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Corrosion inhibition properties of *Commiphora africana* (a. rich.) engl. gum exudates on mild steel in alkaline medium

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The effect of *Commiphora africana* (CA) gum exudates on the corrosion of mild steel in 2.5 M Na_2CO_3 has been studied using weight loss (gravimetric) and thermometric methods at 303 and 333 K. Results obtained suggest that *C. africana* acts as a good corrosion inhibitor as the inhibition efficiency increased with increase in the concentration of the inhibitor. A decrease in the %I was observed with increase in temperature from 303 to 333 K. Values of inhibition efficiency from weight loss method were found to be significantly higher ($p \leq 0.05$) than values obtained from gasometric method, even as the (I%) values from the two methods correlated strongly. Also values of ? G_{ads}, Ea and Q_{ads} suggest physical mechanism for the adsorption of the inhibitor molecules on the surface of mild steel even as Temkin adsorption isotherm was found to best suit the adsorption mechanism within the temperature range under study.

Key words: Mild steel, adsorption isotherm, corrosion inhibition, activation energy.

INTRODUCTION

Corrosion scientists and engineers have continued to grapple with the manifestation of corrosion and corrosion products on steel structures (Tretchewey and Chamberlain, 1995; Ita and Offiong, 2000). One of the most practical methods of protection of metals against corrosion in various media is the use of inhibitor which helps to effectively isolate the metal from the corrosive agents. Inhibitors are important in corrosion monitoring because they prevent or reduce corrosion without significant reaction with the components of the environment. Compounds containing heteroatoms are known to be effective and efficient organic inhibitors (Fekry and Ameer, 2010). An effective inhibitor should be able to not only displace water from the surface of a metal, but should interact with the anodic or cathodic reaction sites to retard the oxidation and reduction corrosion reactions, as well as prevent transportation of water and corrosion active species on the surface of metal. Synthetic organic inhibitors have been continually replaced with naturally occurring substances which are cheap, readily available, ecologically and environmentally friendly. Most importantly, they are biodegradable and renewable sources of materials. Recent studies have shown plant materials as effective good inhibitors for

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metals in aggressive media (Avwiri and Igbo, 2003; Oguzie, 2007; Emregul and Abbas, 2008; Abdel-Gaber et al., 2008; Singh et al., 2011). Also reports abound on the corrosion inhibitive effectiveness of metals by *Gum arabic* (Umuoren et al., 2006) *Raphia hookeri* (Ebenso et al., 2009), *Acacia seyal var seyal* (Buchweishaija and Mhinzi, 2008). *Guar gum* (Abdallah, 2004), *Anogessus leocarpus* (Eddy et al., 2011), *Pachylobus edulis* (Umoren et al., 2008). The growing interest in environmentally friendly corrosion inhibitors has necessitated this work which seeks to investigate the inhibiting effect of gum exudates from *Commiphora africana* (CA) on mild steel corrosion in alkaline medium using gravimetric and thermometric techniques at 303 - 333 K. Also considered were the thermodynamic, activation and adsorption parameters that govern metal corrosion.

MATERIALS AND METHODS

Mild steel sheets of composition (wt%) Mn (0.6), P (0.36), C (0.15), Si (0.03) and the rest iron were used in this study. The sheet was mechanically cut into different coupons, each of dimensions 4 x 3 cm. Each coupon was degreased by washing with ethanol, rinsed with acetone and allowed to dry in air before they were preserved in desiccators. All reagents used for the study were Analar grade and double distilled water was used for the preparations. The samples were purified using the procedure earlier described by Eddy et al. (2011).

Corrosion inhibition studies

Gravimetric method

Gravimetric study using *C. africana* gum was done by dipping a previously weighed metal (mild steel) coupon into 20 ml of the test solution maintained at 303 and 333 K in a thermo stated bath. The weight loss was determined by retrieving the coupons at 1 hour intervals progressively for 7 h. Prior to measurement, each coupon was immersed in a solution of 20 % sodium hydroxide containing 200 g/L of zinc dust to terminate the corrosion reaction and then rinsed in acetone before drying. The difference in weight was taken as the weight loss of the mild steel. From the average weight loss (mean of three replicate analyses) results, the degree of surface coverage (è), the inhibition efficiency (%I) of the inhibitor, and the corrosion rate of mild steel (CR) were calculated using the following equations.

$$\Theta = \frac{W_0 - W_1}{W_0} \quad (1)$$

$$\%I = \left\{\frac{W_0 - W_1}{W_0}\right\} \times 100 \quad (2)$$

$$CR = \frac{W}{At} \quad (3)$$

where W_0 and W_1 are the weight losses (g) for mild steel in the absence and presence of the inhibitor in Na_2CO_3 solution, ? is the degree of surface coverage of the inhibitor, Ais the area of the mild steel coupon (in cm^2), t is the period of immersion (in hours) and W is the weight loss of mild steel after time, t.

Thermometric method

Thermometric analysis was also carried out as reported elsewhere [15]. From the rise in temperature of the reaction system per minute, the reaction number (RN) and the percentage inhibition efficiency were calculated using the following equations.

$$RN(°C/Min) = \frac{T_m - T_I}{t} \quad (4)$$

$$\%I = \frac{RN_{aq} - RN_{wi}}{RN_{aq}} \quad (5)$$

Where: T_m = Maximum temperature attained by the system. T_i = the initial temperature.
t = the time (min) taken to reach the maximum temperature. RN_{aq} = Reaction number in the absence of inhibitor, RN_{wi} = Reaction number in the presence of inhibitor.

RESULTS AND DISCUSSION

The variation of weight loss with time for the corrosion of mild steel in 0.1 M Na_2CO_3 containing various concentrations of *C. africana* gum exudates at 303 and 333 K are as shown in Figures 1 and 2 respectively. From these figures, it was observed that the rate of corrosion of mild steel increased as the period of immersion increased, but decreased with increase in the concentration of *C. africana* gum exudates, confirming the inhibition of corrosion of mild steel by gum exudates of CA in Na_2CO_3 within the temperature range under review. However, the inhibition efficiency of the gum exudates was found to have a direct proportional relationship with the concentration of the exudates gum, but varies inversely with the temperature, suggesting physical adsorption on the surface of mild steel. Similar findings were equally deduced from thermometric study.

Effect of temperature

The effect of temperature on the rate of corrosion of metal cannot be overemphasized. In corrosion involving basic medium, there is an exponential increase in corrosion rate with increase in temperature and so the integrated Arrhenius type equation which is experimental dependent is observed between the corrosion rate and temperature.

$$\log\frac{CR_2}{CR_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \quad (6)$$

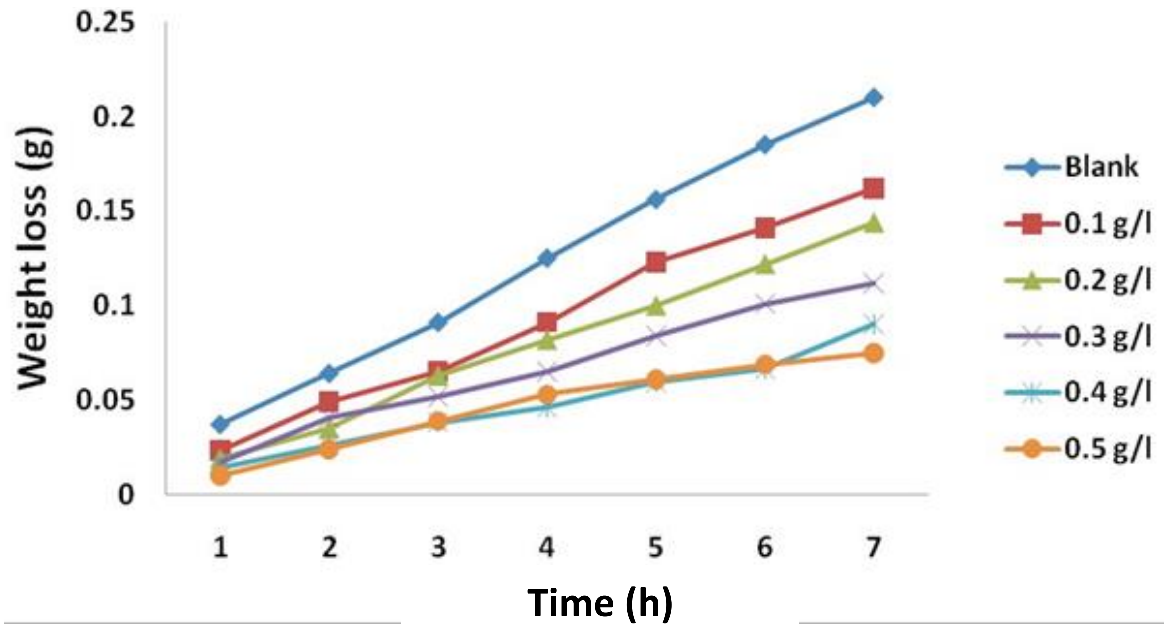

Figure 1. Variations of weight loss of mild steel with time for the corrosion of mild steel in 0.1 M Na_2CO_3 containing various concentrations of *C.africana* at 303 K.

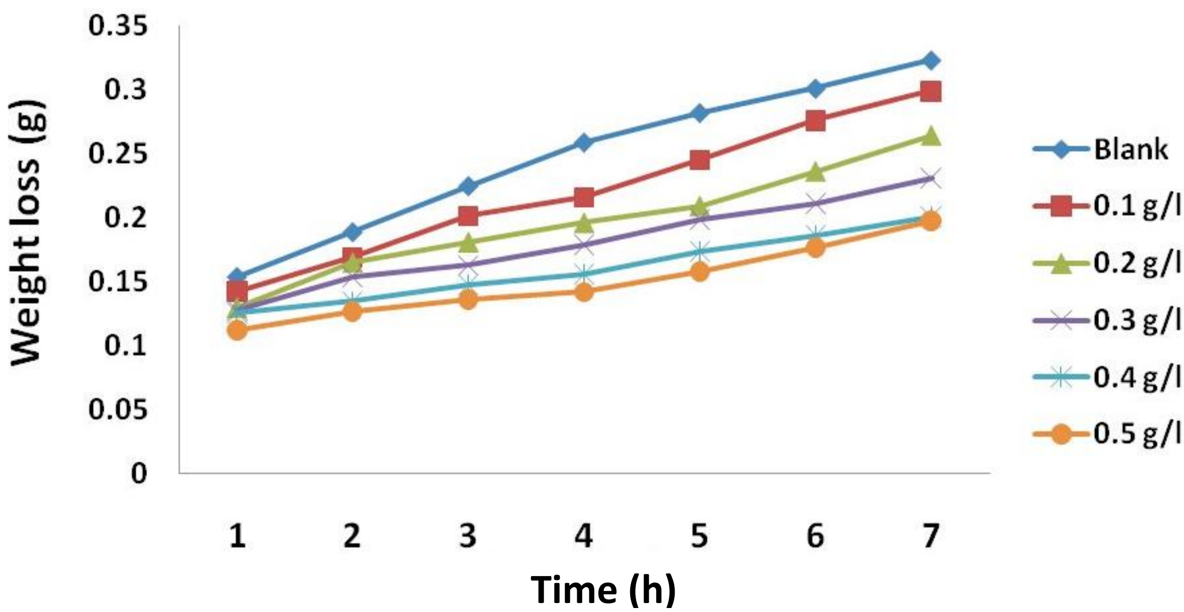

Figure 2. Variations of weight loss of mild steel with time for the corrosion of mild steel in 0.1 M Na_2CO_3 containing various concentrations of *C. africana* at 333 K.

Where E_a is the activation energy, CR_1 and CR_2 are the corrosion rates of mild steel at the temperatures T_1 (303 K) and T_2 (333 K) respectively.

The heat of adsorption of *Commiphora africana* on the surface of mild steel was calculated using Equation 7, since the corrosion inhibition was carried out at constant pressure, the heat adsorbed should approximate the enthalpy change (Umuoren et al., 2006a; Umuoren et al., 2006b).

$$Q_{ads} = 2.303R\left(\mathrm{Log}\left[\frac{Q_2}{1-Q_2}\right] - \mathrm{Log}\left[\frac{Q_1}{1-Q_1}\right]\right) \times \frac{T_1T_2}{T_2-T_1}\ \mathrm{kjmol}^{-1} \quad (7)$$

Table 1. Calculated values of activation energy and heat of adsorption for mild steel corrosion in 0.1 M Na_2CO_3 with various concentrations of *C. africana* gum exudates.

Conc. of (CA) (g/l)	Ea $Kjmol^{-1}$	Qa ($Kjmol^{-1}$)
Blank	11.97	
0.1	13.71	-18.19
0.2	16.84	-20.16
0.3	20.13	-22.01
0.4	22.27	-22.01
0.5	22.71	-32.18

Table 2. Corrosion rates, inhibition efficiencies and reaction numbers of various concentrations of *C. africana* for the corrosion of mild steel in Na_2CO_3.

Conc. of weight Loss (CA) g/L				Thermometric		
303 K				333 K	%I	RN
CR X 10^{-3}	**%I**	**CR X 10^{-3}**		**%I**		
Blank	250					
0.1	2.17	13.33	3.56	7.43	66.67	0.075
0.2	1.71	31.49	3.14	18.27	77.78	0.055
0.3	1.33	46.67	2.75	28.48	82.22	0.040
0.4	1.07	57.14	2.39	37.78	86.67	0.030
0.5	1.04	58.57	2.36	38.69	91.11	0.020

Where $?_1$ and $?_2$ 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 negative as recorded in Table 1, indicating that the adsorption of *C. africana* gum on mild steel surface is exothermic.

In the present study, it could be seen that the values of E_a in the presence of different concentrations of CA were progressively higher than that in its absence. This could be attributed to the formation of an adsorptive electrostatic film of physical character [16]. Thus, a physical barrier to charge and mass transfer is created by the adsorbed molecule. The degree of surface coverage decreased with increase in temperature as signified by the negative values of Q_{ads}. This could be attributed to the fact that attainment of physical adsorption equilibrium is usually rapid and the process is readily reversible and exothermic, whereas in chemical adsorption, the occurrence of chemical reactions at the metal surface makes the process relatively slow and not readily reversible. This is in line with earlier suggestion (Oguzie, 2007).

Adsorption and inhibition efficiency

The adsorption capacity of molecules determines their protective ability in metal corrosion (Haider, 2011). The adsorption film that results isolates the metal surface from the corrosive medium such that the corrosion rate indicates the number of free corrosion sites remaining after some sites have been effectively shut out by the adsorbed inhibitor. Table 2 indicates that the %I increased with increase in the concentration of *C. africana,* but decreased with increase in temperature. This is attributed to the decrease in formation of the protective film on the metal surface (or desorption of the inhibitor molecule from the metal surface) at elevated temperatures (Doche et al., 1999). Physical adsorption mechanism is thus suggested. Values of inhibition efficiency obtained from thermometric method were found to be significantly higher than values from weight loss method ($p \leq 0.05$). Thus the inhibitor could be said to be more efficient in instantaneous inhibition than inhibition over a length of time.

Attempts were made to fit the degree of surface coverage values (?) to various adsorption isotherms. Temkin adsorption isotherm was found to best suit the experimental data using Equation 8 (Okafor et al., 2009).

$$\exp(-2f?) = K_{ads}\ C. \quad (8)$$

Where K_{ads}, C, f and ? represent the equilibrium constant of adsorption process, additive concentration, molecules interaction parameter and degree of surface coverage respectively. Taking the logarithm of Equation 8 with rearrangement results to Equation 9.

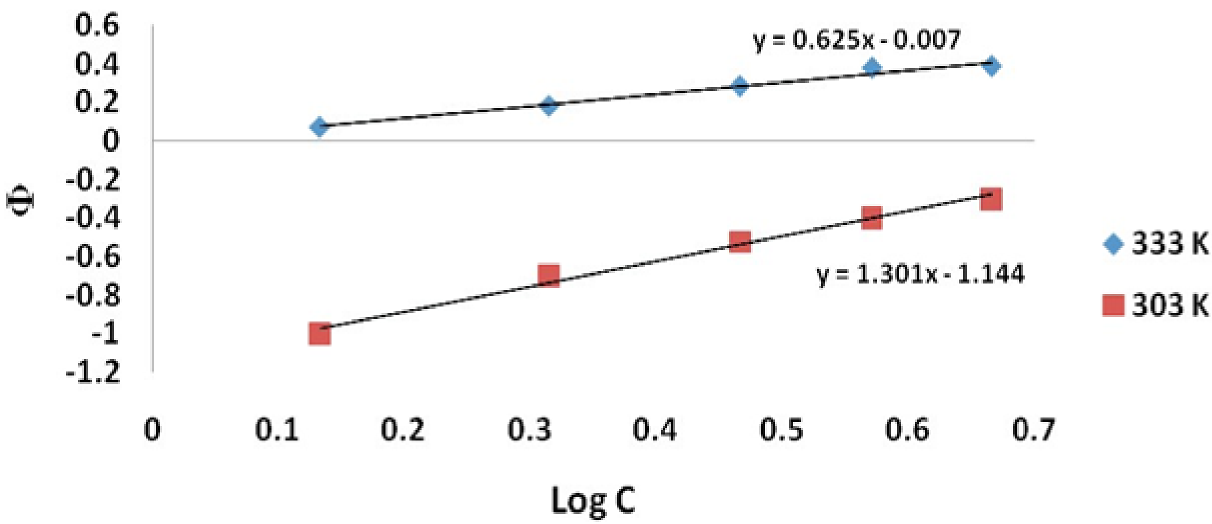

Figure 3. Temkin isotherm plots for the adsorption of *C. africana* on mild steel surface in 0.1 M Na_2CO_3.

Table 3. Thermodynamic Parameters for adsorption of Commiphora africana (CA) on mild steel surface at 303 and 333 K.

Temp (K)	Log K	? G^0_{ads}	f	R^2
303	-1.18	-3.27	2.912	0.990
333	-0.05	-10.80	1.045	0.981

$$\theta = \frac{-LnK}{2f} - \frac{LnC}{2f} \quad (9)$$

A plot of ? against Log C would give a straight line with intercept Log K. Figure. 3 is an indication that Temkin adsorption isotherm is obeyed.

Calculated values of equilibrium constant and standard free energy of adsorption are as shown in Table 3 as obtained from Equation 10.

$$? G_{ads} = -2.303RT\log(55.5K) \quad (10)$$

Where R is the gas constant, 55.5 is the concentration of water in the solution in Mol/L.

The positive value of f shows the existence of attractive force at the neighbouring adsorption sites in the adsorption layer (Umoren et al., 2008).

Generally,? G^0_{ads} values up to -20 $Kjmol^{-1}$ are consistent with physical adsorption (Scendo, 2008). The values of standard free energy from Table 3 are in consonance with physical adsorption mechanism and also show that the adsorption of *C. africana* (CA) on the surface of mild steel in an alkaline medium is spontaneous. Also higher value of (f) at 303 K shows a better interaction of the molecules at lower temperature confirming the mechanism of physical adsorption.

Conclusion

The following conclusions were made from the results of this study:

(i) Gum exudates of *C. africana* is a good inhibitor for the corrosion of mild steel in alkaline medium within the temperature range under study.
(ii) The inhibitor follows the physical mechanism of adsorption onto the surface of mild steel as the inhibition efficiency decreased with increase in temperature.
(iii) The efficiency of the inhibitor increased with increase in the concentration of the inhibitor.
(iv) The adsorption behaviour of the inhibitor is consistent with Temkin adsorption model.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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