Studies on the Inhibitive Effect of Exudate Gum from *Dacroydes edulis* on the Acid Corrosion of Aluminium

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Abstract

The inhibitive effect of exudate gum from *Dacroydes edulis* in the corrosion of aluminium in HCl solutions was studied using weight loss and thermometric methods at 30-60 $^{\circ}$C. The results reveal that the exudate gum acts as an inhibitor for corrosion of aluminium in HCl solution. The inhibition efficiency increases with an increase in the concentration of the exudate gum but decreases with increase in temperature. The Temkim adsorption isotherm was tested for its fit to the experimental data. The result confirms that the corrosion inhibition of the exudate gum from DE is attributed to the adsorption of molecules of phytochemicals present in the exudate gum on the surface of the metal. The free energies and equilibrium constant for the adsorption process were determined. A mechanism of physical adsorption is proposed..

Keywords: corrosion inhibition, aluminium, *Dacroydes edulis,* adsorption, Temkin isotherm.

Introduction

Investigation of natural substances as corrosion inhibitors has attracted considerable attention because they have been shown to be cheap, ecologically friendly and possess no threat to the environment. Plant extracts including their leaves and tubers and their corrosion inhibitive properties have been widely examined. The inhibitive properties of *Telfaria occidentalis* extract [1], *Occimum basilicum* [2], *Anacardium occidentale* [3], *Zenthoxylium alatum* [4], *Rosmarinus*

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officinalis [5], *Andrographis panizulata* [6], *Mimosa* tannin [7], *Prunus cerasus* [8], *Allium sativum* [9], oil from *Mentha pulegium* [10], natural honey [11], extract of *Rhizome* powder [12], *Lawsonia* extract [13], *Vernonia amydalina* [14], *Magnifera indica* [15], *Azadirachta indica* [16,17], *Carica papaya* [17], *Datura metel* [18], have been reported. Also reported are the inhibitive effects of natural *Artemisia* oil [19] on steel and *Jojoba* oil [20] on aluminium in acidic medium. El-Etre has also reported on the effect of *Khillah* extract [21] and *Opuntia* extract [22] as ecofriendly corrosion inhibitors for steel and aluminium, respectively. *Guar gum* [23], *Quinine* [24] and *Sansevieria trifasciata* extract [25] have been shown to be effective corrosion inhibitors for metal in aggressive acid environments. Results obtained show that all the natural substances act as effective corrosion inhibitors in the different test media. Inhibition efficiency was found to increase with increase in the concentration of the tested materials. We have recently reported on the potential of *Gum arabic* as corrosion inhibitor for aluminium in alkaline medium [26]. The inhibition of aluminium corrosion by *Gum arabic* was attributed to the presence of arabinogalactan, oligosaccharides, polysaccharides and glucoproteins since these compounds contain oxygen and nitrogen atoms which are the centers of adsorption. It has also been shown by other researchers that the inhibitive effect of some plants solution extract is due to the adsorption of molecules of phytochemicals present in the plant on the surface of the metal [27-29].

Dacroydes edulis (DE) (pear tree) is widely planted and found mainly in tree crops fields and in home gardens in Nigeria, Cameroon and in Central Africa. The dead branches of the species are used as firewood and its bark is used as medicine [30]. This plant produces gummy exudates which are used locally. The present work is therefore another trial aimed at finding a cheap and environmentally safe inhibitor for aluminium corrosion in acidic medium using exudates gum from *Dacroydes edulis*.

Experimental

Pure aluminium metal (purity 98.5%) of the type AA 1060 obtained from System Metals Industries Calabar, Nigeria, was used for the investigation. Each sheet was 0.4 mm in thickness and was mechanically press cut into 5 cm × 4 cm coupons. These coupons were used in as cut condition, i.e., without further polishing. However, for surface treatment they were degreased in absolute ethanol, dried in acetone and stored in a desiccator devoid of moisture before use in corrosion studies. *Dacroydes edulis* (DE) was obtained locally. The impurities in the exudate gum, which are principally, sand, wood and bark fibres were removed by dissolving the exudate in hot 95% ethanol following the method of Ekpe et al. [31]. Thereafter, the gum was dried in an N53C-Genlab laboratory oven at 40 $^{\circ}$C to obtain a solid gum. Different concentrations (0.1 to 0.5 g/L) of the exudate gum used as inhibitor was weighed and dissolved in 2 M HCl. The concentration of HCl (BDH) used was 2M.

Weight loss measurements

In the weight loss experiments, a clean weighed aluminium coupon was immersed completely in a 250 mL beaker containing the corrodent and inhibitors with the aid of glass rods and hooks. The beakers were placed in a constant-temperature bath maintained at 30 – 60 ^{o}C. The coupons were retrieved at 24 h interval progressively for 168 h (7 days), immersed in concentrated nitric acid (S.G 1.42) at room temperature, scrubbed with bristle brush under running water, dried in acetone and weighed [32,33]. The differences in weight of the coupons were taken as the weight loss which was used to compute the corrosion rate given by [33]

$$\text{corrosion rate (mm/yr)} = \frac{87.6W}{\rho At} \tag{1}$$

where W is the weight loss (g dm^{-3}), ρ is the density of the specimen (2.25 g cm^{-3}), A the area of specimen (cm^2) and t the exposure time (hrs).
The inhibition efficiency of DE acting as inhibitor in 2 M HCl was calculated using the following expression [17]:

$$I(\%) = \left(1 - \frac{W_i}{W_0}\right) x100 \tag{2}$$

where W_0 and W_1 are the weight losses of the aluminium coupons in the absence and presence of inhibitor, respectively, in HCl at the same temperature.
The degree of surface coverage (θ) was calculated using the expression [17]

$$\theta = 1 - \frac{W_i}{W_0} \tag{3}$$

Thermometric measurements

The reaction vessel and procedure for determining the corrosion behaviour by this method has been described elsewhere by other authors [34-36]. In the thermometric technique the corrodent (HCl) concentration was kept at 2 M. The volume of test solution used was 50 mL. The initial temperature in all experiments was kept at 30 ^{o}C. The progress of corrosion reaction was monitored by determining the changes in temperature with time using a calibrated thermometer (0-100 ^{o}C) to the nearest ± 0.05 ^{o}C. This method enabled the computation of the reaction number (RN) defined as [26,34]

$$RN(^oC\,\text{min}^{-1}) = \frac{T_m - T_i}{t} \tag{4}$$

where T_m and T_i are the maximum and initial temperatures, respectively, and 't' is the time (min) taken to reach the maximum temperature.

Results and discussion
Effect of exudate gum on the corrosion rate
The corrosion rates of the aluminium samples in 2 M HCl in the absence and presence of different concentrations of the exudate gum were determined. The results obtained are presented in Table 1. The corrosion rate decreases with increasing concentration of the gum. This indicates that the exudate gum in the solution inhibits the corrosion of aluminium in HCl and that the extent of corrosion inhibition depends on the amount of the extract present.

Table 1. Calculated values of corrosion rate (mm/yr) and inhibition efficiency (% I) for exudate gum from weight loss data.

Concentration of DE (g/L)	Corrosion rate (mm/yr) $\times 10^{-3}$ and inhibition efficiency (% I)							
	30 ^{o}C		40 ^{o}C		50 ^{o}C		60 ^{o}C	
Blank	5.1	-	11.0	-	12.0	-	16.0	-
0.1	3.9[a]	(22.0)[b]	9.3	(17.3)	11.0	(10.2)	15.0	(8.7)
0.2	3.7	(27.0)	8.6	(24.1)	10.0	(17.3)	14.0	(16.0)
0.3	3.5	(31.0)	8.1	(29.0)	9.4	(25.0)	12.0	(24.0)
0.4	3.3	(38.0)	7.2	(34.0)	8.3	(33.0)	11.0	(32.0)
0.5	3.0	(42.0)	6.2	(41.0)	7.1	(40.0)	9.5	(39.0)

(a) = corrosion rate obtained from equation (1)
(b) = inhibition efficiency (%I) obtained using equation (2)
DE = *Dacroydes edulis* gum

Fig. 1 shows the variation of the inhibition efficiency with the concentration of the exudate gum. It is observed that the inhibition efficiency increases with increasing concentration of the gum. The maximum inhibition efficiency was observed to be 42% at 0.5 g/L recorded at 30 ^{o}C. The inhibitive effect of the *Dacroydes edulis exudate* gum could be attributed to the presence of some phytochemical constituents in the exudate. Previous studies have shown that the exudate gum contains tannin, oligosaccharides, polysaccharides and glucoproteins as part of its phytochemical composition [30,31]. Owing to the complex chemical composition of the exudate gum, it is quite difficult to assign the inhibitive effect to a particular constituent.
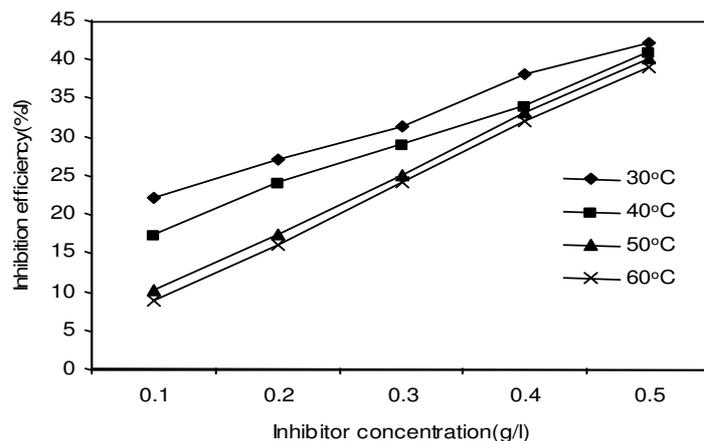
Figure 1. Variation of the inhibition efficiency with the concentration of DE gum for Al in 2 M HCl solution at 30 – 60 ^{o}C.

Kinetic analysis of weight loss results

A plot of the logarithm of the measured weight of the aluminium against time, as depicted in Fig. 2, helps to explain the kinetics of the corrosion in HCl in the absence and presence of the inhibitors. Fig. 2 shows that a linear variation is observed from the plot both in the absence and presence of the gum, which confirms a first order kinetics which may be formulated as:

$$\log W_f = \log W_o - kt \tag{5}$$

where W_f and W_o are the weights of the coupons after and before immersion respectively, k is the rate constant and t is time [37].
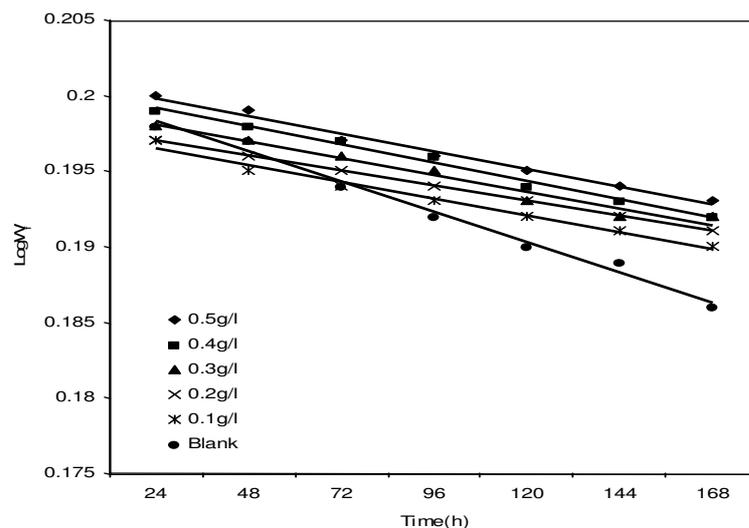
**Figure 2**. Plot of log W_f against time for Al in 2 M HCl solution in the absence and presence of exudate gum from *Dacroydes edulis.*

Table 2. Kinetic and thermodynamic parameters for the corrosion of aluminium in 2 M HCl solution containing exudate gum from *Dacroydes edulis*.

Concentration of DE (g/L)	Rate constant k (s^{-1})	Half life (h)	Temp. (^{o}C)	Temkin isotherm		
				ΔG^o_{ads} (kJmol^{-1})	K	a
Blank	7.2	346		–	–	–
0.1	3.9	630	30	-18.2	1.9	-0.3
0.2	3.6	693	40	-17.8	1.7	-0.3
0.3	3.9	630	50	-17.4	1.5	-0.2
0.4	4.3	576	60	-16.8	1.5	-0.4
0.5	4.3	576				

The values of the rate constants obtained from the slope in Fig. 2 are presented in Table 2. It was observed that the rate constants vary linearly with the logarithm of the exudate gum concentration, c, as depicted in Fig. 3, and obeys the relationship:

$$k = -0.204c + 4.476 \qquad (6)$$
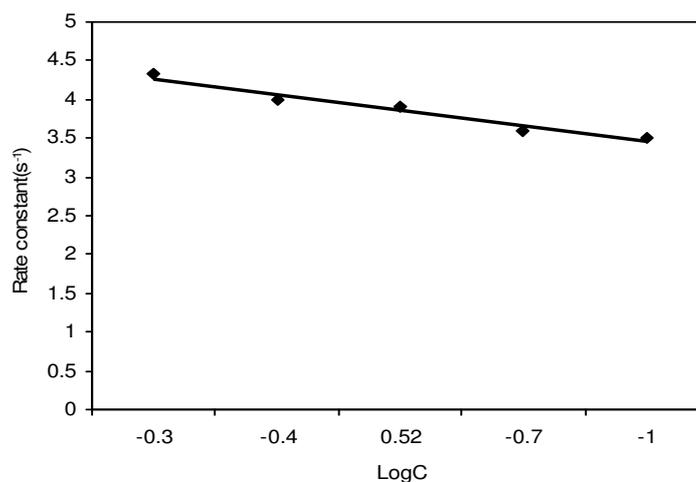
Figure 3. Plot of rate constant against log C for Al in 2 M HCl solution containing DE gum.

From values of the rate constants, half-life of corrosion reaction involving aluminium in the absence and presence of different concentrations of the exudate gum were estimated. The values are also presented in Table 2. It was found to be linearly dependent on the concentration of the gum, decreasing with increase in the concentration of the exudate gum as shown in Fig. 4. A similar trend has earlier been reported [38,39]. The results obtained are not very clear. However, it is assumed that adsorbed organic molecule can influence the behaviour of electrochemical reactions involved in corrosion processes in several ways. The action of organic inhibitor also depends on the type of interactions between the

substance and the metallic surface. The interaction can bring about a change either in electrochemical mechanism or in the surface available for the processes [40]. The half-life obeys the relationship:

$$t_{1/2} = -22.5c + 688.5 \tag{7}$$

where c is the concentration of the exudate gum.
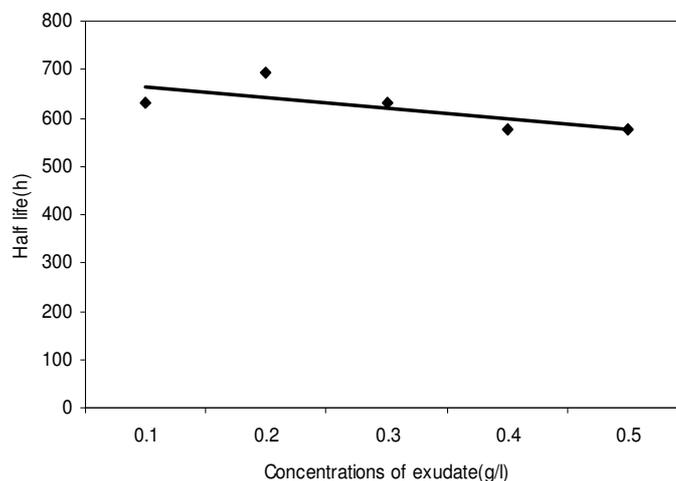
Figure 4. Variation of the half-life with the concentration of exudate gum from DE for Al in 2 M HCl solution at 30 ^{o}C.

Adsorption studies

The mechanism of the interaction between inhibitor and the metal surface can be explained using adsorption isotherms. The degree of surface coverage, θ, for the different systems studied was computed from the weight loss measurements. The surface coverage values for the tested exudate gum obtained from *Dacroydes edulis* was applied to various adsorption isotherm models. It was found that the experimental data fitted the Temkin adsorption isotherm, which may be formulated as [17]

$$\exp(-2a\theta) = KC \tag{8}$$

where 'a' is the molecules interaction parameter, θ, is the degree of surface coverage, 'K' is equilibrium constant of adsorption process and 'C' is the concentration of the inhibitor. Fig. 5 shows the plot of θ against log C for the exudate at 30-60 ^{o}C (Temkin adsorption isotherm). Linear plots were obtained indicating that the experimental results fit the Temkin isotherm. This result confirms that the corrosion inhibition of the exudate gum from DE is attributed to the adsorption of molecules of phytochemicals present in the exudate gum on the surface of the metal. The calculated values of molecular interaction parameter 'a' and equilibrium constant of adsorption process, K obtained from Temkin plot are shown in Table 2. The values of 'a' are negative in all cases showing that repulsion exist in adsorption layer [41].
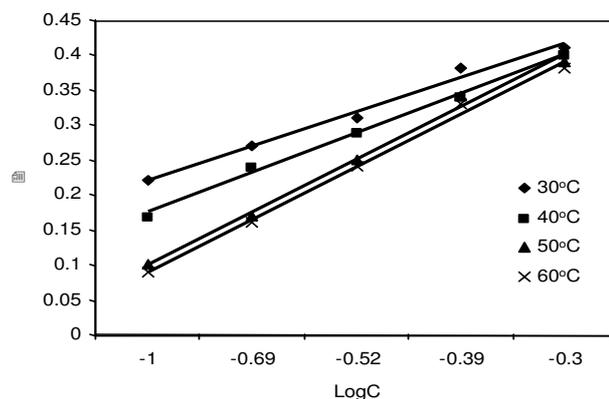
**Figure 5**. Temkin adsorption isotherm for Al in 2 M HCl solution containing DE gum at 30 – 60 ^{o}C.

The thermodynamic parameters for adsorption shown in Table 2 were calculated using the values of K according to the following equation [29]

$$\Delta G^{o}_{ads} = -RT \ln(Kx55.5) \tag{9}$$

The values obtained are presented in Table 2. The values of ΔG^{o}_{ads} indicate that the inhibitors function by physically adsorbing on the metal. The adsorption of these compounds on the aluminium surface reduces the surface area available for corrosion. Generally, values of ΔG^{o}_{ads} up to –20 kJmol^{-1} are consistent with electrostatic interaction between charged molecules and a charged metal (which indicates physical adsorption), while those more negative than –40 kJmol^{-1} involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of bond (which indicates chemisorption) [24,26]. Further work on the mechanistic aspect of the corrosion inhibition of exudate gum from *Dacroydes edulis* can be better understood using electrochemical studies such as polarization and AC impedance spectra. Also addition of halides may improve the performance of the inhibitor significantly as reported elsewhere [1,2,25]

Thermometric measurements
Thermometric methods have proved useful in evaluating the inhibitor efficiency of a number of surface-active agents and results obtained using these techniques are corroborated by other well-established methods such as weight loss, potentiostatic polarization measurements [34].
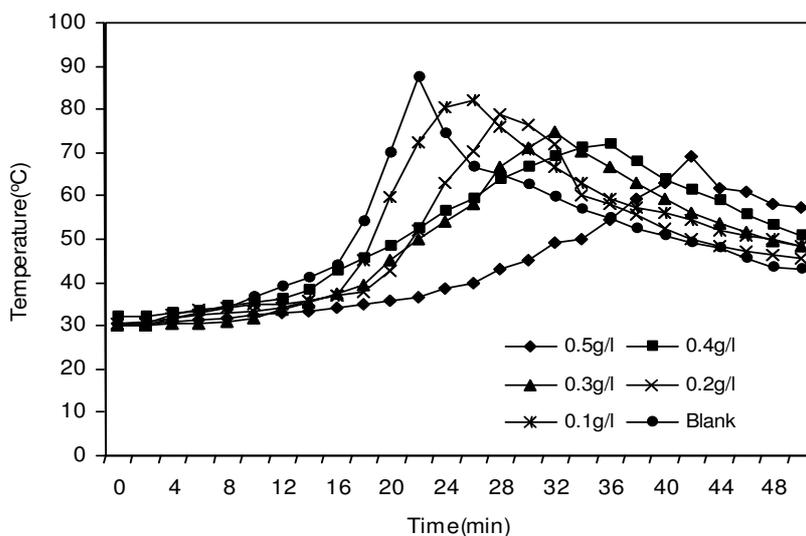
Figure 6. Temperature – time curves for the dissolution of aluminium in blank and different concentrations of the exudate gum.
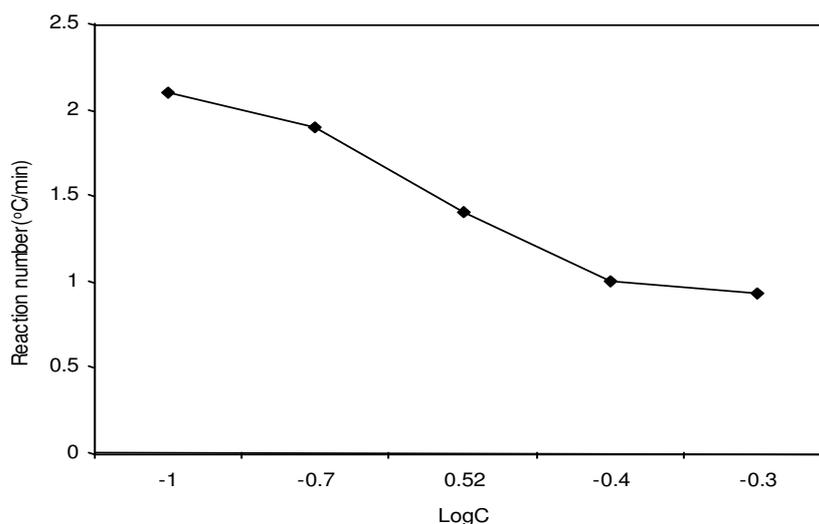
Figure 7. Plot of RN against Log of inhibitor concentration.

Fig. 6 shows the temperature-time curves for the dissolution of aluminium in 2 M HCl in the absence and in the presence of different concentrations of the inhibitor (DE). Inspection of Fig. 6 shows that as the concentration of the inhibitor increases, the time required to reach maximum temperature (T_m) increases and the rate of temperature rise decreases, that is, the inhibition efficiency increases with the increase in the concentration of the inhibitor. Fig. 7 shows the relationship between the RN and the logarithm of inhibitor concentration. The curve consists of an initial decreasing portion along which the RN decreases with increasing concentration of DE and then the rate of decrease became smaller. As the concentration of DE increased further, the value of RN decreased with

concentration. This is an indication that the exudate gum inhibits the corrosion of Al in the acidic environment, probably by adsorption on the metal surface [26].

Conclusions

From the experimental results obtained in the present study, the following conclusions could be drawn:

1. *Dacroydes edulis* exudate gum acts as inhibitor for aluminium corrosion in HCI solution.
2.   Inhibition efficiency increased with increase in concentration of the *Dacroydes edulis* exudate gum but decreased with increase in temperature which confirmed that the adsorption process was physical in nature. Phytochemical constituents in the exudate play a very vital role in the inhibiting action.
3. Phenomenon of physical adsorption is proposed from the calculated values of ΔG_{ads}^{o}. The values were negative which suggests that DE exudate gum was strongly adsorbed on the metal surface. The values of ΔG_{ads}^{o} at all temperatures studied indicate spontaneous adsorption of the inhibitor, and this is usually characteristic of strong adsorption with the metal surface.
4. Kinetic analysis of the data showed a linear variation, which confirms a first order kinetics.
5. The adsorption process for *Dacroydes edulis exudate* gum followed the Temkin adsorption isotherm.

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