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Corrosion Inhibition of Aluminium Using Exudate Gum from *Pachylobus edulis* in the Presence of Halide Ions in HCl

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Abstract: The anti-corrosive effect of *Pachylobus edulis* exudate gum in combination with halides ions (Cl^-, Br^- and I^-) for aluminium corrosion in HCl was studied at temperature range of 30-60°C using weight loss method. Results obtained showed that the naturally occurring exudate gum acts as an inhibitor for aluminium corrosion in acidic environment. Inhibition efficiency (%I) increases with increase in concentration of the exudate gum and synergistically increased to a considerable extent on the addition of the halide ions. The increase in inhibition efficiency (%I) and surface coverage (θ) in the presence of the halides was found to be in the order $I^- > Br^- > Cl^-$ which indicates that the radii as well as electronegativity of the halide ions play a significant role in the adsorption process. *Pachylobus edulis* exudate gum obeys Temkin adsorption isotherm. Phenomenon of physical adsorption is proposed from the values of kinetic and thermodynamic parameters obtained. The values of synergism parameter (S_1) obtained for the halides are greater than unity suggesting that the enhanced inhibition efficiency of the *P. edulis* caused by the addition of the halide ions is only due to synergistic effect.

Keywords: *Pachylobus edulis*, Exudate, Aluminium, Acid corrosion, Adsorption isotherms, synergism.

Introduction

In order to mitigate aluminium corrosion, the main strategy is to effectively isolate the metal from corrosive agents by the use of corrosion inhibitors. Inorganic substances such as phosphates, chromates, dichromate and arsenates have been found effective as inhibitors of metal corrosion, but a major disadvantage is their toxicity and as such their use has come under severe criticism. Among the alternative corrosion inhibitors, organic substances containing polar function with nitrogen, oxygen and/or sulphur atoms in a conjugated system have been reported to exhibit good inhibiting properties[1-9]. Corrosion inhibition occurs via adsorption of their molecules on the corroding metal surface and efficiency of inhibition depends on the mechanical, structural and chemical characteristics of the adsorption layers formed under particular condition[10].

Research activities in recent times are geared towards finding alternative corrosion inhibitors to replace the inorganic and organic compounds. Naturally occurring substances have been found to readily satisfy this need. Apart from being readily available, cheap and a renewable source of materials, naturally occurring substances are ecofriendly and ecologically acceptable. The successful use of naturally occurring substances to inhibit the corrosion of metals in acidic and alkaline environment have been reported by some authors[6,11-14]. However, reports on effects of halide ions in combination with naturally occurring substances for corrosion inhibition of metals is very scanty[10,15-18].

Efforts geared towards finding naturally occurring organic substances or biodegradable organic materials as a suitable replacement of organic/inorganic corrosion inhibitors has been intensified in our research. *Pachylobus edulis* represents a category of substances that fulfill the aspect required for such purpose, since it occurs naturally and is relatively cheap. *Pachylobus edulis* (PE)(local pear tree) is widely planted and found mainly in tree crops fields and in home gardens in Nigeria, Cameroon and in Central Africa. It is also known as *safou* or African plum and is of the specie *Burseraceae*. The dead branches of the species are used as firewood and its bark is used as medicine[19]. This plant produces gummy exudates which are used locally.

As a contribution to the current interest on environmentally friendly, green, corrosion inhibitors, the present study investigates the inhibiting effect of exudates gum from *Pachylobus edulis* on aluminium corrosion in acidic solution using the weight loss technique at 30-60 ^{o}C. Synergistic effect of halide additives namely KCl, KBr and KI on the inhibition efficiency has also been studied. Kinetic and activation parameters that govern metal corrosion have been evaluated.

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 0.4mm in thickness and was mechanically press cut into 5cm x 4cm 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) was obtained from Ikpetime Village, Ikot Abasi Local Government of Akwa Ibom State, Nigeria. 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.*[20]. The concentrations of inhibitor (PE) prepared and used in the study were 0.1 to 0.5g/L. The concentrations of HCl (BDH supplies chemicals, England) used were 0.001M to 0.1M. The halides used (KCl, KBr and KI) were all BDH supplies chemicals, England and the concentrations prepared was 0.1M. For the synergistic studies, 0.06M KCl, 0.06M KBr and 0.06M KI were used.

Table 1. Calculated values of corrosion rate (mm/yr), inhibition efficiency (% I) and degree of surface coverage (θ) for aluminium in 0.1M HCl containing PE, halides and PE-halide mixtures at different temperatures.

Systems/ concentration	Corrosion rate (mm/yr) x 10^{-3},				Inhibition efficiency (% I)				Degree of surface coverage θ			
	Temperature, ^{0}C											
	30	40	50	60	30	40	50	60	30	40	50	60
Blank	5.1	11.0	12.0	16.0	-	-	-	-	-	-	-	-
0.06M KCl	3.7	8.9	9.9	13.0	27.0	24.0	22.1	20.4	0.27	0.24	0.22	0.20
0.06M KBr	3.3	8.6	9.6	12.0	34.0	25.0	23.3	23.0	0.34	0.25	0.23	0.23
0.06M KI	3.2	8.4	9.0	11.0	37.0	31.3	26.0	25.0	0.37	0.31	0.26	0.25
(Exudate) PE	3.0	6.2	7.1	9.6	41.0	40.0	39.0	38.0	0.41	0.40	0.39	0.38
PE + 0.06M KCl	2.9	5.9	7.0	9.5	48.0	46.1	44.2	41.7	0.48	0.46	0.44	0.42
PE + 0.06M KBr	2.4	5.8	6.8	9.3	53.0	48.8	45 .0	42.2	0.53	0.49	0.45	0.42
PE + 0.06M KI	1.9	3.7	6.6	9.0	63.0	9.6	47.9	45.1	0.63	0.50	0.48	0.45

Weight loss measurements

In the weight loss experiments, a clean weighed aluminium coupon was immersed completely in a 250mL beaker containing the corrodent and inhibitors with the aid of glass rod and hooks. The beakers were placed in a constant thermostated bath maintained at 30 – 60 ^{o}C. The coupons were retrieved at 24h interval progressively for 168h (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 [21]. The differences in weight of the coupons were taken as the weight loss which was used to compute the corrosion rate given by:

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

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

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

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

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 from equation (3):

$$\theta = 1 - \frac{W_i}{W_0} \qquad (3)$$

Results and Discussion

Weight loss and corrosion rate

The loss in weight of aluminium in 0.1M HCl in the absence and presence of *P. edulis* exudate gum, halides and exudate gum–halide mixtures after 168h of immersion was determined at temperature range of 30-60 ^{o}C. Fig.1 shows weight loss time curves for aluminium dissolution in the absence and presence of various additives at 30 ^{o}C. Similar plots were obtained at 40-60 ^{o}C. Inspection of the figure shows a decrease in weight loss of aluminium in the presence of halides, exudate gum and exudates gum-halide mixtures compared to the blank.

The corrosion rate was evaluated using equation (1). The calculated values for corrosion rate for the different systems studied are presented in Table 1. Results shown in the table indicate that corrosion rate of aluminium dissolution in HCl was reduced in the presence of halides and *Pachylobus edulis* exudate gum compared to the free acid. Further reduction in corrosion rate was observed on addition of halide ions to the exudate gum. The reduction in corrosion rate in the presence of the halides was observed to follow the trend: exudate + KCl > exudate + KBr > exudate + KI. Corrosion rates were also observed to increase with rise in temperature. With highest values obtained at 60 ^{o}C both in the absence and presence of the additives.

Inhibition efficiency (%I)

The calculated values of inhibition efficiency for halides, exudate gum (0.5g/L) and exudate gum in combination with halides are presented in Table 1. From the table, it is clearly seen that inhibition efficiency increased in the presence of the exudate gum compared to the blank alone. The maximum inhibition efficiency was observed to be 63.00% (0.5g/L of exudate gum + 0.06M KI). However, inhibition efficiency of exudate gum was significantly improved on the addition of halide ions. The table also revealed that inhibition efficiency decreases with increase in temperature. Decrease in inhibition efficiency with increase in temperature is suggestive of physical adsorption mechanism. The inhibitive effect of the *P. 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[19,20]. Owing to the complex chemical composition of the exudate gum, it is quite difficult to assign the inhibitive effect to a particular constituent. The adsorption of these compounds on the aluminium surface reduces the surface area available for corrosion.

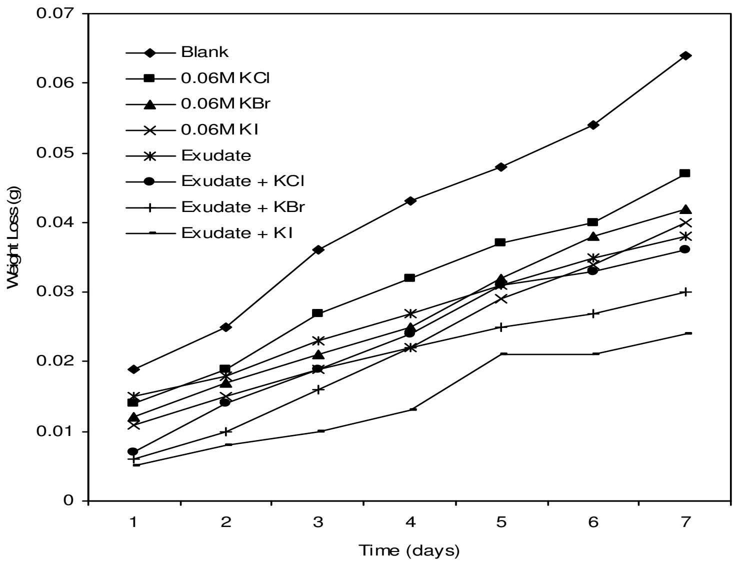


Figure 1. Variation of weight loss with time for aluminium corrosion in 0.1M HCl in the absence and presence of halides, exudates and exudates – halide mixtures at 30 °C.

Effect of Halide Ions and Synergistic Considerations

Results obtained in the present study clearly show that surface coverage and inhibition efficiency of the *P. edulis exudates* gum was greatly enhanced on addition of halide ions. Similar observation had been reported by some authors[10,17,18,22-24] and was ascribed to a synergistic effect. It is thought that the anions are able to improve adsorption of the organic cations in solution by forming intermediate bridges between the metal surface and the positive end of the organic inhibitor. The degree of surface coverage values was found to increase in the order KI > KBr > KCl. It is also seen in Table 1 that inhibition efficiency of the exudate gum increases with the addition of the halide salts with the highest inhibition efficiency obtained when the exudates gum combined with iodide ions at all the temperatures studied. This can be attributed to the stabilization of adsorbed halide ions by electrostatic interaction with the exudates gum, which leads to greater surface coverage and hence greater inhibition efficiency. Halide ions are good ligands because they exhibit low electronegativity (less than 3.5) except fluoride ion [22]. Electronegativity decreases while the atomic radius increases from Cl^- to I^- [25]. Hence, Al can form compounds with halide ions, thereby inhibiting the corrosion of Al in the presence of exudates gum. The synergistic effect increased in the order $Cl^- < Br^- < I^-$ suggesting a possible role by ionic radii in the adsorption process which also increase in the order, Cl^- (0.09nm) < Br^- (0.114nm) < I^- (0.135nm).

Corrosion inhibition synergism then results from increased surface coverage arising from ion-pair interactions between the organic cations and the anions. Synergism of corrosion inhibition has been assessed in terms of a synergistic parameter, S_I, according to the relationship earlier reported[26,27]. This parameter was evaluated from the inhibition efficiency values obtained from weight loss measurements.

The calculated values of S_I for the halides KCl, KBr and KI are 1.854, 1.556 and 1.354 respectively. These values are greater than unity. This suggests that the enhanced inhibition efficiency caused by the addition of halide ions to the exudates gum is only due to synergistic effect.

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 using equation (3) and presented in Table 1. The experimental data for the tested exudate gum obtained from *Pachylobus 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

$$\exp(-2a\theta) = KC \tag{4}$$

where 'a' is 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. 2 shows the plot of θ against log C for (a) halides (b) exudates and exudates – halide mixtures at 30°C (Temkin adsorption isotherm). Similar plots were obtained at other temperatures (40-60°C). Linear plots were obtained for the different systems studied at 30°C indicating that the experimental results fit the Temkin isotherm. 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 (for (a) halides (b) exudates and exudates – halide mixtures) showing that repulsion exist in adsorption layer[5].

The thermodynamic parameters for adsorption were calculated using the values of K according to the following equation:

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

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. 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 $kJmol^{-1}$ involves charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of bond (which indicates chemisorption)[28-30]

Effect of Temperature

The results obtained from temperature studies revealed that increasing temperature increases corrosion rate and decreases inhibition efficiency at all the concentrations studied.

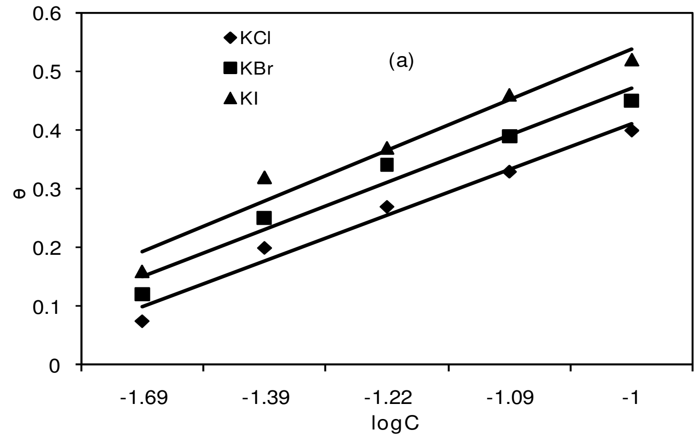
The activation energy (E_a) of the corrosion process in the absence and presence of the additives was evaluated using Arrhenius equation,

$$\log CR = \log(A) - \frac{E_a}{2.303RT} \tag{6}$$

where CR is the corrosion rate, A is the Arrhenius constant, R is the molar gas constant and T is the absolute temperature. Fig.3 shows the plot of log CR versus I/T. Linear plots were obtained. The values of E_a were computed from the slope of the straight lines and are listed in Table 3.

Table 2. Some Thermodynamic parameters and adsorption coefficients deduced from the adsorption isotherms at 30 °C.

Systems/Concentrations	Temkin adsorption Isotherm		
	$\Delta G^o_{ads,}$ $kJmol^{-1}$	K	a
0.06M KCl	-15.01	1.09	-0.35
0.06M KBr	-16.24	1.03	-0.37
0.06M KI	-16.88	1.57	-0.39
Exudate	-17.43	1.51	-0.23
Exudate +KCl	-17.78	1.65	-0.27
Exudate +KBr	-18.21	1.87	-0.27
Exudate +KI	-18.94	2.73	-0.31



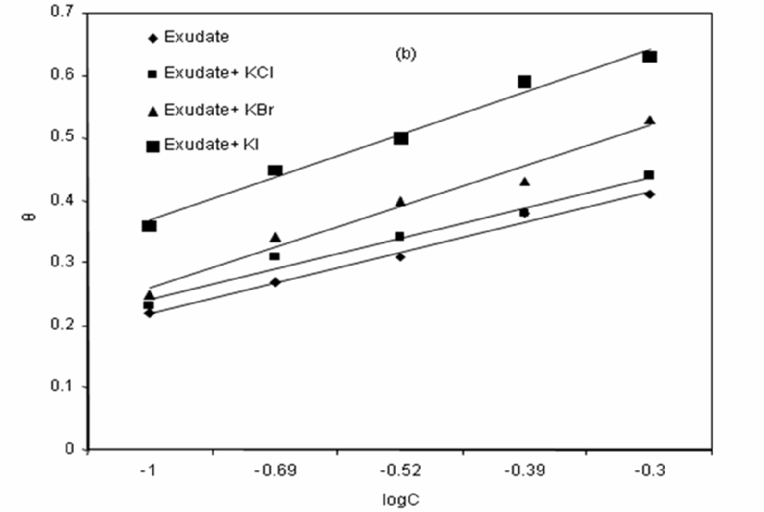


Figure 2. Temkin adsorption isotherm plot as θ against logC for (a) halides (b) exudates and exudates – halide mixtures at 30°C.

Table 3. Calculated values of Activation parameters of the dissolution reaction of aluminium in 0.1 M HCl in the absence and presence of exudates, halides and exudate halides mixture.

Systems/Concentrations	Activation Energy, E_a ,kJmol^{-1}	Enthalpy of adsorption, ΔH^o , kJmol^{-I}
Blank	1.06	1.50
0.06M KCl	2.81	2.45
0.06M KBr	3.01	2.70
0.06M KI	3.03	2.80
Exudate (0.5g/l)	3.26	2.88
Exudate + KCl	3.50	3.24
Exudate + KBr	3.73	3.49
Exudate + KI	3.96	3.73

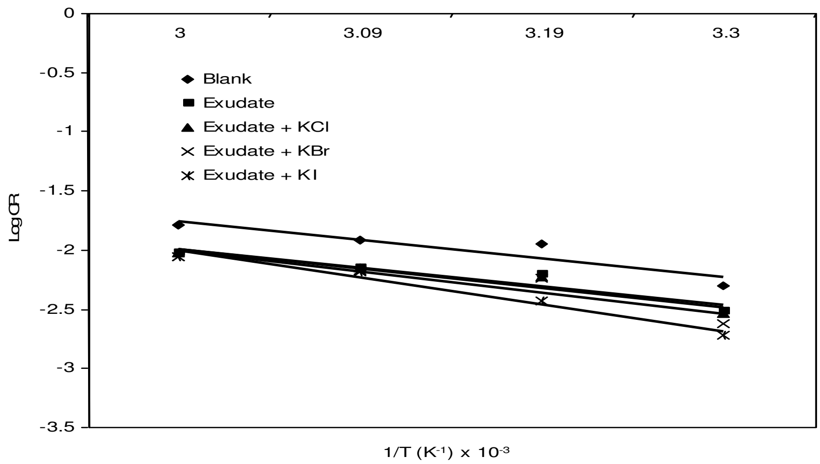


Figure 3..Arrhenius plot for aluminium dissolution in 0.1M HCl in the absence and presence of halides, exudate and exudate- halide mixtures at 30 ^{o}C.

It is clear from Table 3 that E_a values in the presence of the additives are higher than that in their absence. The higher activation energies imply a slow reaction and that the reaction is very sensitive to temperature. The increase in the activation energy in the presence of halide, *P. edulis* exudate and exudate-halide mixtures signifies physical adsorption[31]. This conclusion is denoted by the decrease in inhibition efficiency with increasing temperature. Enthalpy of activation, ΔH^* is another criterion from which the mode of adsorption can be probed. ΔH^* was obtained by applying the transition state equation.

$$CR = \frac{RT}{Nh}\exp\left(\frac{\Delta S^*}{R}\right)\exp\left(-\frac{\Delta H^*}{RT}\right) \tag{7}$$

Where h is the Planck's constant, N is the Avogadro's number, ΔS^* is the entropy of activation, T is the absolute temperature and R is the universal gas constant. A plot of Log (CR/T) against I/T (not shown) was made for the blank and various additives with a slope of (-ΔH^*/R) and an intercept of (Log(R/Nh) + ΔS^*/R. The values of ΔH^* are presented in Table 3. Enthalpy of activation of absolute values lower than 41.86kJmol^{-1} indicates physical adsorption and values approaching 100kJmol^{-I} indicate chemical adsorption[31]. In this study, the values of ΔH^* are lower than 41.86 kJmol^{-1} confirming physical adsorption.

Conclusions

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

1. *Pachylobus edulis* exudate gum acts as inhibitor for aluminium corrosion in HCI solution.
2. Inhibition efficiency increased with increase in concentration of the *P. edulis* exudate gum but decreased with increase in temperature. Phytochemical constituents in the exudate play a very vital role in the inhibiting action.
3. Synergistic effects increased the inhibition efficiency of the exudate in the presence of halide ions in the order KI > KBr > KCl.
4. Activation energies were higher in the presence of the exudates gum suggesting physisorption mechanism.
5. This present study provides new information on the inhibiting characteristic of a *Pachylobus edulis* exudate gum under the specified conditions. The adsorption of halides, *P. edulis* exudate gum and exudate-halide mixtures fits into the Temkin isotherm model.

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