Eco-friendly Inhibitors from Naturally Occurring Exudate Gums for Aluminium Corrosion Inhibition in Acidic Medium

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Abstract

Exudates gums from *Pachylobus edulis* (PE) and *Raphia hookeri* (RH) were evaluated as corrosion inhibitors for aluminium in HCl using weight loss and thermometric measurements at 30 – 60 ^{o}C. The exudates were found to retard corrosion rate of aluminium. The inhibition efficiency (%1) increased with increase in concentration of the exudates. Increase in temperature increased the corrosion rate in the absence and presence of inhibitors but decreased the inhibition efficiency. Both PE and RH exudate gums were found to obey Temkin adsorption isotherm and Kinetic-Thermodynamic Model of El-Awady *et al.* at all the concentrations and temperatures studied. Phenomenon of physical adsorption is proposed from the activation parameters obtained. Thermodynamic parameters reveal that the adsorption process is spontaneous. Exudate gum from RH was found to be a better inhibitor than PE.

Keywords: corrosion inhibition, *Pachylobus edulis*, *Raphia hookeri*, adsorption isotherm, aluminium.

Introduction

One of the methods used to reduce the rate of metallic corrosion is the addition of inhibitors. The use of naturally occurring substances as inhibitors for metals exposed to acid environment has continued to receive attention as replacement for synthesized organic inhibitors. Some investigations have been made in recent time into the corrosion inhibition effects of some local plants and are generally reported to exhibit good inhibition efficiencies [1-7]. The greatly expanded

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interest on naturally occurring substances, otherwise tagged 'green inhibitors' is attributed to the fact that they are cheap, ecologically friendly and posses no threat to the environment. In addition, they are readily available and renewable source of materials.

It has been shown that the inhibitory action of some plants solution extract is due to the presence of tannin in their chemical constitutions [8]. Other authors have also shown 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 [9-11], which protect the metal surface and thus do not permit the corrosion process to take place.

Recently, we have reported on the adsorption characteristics and corrosion inhibition ability of Gum Arabic for aluminium corrosion in alkaline medium [12]. 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. The encouraging results obtained by this research permit to test more plants materials.

In this paper, gravimetric and thermometric techniques are applied to study and compare the abilities of exudate gums from *Pachylobus edulis* (PE) and *Raphia hookeri* (RH) to inhibit the corrosion of aluminium in HCl in furtherance of our quest to explore naturally occurring substances (green inhibitors) as corrosion inhibitors for metals in different aqueous media. The effect of temperature is also reported.

Experimental

Pure aluminium metal (purity 98.5%) of the type AA 1060 obtained from System Metals Industries Limited, 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 per 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. *Pachylobus edulis* (PE) and *Raphia hookeri* (RH) were obtained from Ikpetime Village, Ikot Abasi Local Government of Akwa Ibom State, Nigeria. The impurities in the exudates, 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. [13]. The concentrations of inhibitors (PE and RH) prepared and used in the study were 0.1 to 0.5 g/L. The concentrations of HCl (BDH supplies chemicals, England) used were in the range 0.02 – 2 M.

Weight loss measurements

The apparatus and procedure followed for the weight loss measurements were as previously reported [14-19]. The corrodent concentration was kept at 0.1 M and the volume of the test solution used was 100 mL. All tests were made in aerated solutions. The difference between the weight at a given time and the initial

weight of the coupons was taken as the weight loss which was used to compute the corrosion rate given by:

$$\text{Corrosion rate (mm/yr)} = \frac{87.6W}{\rho A t} \tag{1}$$

where W is the weight loss (gdm^{-3}), ρ is the density of the specimen (gcm^{-3}), A the area of the specimen (cm^2), and t the exposure time (hrs).

The inhibition efficiency of PE and RH exudate gums acting as inhibitor in 0.1 M HCl was calculated using the following expression:

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

where W_0 and W_1 are the weight losses of the aluminium coupons in the absence and presence of inhibitors, respectively, in HCl at the same temperature.

The degree of surface coverage (θ) was calculated from equation (3):

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

Thermometric measurements

The reaction vessel and procedure for determining the corrosion behaviour by this method has been described elsewhere by other authors [20-23]. 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

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

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. The inhibition efficiency (%I) was evaluated from percentage reduction in the reaction number, namely

$$\%I = \frac{RN_{aq} - RN_{wi}}{RN_{aq}} \times 100 \tag{5}$$

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 studied inhibitors.
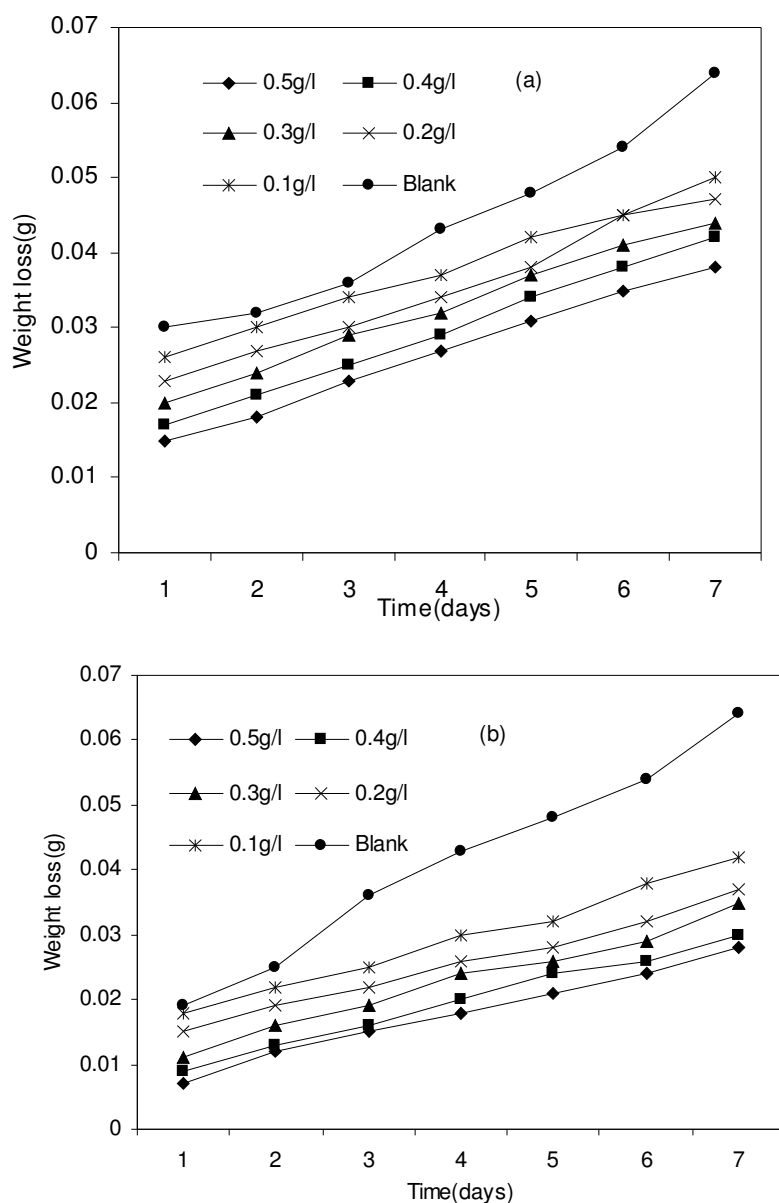

Figure 1. Plot of weight loss against time for aluminium corrosion in 0.1 M HCl containing (a) PE and (b) RH exudates gums at 30 ^{o}C.

Results and discussion
Weight loss, corrosion rate and inhibition efficiency
Weight loss measurements of aluminium subjected to the effect of acid medium in the absence and presence of PE and RH exudate gums of various concentrations were made after 168 h of immersion at temperature range of 30-60 ^{o}C. Results obtained are presented in Fig. 1 and Table 1. Fig. 1 shows the plot of weight loss against time for aluminium in 0.1 M HCl containing (a) PE and (b) RH exudate gums at 30 ^{o}C. Similar plots were obtained for other temperatures

(40-60 ^{o}C). The figures clearly show a reduction in weight loss of the metal coupons in the presence of these inhibitors compared to the free acid solution (blank). Inspection of the figures further revealed that the loss in weight of the coupons decreases as the concentration of the inhibitors increases. Similar trend was observed for other temperatures but with greater values of weight loss.

The calculated values of corrosion rate (mm/yr), for aluminium in 0.1 M HCl in the absence and presence of PE and RH exudate gums of different concentrations are shown in Table 1. The result shows that the corrosion rate (mm/yr) for aluminium was lower in the presence of the exudates compared to the blank (HCl) . It is also seen in the table that the corrosion rate increases with increase in temperature, and decreases as the concentration of the exudate gum increases with the most significant effect observed for both additives. This is an indication that the extent of corrosion inhibition depends on the amount of PE and RH exudate gums present. The decrease in weight loss and corrosion rate of aluminium in the presence of these additives is evidence that the exudate gums derived from PE and RH actually inhibited the corrosion of aluminium in acidic environment.

Also presented in Table 1 are the calculated values of inhibition efficiency for PE and RH exudate gums. Inhibition efficiency was observed to increase with increase in concentration of exudates, probably due to an increase in the metal surface area covered by the exudates. From Table 1, it is seen that inhibition efficiency of PE and RH exudate gums decreases with increase in temperature. Decrease in inhibition efficiency with increase in temperature is suggestive of physical adsorption mechanism. The inhibitive effect of the exudates could be attributed to the presence of some phytochemical constituents in the exudates. Previous studies [13, 24] have shown that the RH exudate contains hexuronic acid residues in combination with neutral sugar residues. The presence of volatile monoterpenes, canaric and related triterpene acid has been reported. It also contains reducing and non-reducing sugars. On the other hand, PE exudate has been reported to contain tannin, oligosaccharides, polysaccharides and glucoproteins as part of its phytochemical composition [13,25]. These compounds contain oxygen and nitrogen atoms which are the centers of adsorption. Therefore it could be assumed that the exudate gums establish their inhibitive action via adsorption of these phytochemical component molecules on the metal surface. This adsorption process creates a barrier between the metal and the corrosive medium leading to inhibition of corrosion. Consequently, inhibition efficiency increases as the metal surface area covered by the adsorbed molecules increases, the later is in turn increased as the exudate concentration increases.

Thermometric studies

Thermometric methods have proved to be of considerable value and help in studying corrosion behaviour of a number of metals and alloys in various corroding environments [26,27]. The technique is also useful in evaluating the inhibitor efficiency of a number of surface-active agents [28,29]. Results obtained using thermometric methods were confirmed by other well-established

methods such as weight loss [27,29,30], and potentiostatic polarization measurements [29,31].

Table 1. Calculated values of corrosion rate (mm/yr), inhibition efficiency (% I), and degree of surface coverage (θ), for exudates gums from weight loss data.

Concentration of exudates (g/L)	Corrosion rate (mm/yr) × 10⁻³, inhibition efficiency (% I) and degree of surface coverage (θ)											
	30 °C			40 °C			50 °C			60 °C		
PE Exudate Blank	5.10	-	-	11.00	-	-	12.00	-	-	16.00	-	-
0.1	3.90^a	(22.00)^b	[0.22]^c	9.30	(17.30)	[0.17]	11.00	(10.20)	[0.10]	15.00	(8.70)	[0.09]
0.2	3.70	(27.00)	[0.27]	8.60	(24.10)	[0.24]	10.00	(17.30)	[0.17]	14.00	(16.00)	[0.16]
0.3	3.50	(31.02)	[0.31]	8.10	(29.00)	[0.29]	9.40	(25.00)	[0.25]	12.00	(24.00)	[0.24]
0.4	3.30	(38.00)	[0.38]	7.20	(34.00)	[0.34]	8.3 0	(33.00)	[0.33]	11.00	(32.00)	[0.32]
0.5	3.00	(41.00)	[0.41]	6.20	(39.00)	[0.39]	7.10	(37.00)	[0.37]	9.5	(34.00)	[0.34]
RH Exudate												
0.1	3.00^a	(34.40)^b	[0.34]^c	7.30	(32.20)	[0.32]	8.60	(26.20)	[0.26]	12.80	(22.30)	[0.22]
0.2	2.70	(42.20)	[0.42]	6.90	(40.90)	[0.40]	8.30	(31.10)	[0.31]	12.00	(26.20)	[0.26]
0.3	2.50	(45.30)	[0.45]	6.10	(42.30)	[0.42]	8.00	(37.80)	[0.38]	11.70	(34.50)	[0.35]
0.4	2.20	(53.10)	[0.53]	5.50	(51.70)	[0.52]	7.50	(48.80)	[0.49]	11.40	(45.50)	[0.56]
0.5	2.00	(56.30)	[0.56]	5.20	(55.20)	[0.55]	7.10	(51.70)	[0.52]	10.50	(46.10)	[0.46]

(a) Corrosion rate obtained from equation (1); (b) Inhibition efficiency (%I) obtained using equation (2); (c) Degree of surface coverage (θ) obtained using equation (3); PE = *Pachylobus edulis;* RH = *Raphia hookeri.*

Fig. 2 shows the change of temperature due to corrosion reaction of aluminium in 2 M HCl solution devoid of and containing different concentrations of PE and DE exudate gums. Inspection of the figure revealed that the dissolution of aluminium starts after a certain time from the immersion of the aluminium coupons in the test solution as evident in the constant temperature with time. It may be expected that this time corresponds to the period required by the acid to destroy the pre-immersion oxide film and it is known as the 'incubation period'. After the breakdown of the pre-immersion oxide film, the temperature of the system rises gradually due to the exothermic corrosion reaction to reach a maximum value, T_m. It is seen from the figure that the maximum temperature T_m was attained at a very short time (t) by the free acid solution. This corresponds to a reaction number (RN) of 2.80 ^{o}C min^{-1} (Table 2). Further inspection of the figure revealed that on addition of the PE and RH exudates gums the maximum temperature attained decreases and the time required to reach

it increases. This is an indication that the various additives inhibit the corrosion of Al in the acidic environment, probably by adsorption on the metal surface [19]. The extent of inhibition depends on the degree of coverage of the metal by the adsorbed molecules. Strong adsorption is noted at higher concentration of exudates as depicted by decrease in maximum temperature (T_m) attained and a corresponding increase in time (t) taken to reach it, and both factors cause a large decrease in the RN of the system (Table 2). The temperature of all the systems decreases after reaching their maximum values. The results obtained in this study corroborate those of other workers earlier published [1,22].
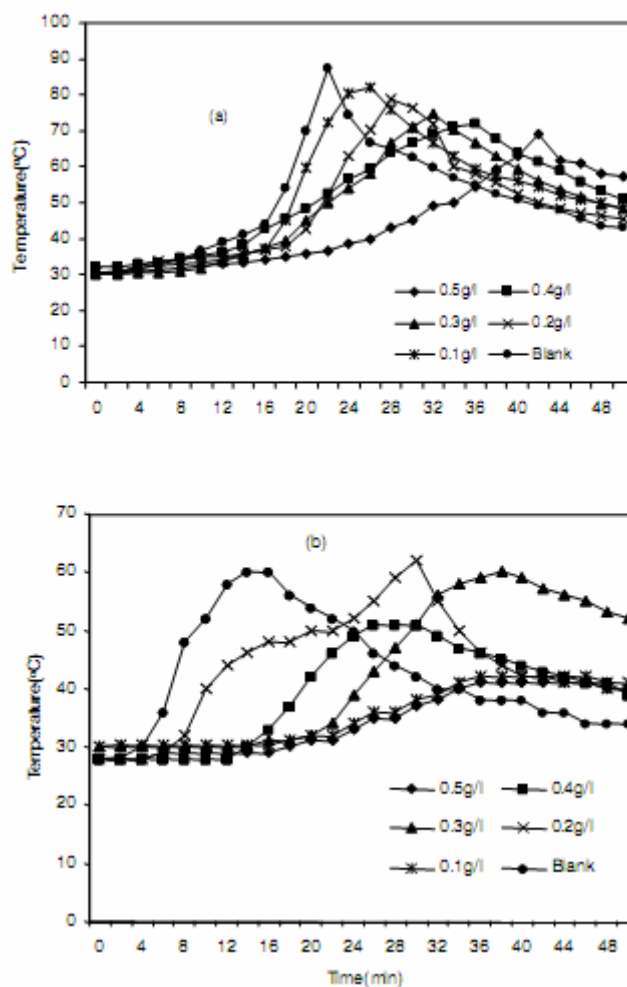

Figure 2. Temperature-time curves for aluminium corrosion in 2 M HCl in the presence of (a) PE exudates and (b) RH exudates of different concentrations.

Table 2 shows the calculated values of reaction number (RN) and the percentage reduction in reaction number (inhibition efficiency) for the various systems investigated. It is very clear from the table that reaction number decreased in the presence of the exudates compared to the blank solution. Also, the percentage reduction in reaction number increases with increase in concentration of the two exudates studied. However, *Raphia hookeri* has the highest value at all the concentrations studied. This confirms that RH is a better inhibitor than PE. This assertion is also corroborated by weight loss measurements.

Table 2. Calculated values of reaction number and percentage reduction in reaction number for Al dissolution in 2 M HCl containing exudates gums from PE and RH from thermometric method.

Concentrations of exudates (g/L)	Reaction number (RN) (^{o}Cmin^{-1})	% Reduction in RN (Inhibition efficiency)
PE Exudate		
Blank	2.80	
0.1	2.10	19.36
0.2	1.75	32.92
0.3	1.40	46.34
0.4	1.17	55.22
0.5	0.93	64.24
RH Exudate		
0.1	1.27	40.60
0.2	1.06	50.46
0.3	0.79	63.08
0.4	0.70	67.29
0.5	0.31	85.51

Adsorption /Thermodynamic studies

Adsorption isotherms are very important in understanding the mechanism of organo-electrochemical reactions [32]. In discussing adsorption isotherms, the degree of surface coverage (θ) is very useful (Table 1). The degree of surface coverage values was obtained from weight loss measurements using equation (3). The surface coverage values for PE and RH exudate gums were fitted into Temkin adsorption isotherm model, which has the form [33]

$$\exp(-2a\theta) = KC \qquad (6)$$

where 'a' is the molecules interaction parameter, θ, is the degree of surface coverage, 'K' is the equilibrium constant of adsorption process, and 'C' is the concentration of the exudates.

K is related to the free energy of adsorption by the equation:

$$k = \frac{1}{55.5} \exp\left[\frac{-\Delta G^o_{ads}}{RT} \right] \qquad (7)$$

The plot of surface coverage (θ) as a function of logarithm of exudates concentration is shown in Fig. 3. From the plot, straight lines were obtained for (a) PE and (b) RH exudate gums, indicating that the experimental data fit well into Temkin adsorption isotherm.
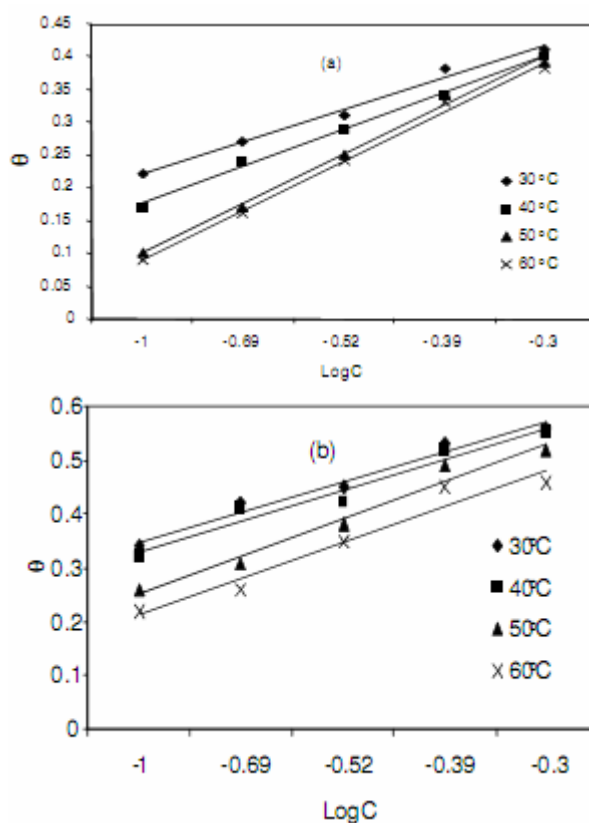
Figure 3. Plot of surface coverage (θ) as a function of logarithm of exudates concentration for (a) PE and (b) RH at 30-60 ^{o}C.

The Temkin isotherm characterizes the chemisorptions of uncharged molecules on a heterogeneous surface [34]. The complex composition of the exudates gum entails that the gum will comprise both protonated and molecular species which can affect the corrosion process to different extents, depending on their relative proportion. Physical adsorption is a result of electrostatic attraction between charged metal surface and protonated species in the bulk solution. Though physisorption of protonated species by electrostatic interaction with chloride ion adsorbed on the aluminium surface should prevail, the observed adherence to the Temkin isotherm suggests participation of some molecular species. These do not however, significantly influence the corrosion process, as ΔG^{o}_{ads} is quite low. It could therefore be concluded that in addition to molecular form, the exudates gum can also be present as protonated species in acid solution. Both molecular and protonated species can adsorbed on the aluminium surface and affect the corrosion process differently.

The calculated values of molecular interaction parameter 'a' and equilibrium constant of adsorption process, K, obtained from Temkin's plot is shown in Table 3. The values of 'a' are negative in all cases (for both PE and RH exudates) showing that repulsion exists in adsorption layer [15]. The values of K decrease with increasing temperature, suggesting that the inhibitor is physically adsorbed on the mild steel surface. Generally, K denotes the strength between adsorbate and adsorbent. Large values of K imply more efficient adsorption and hence

better inhibition efficiency [35]. Thus, exudates from RH with higher values of K at all the temperatures studied is a better inhibitor than exudates from PE.

Table 3. Some thermodynamic parameters and adsorption coefficients for aluminium corrosion of PE exudates and RH exudates in 0.1 M HCl.

Inhibitor	Temperature ^{o}C	Temkin			El-Awady		
		ΔG_{ad}^{o} (kJmol^{-1})	a	K	ΔG_{ad}^{o} (kJmol^{-1})	1/y	k$_{ad}$
PE	30	-11.11	-0.056	1.48	-10.09	10.00	4.14×10^{-7}
	40	-11.17	-0.064	1.32	-10.43	7.69	0.12×10^{-7}
	50	-10.94	-0.086	1.06	-10.76	5.26	0.16×10^{-7}
	60	-11.23	-0.086	1.04	-10.76	5.00	0.16×10^{-7}
RH	30	-11.83	-0.015	1.85	-10.09	11.11	1.09×10^{-4}
	40	-12.08	-0.009	1.73	-10.43	10.00	0.81×10^{-4}
	50	-11.91	-0.013	1.45	-10.76	7.69	0.32×10^{-4}
	60	-12.07	-0.015	1.13	-11.09	7.14	0.15×10^{-4}

The surface coverage values obtained from the gravimetric measurements were also fitted into the adsorption isotherm of the thermodynamic-kinetic model of El-Awady et al. [36-38] given by:

$$\log \frac{\theta}{1-\theta} = \log K + y \log C \qquad (8)$$

where C is the concentration of the exudates, θ is the degree of surface coverage, K_{ad} is the equilibrium constant of adsorption process, and $K_{ad} = K^{1/y}$. 1/y is the number of inhibitor molecules occupying one active site (or the number of water molecules replaced by one molecule of PE and RH exudate gums, respectively). Curve fitting of the data to the thermodynamic-kinetic model is shown in Fig. 4. This data gave straight lines for (a) PE and (b) RH exudates, respectively. The values of 1/y and K_{ad} calculated from the El-Awady et al. model curve is given in Table 3. The values of 1/y obtained are more than unity, indicating that each molecule of the phytochemical compound from the exudates involved in the adsorption process is attached to more than one active site on the metal surface [40].
The free energy of adsorption values, ΔG_{ads}^{o}, were obtained from equation (7).
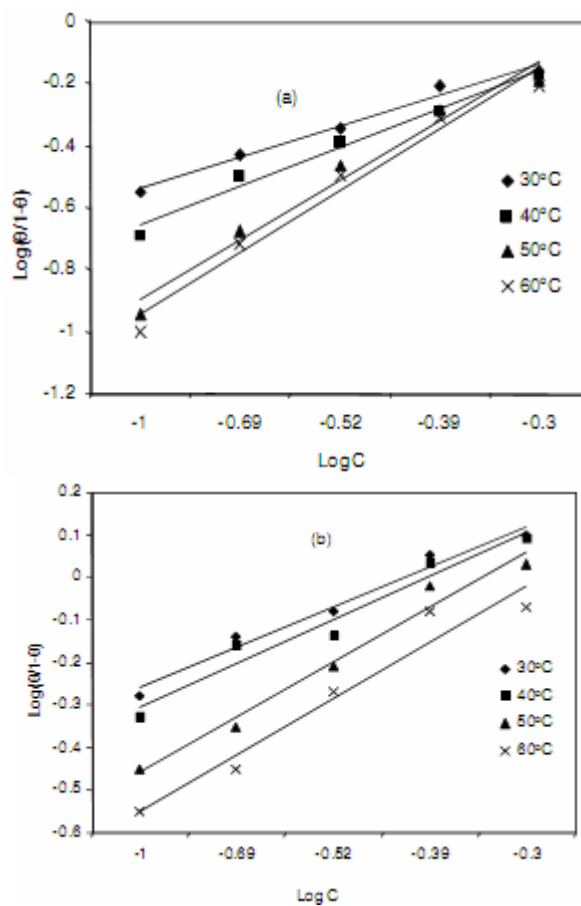
Figure 4. Kinetic/thermodynamic model of El-Awady *et al.* for Al corrosion in 0.1 M HCl in the presence of (a) PE and (b) RH exudates gums at 30-60 ^{o}C.
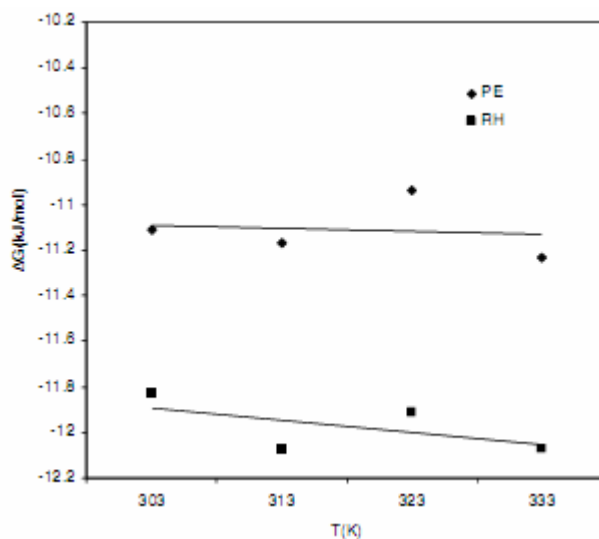

Figure 5 . Plot of ΔG^o_{ads} against temperature for PE and RH exudates.

The values obtained are presented in Table 3. Results presented in the Table indicate that the values of ΔG^o_{ads} are negative in all cases. This suggests that the exudate additives are strongly adsorbed on aluminium surface. The negative values also indicate a spontaneous adsorption of the inhibitor molecules. Results shown in the table also revealed that the values of ΔG^o_{ads} obtained from Temkin adsorption isotherm and kinetic-thermodynamic model of El-Awady et al. are comparable. The value of ΔG^o_{ads} indicates that the inhibitors (PE and RH exudates) function by physically adsorbing on the surface of the metal. 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) [39-41]. Physical adsorption is a result of electrostatic attraction between charged metal surface and charged species in the bulk of the solution. Adsorption of negatively charged species is facilitated if the metal is positively charged. Positively charged species can also protect the positively charged metal surface acting with a negatively charged intermediate such as acid anions adsorbed on the metal surface [41].
The values of enthalpy of adsorption, ΔH^o, and entropy of adsorption, ΔS^o, were obtained from (Fig. 5) the basic thermodynamic equation (9):

$$\Delta G^o_{ads} = \Delta H - T\Delta S^o \tag{9}$$

ΔH^o obtained were -11.08 kJmol^{-1} for PE and -11.84 kJmol^{-1} for RH exudate. Also values obtained for ΔS^o were 0.013 kJmol^{-1}K^{-1} for PE and 0.055 kJmol^{-1}K^{-1} for RH exudate gums. The negative sign of the ΔH^o obtained indicates that the adsorption process is spontaneous, while the positive sign of ΔS^o shows a decrease in the system order [1].

Effect of temperature

In order to get more information about the performance of the exudates, the nature of adsorption and the activation processes, the influence of temperature on the inhibition process is important. Based on temperature effect, inhibitors may be classified into three groups according to Rodovici [42]: (i) inhibitors whose inhibition efficiency (%I) decreases with temperature increase. The value of the apparent activation energy E_a, found is greater than that in the unhibited solution; (ii) inhibitors in whose %I does not change with temperature variation. The apparent activation energy E_a, does not change with the presence or absence of inhibitors; (iii) inhibitors in whose presence the %I increases with temperature increase while the value of E_a for the process is smaller than that obtained in the unhibited solution. Thus, in examining the effect of temperature on the corrosion process in the presence of the exudates, the Arrhenius equation is helpful:

$$\log CR = \frac{-E_a}{2.303RT} + \log A \tag{10}$$

where 'CR' is the corrosion rate, E_a is the apparent activation energy, R is the molar gas constant, T is the absolute temperature, and A is the frequency factor. Fig. 6 represents Arrhenius plot as log CR vs. 1/T for aluminium corrosion in 0.1 M HCl in the absence and presence of various concentrations of (a) PE and (b) RH exudate gums, respectively. Linear plots were obtained. The values of E_a were obtained from the slope of the Arrhenius plot and are presented in Table 4. From the table, it is seen that E_a increases in the presence of the inhibitors compared to the blank. The higher value of the activation energy of the process in an inhibitor's presence when compared to that in its absence is attributed to its physisorption, while the opposite is the case with chemisorption. [43,44].
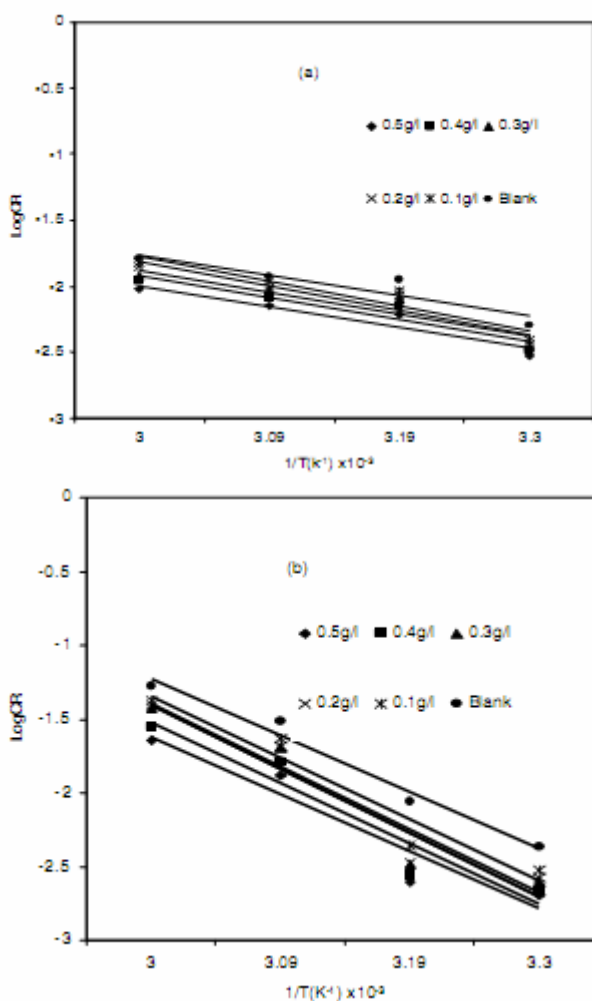

Figure 6. Arrhenius plot as log CR vs. 1/T for aluminium corrosion in 0.1 M HCl in the absence and presence of various concentrations of (a) PE and (b) RH exudates gums.

The decrease of %I value with temperature increase and the higher value of E_a in the presence of PE and RH exudates can be interpreted as an indication for a physical or coulombic type of adsorption. Similar results have been reported by other authors [4, 7, 10,]. However, the temperature and kinetic data obtained for

PE in this study within the limits of experimental error do not really show physisorption character, particularly at high concentration. This could be a further manifestation of the participation of molecular species in the inhibition process.

Table 4. Activation energy, E_a (kJ/mol) for aluminium corrosion in the presence of PE and RH exudates in 0.1 M HCl.

Concentration of exudates (g/L)	E_a (kJ/mol)
PE exudate	
Blank	2.93
0.1	3.52
0.2	3.46
0.3	3.22
0.4	3.12
0.5	3.12
RH exudate	
0.1	7.94
0.2	8.19
0.3	8.25
0.4	7.85
0.5	7.40

Conclusions
1. PE and RH exudate gums act as inhibitors for aluminium corrosion in acidic medium, RH exudates being a better inhibitor than PE exudates.
2. Inhibition efficiency of PE and RH exudates increases with increase in concentration of the inhibitors, but decreases with increase in temperature.
3. The values of ΔG^o_{ads} are negative, which suggests that the inhibitors were strongly adsorbed on the mild steel surface. The values obtained support the physical adsorption mechanism.
4. PE and RH exudates were found to obey Temkin adsorption isotherm and kinetic-thermodynamic model of El-Awady et al. from the fit of experimental data.
5. Thermodynamic parameters revealed that the adsorption process is spontaneous.

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