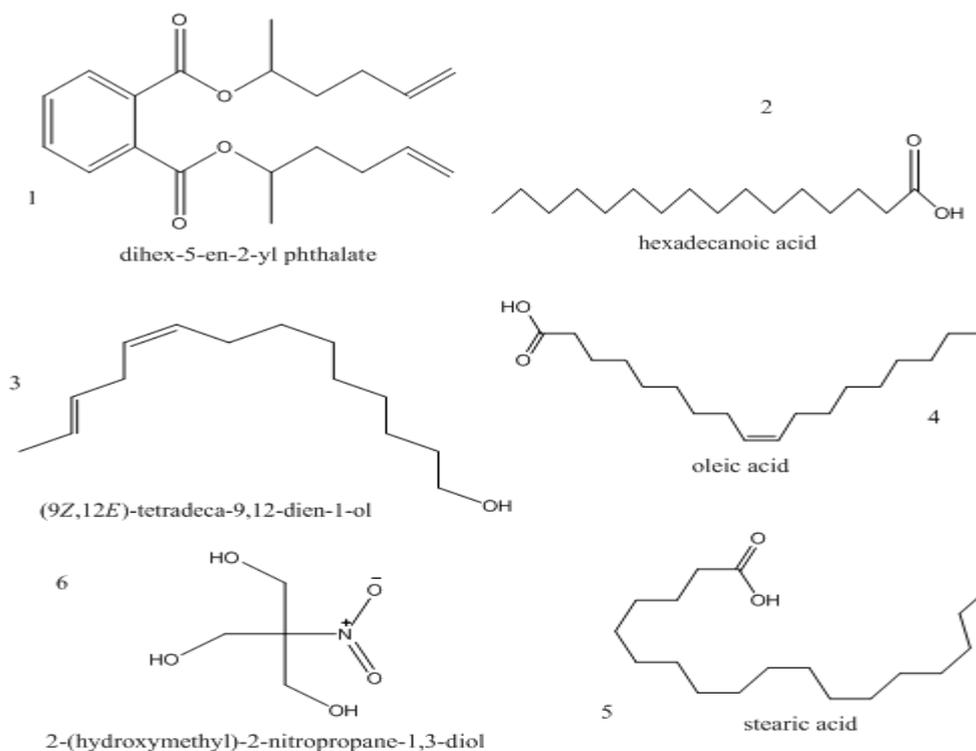
Figure 2. Chemical structures of compounds identified in the GC-MS of *Commiphora africana* gum
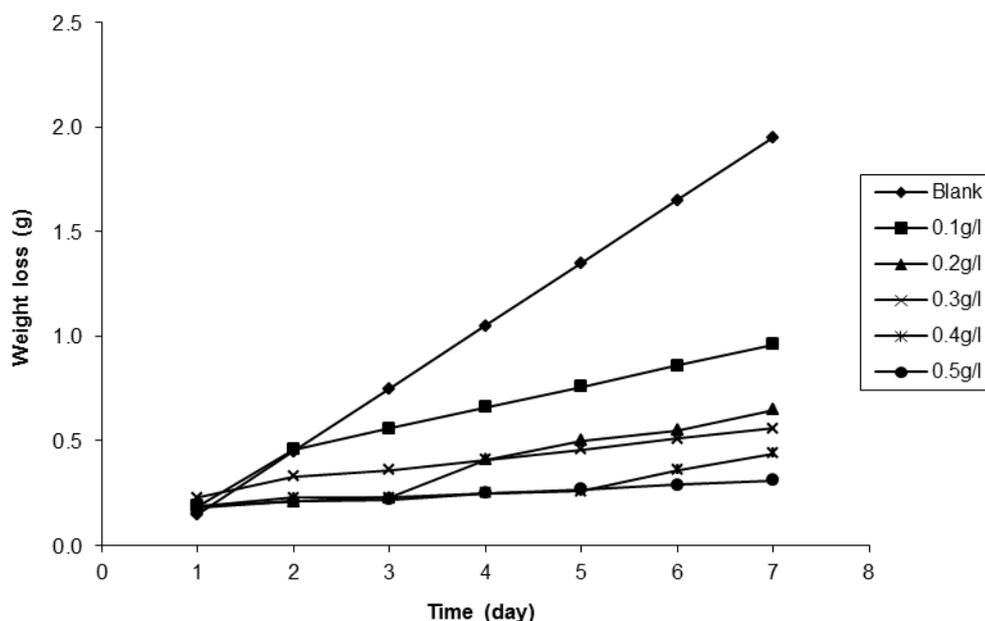
Figure 3. Variation of weight loss with time for the corrosion of aluminium in solution of HCl containing various concentrations of *Commiphora africana* gum at 303 K

At higher temperature (plots not shown), it was evident that the weight loss of aluminium increases with increasing temperature hence inhibition efficiency of *CA* gum decreases with increase in temperature, indicating that the mechanism of adsorption of the gum on aluminium surface favors the transfer of charge from charged inhibitor to charged metal surface, which supports physical adsorption. Several studies have confirmed that a physical adsorption mechanism is associated with increasing value of corrosion rate (hence decreasing value of inhibition efficiency) with increase in temperature [6, 8].

In Table 3, corrosion rates of aluminium and inhibition efficiencies of various concentrations of *CA* gum, calculated from weight loss and gasometric measurements are presented. From the results obtained, it can be seen that the corrosion rate of aluminium in solutions of HCl increases with increase in temperature but decreases with decreasing concentration. Inhibition efficiencies obtained from hydrogen evolution measurements correlated excellently with those obtained from weight loss measurements (r = 0.8946), confirming that the instantaneous and average inhibition efficiencies of *CA* gum are in good agreement.   .

The kinetic of *CA* gum as an inhibitor for aluminium in solutions of HCl was investigated by fitting the data obtained from weight loss measurements into Equation 5 [9].

$$-\log(weightloss) = \frac{k_1 t}{2.303} \qquad\qquad 5$$

where k_1 is the first order rate constant and t is time in days. Figure 4 shows the variation of –log (weight loss) with time for the corrosion of aluminium in solutions of HCl containing various concentrations of *CA* gum at 303 K. From the plots, it can be seen that R^2 values are very close to unity indicating the fitness of the present data to the equation. Therefore, the corrosion of aluminium in solutions of HCl (in the absence and presence of *CA* gum) is consistent with a first order kinetic.

It can also be stated that for a first order reaction, the rate constant (k_1) is related to the half-life as follows [10]:

$$t_{1/2} = \frac{0.693}{k_1} \qquad\qquad 6$$

Table 3. Corrosion rates (CR) of aluminium and inhibition efficiencies (*% I*) of *Commiphora africana* gum in various media

C (g/L)	*CR* x 10000 at 303 K	*CR* x 1000 at 333 K	*% I* (303 K)	*% I* (333 K)	*% I* (Gasometric) (303 K)
Blank	5.80	14.58	-	-	
0.1	2.86	8.57	50.77	41.22	67.24
0.2	1.93	5.80	66.67	60.20	68.56
0.3	1.67	5.00	71.28	65.71	73.02
0.4	1.31	3.93	77.44	73.06	79.01
0.5	0.92	2.77	84.10	81.02	88.36
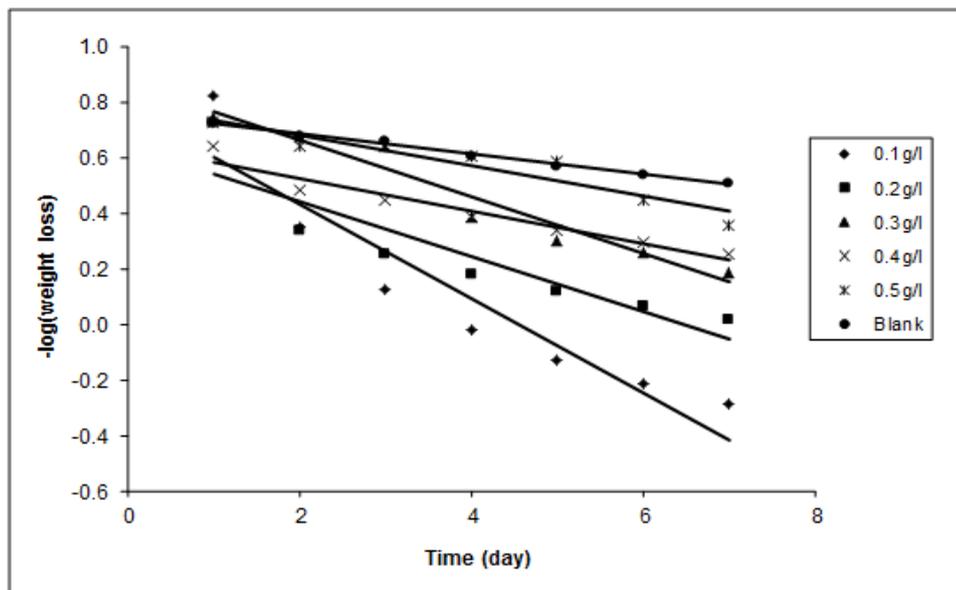
Figure 4. Variation of –log(weight loss) versus time for the corrosion of aluminium in 0.1 M HCl containing various concentrations of *Commiphora africana* gum at 303 K

Values of k_1, R^2 and $t_{1/2}$ deduced from the kinetic plots are recorded in Table 4. From the results obtained, it can be seen that *CA* gum increases the half-life of aluminium in solutions of HCl, Hence it is a good corrosion inhibitor for aluminium in solution of HCl.

Table 4. Kinetic parameters for the corrosion of aluminium in 0.1 M HCl containing various concentrations of *Commiphora africana* gum at 303 and 333 K

C (g/L)	k_1		$t_{1/2}$ (day)		R^2	
	303 K	333 K	303 K	333 K	303 K	333 K
Blank	0.083	0.361	1	2	0.9992	0.8428
0.1	0.389	0.229	2	3	0.8806	0.8177
0.2	0.229	0.234	3	3	0.8177	0.9458
0.3	0.234	0.135	3	5	0.9475	0.9388
0.4	0.135	0.126	5	5	0.9388	0.8879
0.5	0.126	0.083	5	8	0.8879	0.9919

3.4. Effect of temperature

The effect of temperature on the corrosion of aluminium in solutions of HCl containing various concentrations of *CA* gum was studied, using the Arrhenius equation which can be written as follows [11-12]:

$$CR = A \exp\left(\frac{E_a}{RT}\right) \qquad 7$$

where *CR* is the corrosion rate of aluminium in solutions of HCl. *A* is the Arrhenius or Pre-exponential constant, E_a is the activation energy, *R* is the universal gas constant and *T* is the temperature in Kelvin. Taking logarithm of both sides of Equation 6 yielded Equation 8 [13].

$$\log CR = \log A - \frac{E_a}{2.303RT} \qquad 8$$

If the corrosion rates of aluminium at two temperatures (T_1 and T_2) are known, then simplification of Equation 8 gives Equation 9.

$$\log \frac{CR_2}{CR_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad 9$$

where CR_1 and CR_2 are the corrosion rates of aluminium at the temperatures T_1 (303 K) and T_2 (333 K), respectively. The activation energies calculated from Equation 9 (Table 5) are lower than the threshold value (80 kJ/mol) required for the mechanism of chemical adsorption. Therefore, the adsorption of *CA* gum on aluminium surface proceeded through the mechanism of physical adsorption. Values of E_a for the inhibited systems were also found to be higher than the value (25.80 kJ/mol) obtained for the blank. Therefore, inhibition of aluminium corrosion by *CA* gum proceeded through the activation complex.

Table 5. Heat of adsorption and activation energy for the inhibition of the corrosion of aluminium in solutions of HCl by *Commiphora africana* gum

Concentration of *CA* (g/L)	E_a (kJ/mol)	Q_{ads} (kJ/mol)
0.0	25.80	-
0.1	30.66	-8.09
0.2	30.86	-5.86
0.3	30.58	-5.42
0.4	30.72	-4.94
0.5	30.79	-4.50

3.5. Thermodynamic/adsorption considerations

The heat of adsorption of *CA* gum on aluminium surface was calculated using the following equation [13-14]:

$$Q_{ads} = 2.303R\left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)\right] x \left(\frac{T_{1X}T_2}{T_2 - T_1}\right) kJmol^{-1} \qquad 10$$

where θ_1 and θ_2 are the degrees of surface coverage of the inhibitor at temperatures, T_1 (303 K) and T_2 (333 K), respectively and *R* is the gas constant. Calculated values of Q_{ads} are presented in Table 5. These values are negative and ranged from -4.50 to -8.09 kJ/mol. Therefore, the adsorption of *CA* gum on aluminium surface is exothermic.

The adsorption behaviour of *CA* gum was studied by fitting data obtained for the degree of surface coverage into various adsorption isotherms including Langmuir, Fruendlich, El Awardy, Temkin, Florry Huggins and Brokris-Swinkel adsorption isotherms. The tests indicated that the best isotherm for the adsorption of *CA* gum on aluminium surface is the Langmuir adsorption model, which can be written as follows:

$$\theta = \frac{(b_{ads}Cx1)}{(1+k_{ads}C)} \qquad 11$$

where θ is the degree of surface coverage of the inhibitor, b_{ads} is the equilibrium constant of adsorption and *C* is the concentration of the inhibitor in the bulk electrolyte. Upon rearranging and simplification of Equation 11, Equations 12 and 13 were obtained.

$$\frac{C}{\theta} = C + \frac{1}{b_{ads}} \qquad\qquad 12$$

$$\log\frac{C}{\theta} = \log C - \log b_{ads} \qquad\qquad 13$$

Figure 5 presents the Langmuir isotherm for the adsorption of *CA* gum on aluminium surface. Adsorption parameters deduced from the plots are presented in Table 6.
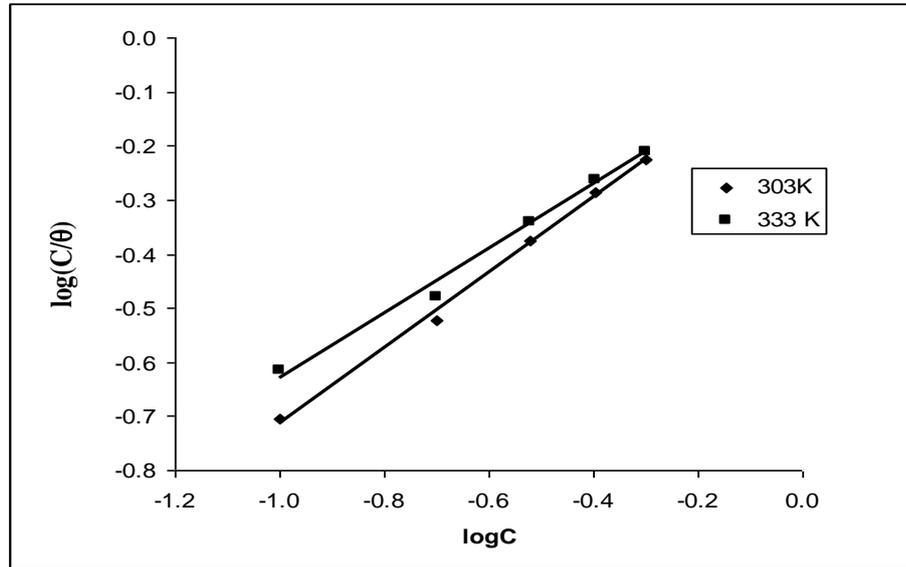

Figure 5. Langmuir isotherm for the adsorption of *Commiphora africana* gum on aluminium surface

Table 6: Langmuir parameters for the adsorption of *Commiphora africana* gum on aluminium surface

T (K)	Slope	*log* b_{ads}	ΔG^0_{ads} (kJ/mol)	R^2
303	0.6992	-0.015	-10.18	0.9966
333	0.5967	-0.0326	-10.28	0.9897

The results revealed that the slope and R^2 values for the plots are close to unity indicating the application of the Langmuir model for the adsorption of *CA* gum. The equilibrium constant of adsorption calculated from the intercept of the Langmuir plot is related to the free energy of adsorption as follows (Equation 14).

$$\Delta G^0_{ads} = -2.303RT\log(55.5b_{ads}) \qquad\qquad 14$$

where ΔG^0_{ads} is the standard free energy of adsorption of *CA* gum on aluminium surface, *R* is the universal gas constant and b_{ads} is the equilibrium constant of adsorption. Calculated values of the free energy of adsorption are also presented in Table 6. The free energies are negatively less than the threshold value (-40 kJ/mol) required for the mechanism of chemical adsorption. Therefore, the adsorption of *CA* gum on aluminium surface is spontaneous and supports the mechanism of charged transfer from the charged inhibitor to the charged metal surface.

3.6. Mechanism of inhibition

The frequencies and peaks of the IR adsorption deduced from the FTIR spectra of *CA* gum and the corrosion product of aluminium when the gum was used as inhibitor are presented in Table 7. From the results obtained, it was observed that the FTIR spectrum of *CA* gum indicated the presence of some functional groups, notably, C-H bends at 606.63, 692.47 and 756.12 cm^{-1}, C-N stretch at 1030.99 cm^{-1}, C-O stretches at 1102.35 and 1253.77 cm^{-1}, the CH bending at 1418.69 cm^{-1}, C=C stretch at 1618.33 cm^{-1}, C-H aliphatic stress at 2943.47 cm^{-1} and OH stretches at 3086.21, 3295.49, 3433.41 and 3559.75 cm^{-1}, respectively.

A comparison of the spectrum of *CA* gum and that of the corrosion product of aluminium when the gum was used as an

inhibitor indicated that the C-H bend at 692.47 is shifted to 651.00 cm^{-1}, the C-N stretch at 1030.99   is shifted to 1018.45 cm^{-1}, the C-O stretch at 1102.35 is shifted to 1149.61 cm^{-1}, the CH bending vibration at 1418.69 was shifted to 1454.38 cm^{-1}, the C=C stretch at 1618.33 was shifted to 1628.94 cm^{-1}, the C-H aliphatic stretch at 2943.47 was shifted to 2902.96 cm^{-1}, the OH stretch at 3086.21 was shifted to 3075.60 cm^{-1}, =C-H aromatic stretch at 3181.69 was shifted to 3167.22 cm^{-1} and OH stretch at 3295.49 was shifted to 3277.17 cm^{-1}.

These shifts in frequencies suggest the existence of an interaction between the inhibitor and the aluminium surface. Also, the C-H bends at 606.63, 756.12 and 979.87 cm^{-1}, the C-O stretch at 1253.77 cm^{-1}, the C=O stretch at 1728.28 cm^{-1}, the C≡C stretch at 2137.20 cm^{-1} and OH stretches at 3433.41 and 3559.75 cm^{-1} were absence in the spectrum of the corrosion product suggesting that these bonds/functional groups were involved in the adsorption of the inhibitor onto the metal surface. On the other hand, new functional groups were found in the spectrum of the corrosion product. These included, C-H bend at 873.78 cm^{-1}, OH stretches at 3006.16 and 3396.76 cm^{-1}.

3.7. Quantum chemical studies

Quantum chemical parameters have some merits and applications in corrosion inhibition study. According to Eddy [5], quantum chemical parameters such as energies of the frontier molecular orbital, dipole moment, cosmo area/volume, ionization potential, total negative charge on hetero atoms, total energy of the molecule as well as electronic energy of the molecule are vital in predicting the ease of adsorption of the inhibitor onto the metal surface, which is the basic mechanism involved in corrosion inhibition process. Of significant interest in studying the direction of corrosion inhibition, is the frontier molecular orbital energies, namely, the energy of the highest occupy molecular orbital (E_{HOMO}), the energy of the lowest unoccupied molecular orbital (E_{LUMO}) and the energy gap, ΔE (which is the difference between E_{LUMO} and E_{HOMO}) [16-17].

Table 7. Peaks and intensity of adsorption of FTIR by *Commiphora africana* gum and corrosion product of aluminium when *Commiphora africana* gum is used as an inhibitor

Peak (cm^{-1})	Intensity	Assignments	Peak (cm^{1})	Peak (cm^{1})	Assignments
606.63	25.336	C-H bend	651	33.607	C-H bend
692.47	23.7	C-H bend	873.78	68.83	C-H bend
756.12	23.517	C-H bend	1018.45	70.51	C-N stretch
979.87	19.986	C-H stretch	1149.61	85.99	C-O stretch
1030.99	18.972	C-N stretch	1454.38	61.33	C-H scissoring and bending
1102.35	18.845	C-O stretch	1628.94	53.54	C=C stretch
1253.77	19.543	C-O stretch	2902.96	27.16	C-H aliphatic stretch
1418.69	19.48	C=C stretch	3006.16	23.22	OH stretch
1618.33	18.881	CH bending	3075.60	21.01	OH stretch
1728.28	28.343	C=C stretch	3167.22	18.24	=C-H aromatic stretch
2137.2	53.733	C=O stretch	3277.17	18.27	OH stretch
2943.47	18.837	C≡C stretch	3396.76	18.75	OH stretch
3086.21	19.135	C-H aliphatic stretch			
3181.69	19.475	O-H stretch			
3295.49	19.022	=C-H aromatic stretch			
3433.41	19.329	OH stretch			
3559.75	20.568	OH stretch			
4010.14	56.693	OH stretch			
4301.4	59.859	OH stretch			

It has been found that corrosion inhibition potential of an inhibitor tends to increase with increasing value of E_{HOMO}, which is an index that characterizes the electron donating ability of an inhibitor [18]. E_{LUMO} on the other hand indicates the tendency of a molecule to accept electron. Therefore, lower values of E_{LUMO} signifies better inhibition efficiency and vice versa [17]. Finally, the energy gap is associated with the hardness and softness of a molecular species [19]. Soft molecules are more reactive than hard molecules because soft molecules are characterize with low value of energy gap, hence, the inhibition efficiency of a molecular species is expected to increase with decreasing value of ΔE. In Table 8, frontier molecular orbital energies for chemical constituents of *CA* gum are presented. The results obtained indicated that dihex-5-en-2-yl phthalate and 2-(hydroxymethyl)-2-nitropropane-1,3-diol have the highest corrosion inhibition potentials. Therefore, these two molecules are singled out for further quantum chemical discussion. Optimized structures of dihex-5-en-2-yl phthalate and 2-(hydroxymethyl)-2-nitropropane-1,3-diol are presented in Figure 6.

Table 8. Frontier molecular orbital energies of chemical constituents of *Commiphora africana* gum

Molecule	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)
dihex-5-en-2-yl phthalate	-10.129	-0.885	9.244
hexadecanoic acid	-10.843	0.544	11.387
(9Z,12E)-tetradeca-9,12-dien-1-ol	-9.297	1.351	10.648
Oleic acid	-9.546	0.536	10.082
Stearic acid	-10.794	0.552	11.346
2-(hydroxymethyl)-2-nitropropane-1,3-diol	-10.27	-0.986	9.284
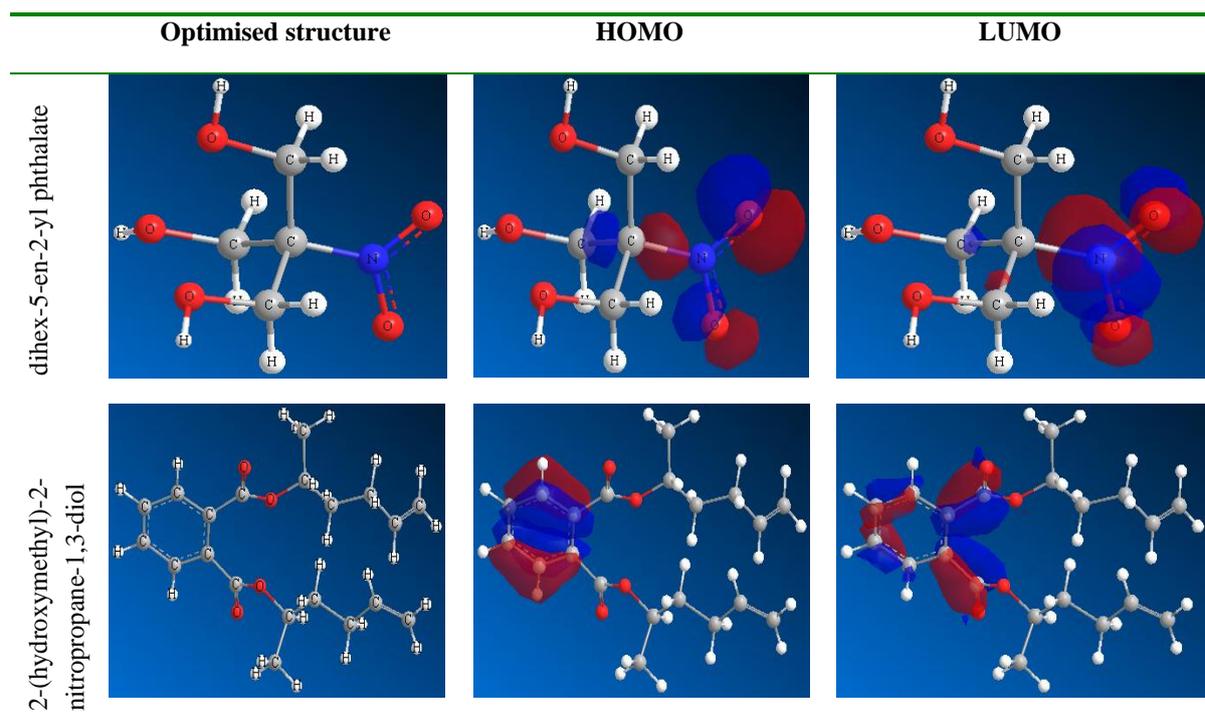
Figure 6. Optimized structures of dihex-5-en-2-yl phthalate and 2-(hydroxymethyl)-2-nitropropane-1,3-diol

Figure 6 also presents the HOMO and LUMO orbital of these molecules. From their chemical structures, significant factors relevant for corrosion inhibition are summarized as follows:

i. The molecular structure of dihex-5-en-2-yl phthalate indicates the presence of aromatic ring, two COOH groups and two π-electron rich olefin bonds (carbon carbon double bond).

ii. The molecular structure of 2-(hydroxymethyl)-2-nitropropane-1,3-diol reveals the presence of three hydroxyl functional groups (-OH), charged radical group (nitromethane group) whose electrons are delocalized between the two oxygen atoms and the nitrogen atom.

iii. The HOMO and LUMO diagrams (red indicate positive and blue, negative) of the two compounds indicated that in dihex-5-en-2-yl phthalate, the lobes are concentrated in the radical nitro group, while in 2-(hydroxymethyl)-2-nitropropane-1,3-diol, the lobes are concentrated in the aromatic ring, indicating that adsorption of the inhibitor might have proceeded through these two groups. This finding agrees with those deduced from FTIR spectrum.

4. Conclusions

From the results and findings of the present study, the following conclusions were made:

i. *CA* gum is yellowish-brown odourless, acidic and ionic gum.

ii. The chemical constituents of *CA* include oleic acid (35.19%), hexadecanoic acid (16.09%), dihex-5-en-2-ylphalate, stearic acid (12.63%), (9Z,12E)-tetradeca-9,12-dien-1-ol (6.73%) and 2-(hydroxymethyl)-2-nitropropane-1, 3-diol (26.53%).

iii. *CA* gum is a good adsorption inhibitor and its inhibition potential can be attributed to the transfer of charge from charged inhibitor to charged metal surface.

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