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Synergistic Inhibition between Naturally Occurring Exudate Gum and Halide Ions on the Corrosion of Mild Steel in Acidic Medium

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The effect of naturally occurring exudate gum from *Raphia hookeri* (RH) on the corrosion of mild steel in H_2SO4 in the temperature range 30-60 ^oC was studied by weight loss and hydrogen evolution techniques. Results obtained reveal that the exudate gum reduces the corrosion rate. The inhibition efficiency increased with an increase in exudate gum content up to 5g/l to reach 70% at 30 ^oC and decreases with increase in temperature. The adsorption of exudate gum from *Raphia hookeri* on the mild steel follows Langmuir adsorption isotherm. Results obtained by weight loss and hydrogen evolution technique are in good agreement. The addition of halide ions to the exudate gum enhanced the inhibition efficiency due to synergistic effect. Mechanism of physical adsorption is proposed from the apparent activation energy (E_a) and the thermodynamic parameters obtained. The adsorption of the exudate gum on the mild steel surface is spontaneous.

Keywords: *Raphia hookeri*, mild steel, halide ions, corrosion inhibition, synergism.

1. INTRODUCTION

Corrosion control of metals is an important activity of technical, economical, environmental and aesthetical importance. Thus, the search for new and efficient corrosion inhibitors has become a necessity to secure metallic materials against corrosion. Over the years, considerable efforts have been deployed to find suitable compounds of organic origin to be used as corrosion inhibitors in various corrosive media, to either stop or delay to the maximum the attack of a metal [1-10]. Nevertheless, the known hazard effects of most synthetic organic inhibitors and the need to develop cheap, non-toxic and environmentally benign processes have now made researchers to focus on the use of natural products. These natural organic compounds are either synthesized or extracted from aromatic herbs, spices and medicinal plants.

The use of natural products as corrosion inhibitors have been widely reported by several authors. These include the inhibitive action of the acid extracts of seeds, leaves and bark from the *Figus virens* plant [11], *Datura metel* [12], *Allium sativum* [13], *Olive* [14], *Zenthoxylum alatum* [15], and juice extracts of *Magnifera indica* (mango) [16] to mention but a few. It was found that all the plant materials act as good corrosion inhibitor for metal corrosion in acidic media. The corrosion inhibition of these plants materials have been attributed to the presence of active principles present in them. These active principles form protective films on metal surfaces by coordinating with metal ions through O, S or N atoms of the functional groups present in the active principles [17].

The presence of halide ions in solution has been found to stabilize the adsorption of some organic cations leading to improved inhibition efficiency. Synergism has become an increasing important phenomenon and serves as the basis for most modern corrosion inhibitor formulation. Trials to enhance the performance of naturally occurring substances by addition of small amount of halide ions have been reported by some authors [18-21].

Our research team had earlier reported on the use of *Gum Arabic* as corrosion inhibitor for aluminium in alkaline medium [22], and the synergistic inhibition of aluminium corrosion in acidic medium by *Gum arabic* and halide ions [23]. In our continued effort to contribute to the current search for green corrosion inhibitors to replace the synthetic ones, the present study reports on the corrosion inhibition and adsorption behaviour of *Raphia hookeri* exudate gum (RH) on mild steel in H_2SO_4 at temperature range of 30 –60^oC using weight loss and hydrogen evolution methods. The synergistic effect of halide ions on the corrosion inhibition of the gum is also reported.

2. EXPERIMENTAL PART

Corrosion tests were performed on a mild steel of the following percentage composition: 0.21% C; 0.38% Si; 0.09% P; 0.01% Al; 0.05% Mn; 0.05% S and the remainder iron. The metal was prepared as previously reported [24-26]. The mild steel sheet was mechanically pressed cut into coupons of dimension 5cm x 4cm. the coupons were used as cut without further polishing. However,, they were degreased using absolute ethanol, dried in acetone and stored in moisture free desiccators prior to use in corrosion testing. *Raphia hookeri* exudate gum was obtained from Ikpetime Village, Ikot Abasi Local Government Area of Akwa Ibom State, Nigeria. The exudate gum was purified following the method of Ekpe et al. [27] and reported elsewhere [28-30]. The concentrations of inhibitor (RH) prepared and used in the study were 0.1- 0.5 g/l. The concentration of H_2SO_4 (BDH) used was 0.1M and 1M for weight loss and hydrogen evolution techniques respectively. The halides used (KCl, KBr and KI) were all BDH supplies chemicals, England and the concentrations prepared were 0.02 – 0.1M. For the synergistic studies, 0.06M solutions of KCl, KBr and KI were used.

The apparatus and procedure followed for weight loss and hydrogen evolution methods were similar to that earlier reported [24-26, 31]. In weight loss measurements, clean and weighed mild steel coupons in triplicates were totally immersed in the free acid solution and in 0.1M H_2SO_4 containing different concentrations of halides, *Raphia hookeri* exudate gum and the exudate gum in combination with the halides. They were withdrawn from the test solutions after 24h progressively for 7 days (168h), washed in 20% NaOH solution containing 200g/l of Zinc dust at room temperature for 2 minutes to remove the corrosion products with bristle brush under running water, dried in acetone and reweighed. The difference in weight of the coupons before and after immersion in the test solutions was taken as the weight loss recorded using digital analytical balance. The values reported are average for three determinations.

In hydrogen evolution method, 100 ml of the corrodent (1M H_2SO_4) was introduced into the reaction vessel and mild steel coupons placed in it, and the reaction vessel was quickly close to prevent any escape of gas. The volume of hydrogen gas evolved was monitored as a function of time by measurement of the depression (in cm^3) in the paraffin oil level. The same experiment was repeated in the presence of inhibitor (RH), halides and RH-halides mixtures. Results recorded are average values of three separate determinations.

In both techniques, the experiments were conducted at 30 – 60° in a thermostated water bath.

3. RESULTS AND DISCUSSION

3.1. Weight Loss Measurements

The corrosion of mild steel in 0.1M H_2SO_4 in the absence and absence of RH, halides, and RH-halides mixtures was investigated at temperature range of 30-60 °C using weight loss measurements. Fig.1 shows a representative plot of weight loss against time (days) for mild steel in 0.1M H_2SO_4 solution containing no inhibitor (blank) and in the presence of the highest concentration (0.5g/l) of *Raphia hookeri* exudate gum (RH) studied, 0.06M KCl, KBr and KI and the highest concentration of RH in combination with 0.06M of the halides at 30°C. Similar plots were obtained for other temperatures (40-60 °C). The figure clearly shows a reduction in weight loss of the metal coupons in the presence of RH and halides when compared to the free acid solution (blank). Further reduction in weight was observed for mild steel in the test solution containing RH in combination with halide ions with the most profound effect noted for RH-KI mixture.

The calculated values of corrosion rate (mpy), inhibition efficiency (%I) and surface coverage (θ) for mild steel corrosion in 0.1M H_2SO_4 (blank) and in the presence of RH, halides and RH-halides mixtures at 30-60 °C from the weight loss measurement are shown in Table 1. The corrosion rate, inhibition efficiency and surface coverage were calculated using the following equations [32]

$$\text{Corrosion rate (mpy)} = \frac{534W}{\rho At} \tag{1}$$

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).

$$\text{Inhibition efficiency (\%I)} = \left(1 - \frac{W_o}{W_1}\right) x100 \qquad (2)$$

where W_0 and W_1 are the weight losses of mild steel in the absence and presence of inhibitor respectively at the same temperature.

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

$$\text{Surface coverage } (\theta) = 1 - \frac{W_0}{W_1} \qquad (3)$$

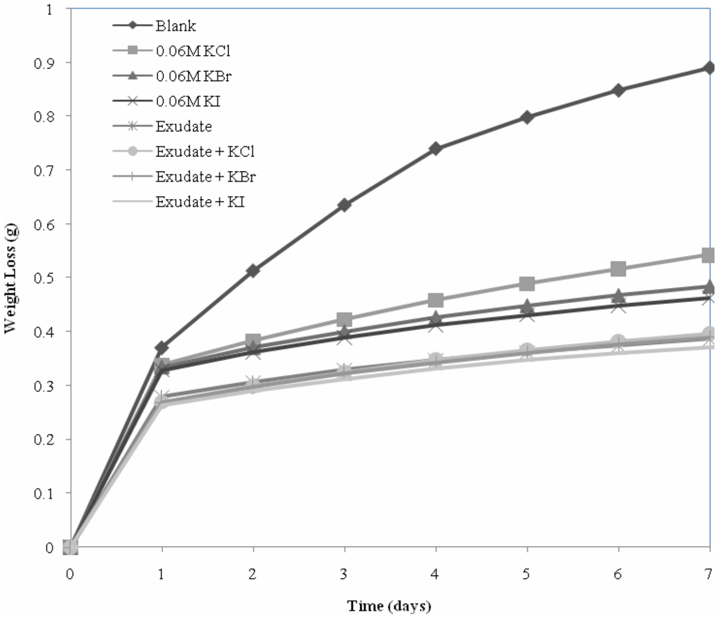

Figure 1. A plot of weight loss against time for mild steel corrosion in 0.1M H_2SO_4 in the absence and in the presence of exudate gum, halides and exudate gum-halides mixtures

Results shown in the table revealed that corrosion rates increase with increasing temperature for all the systems studied. This may be attributed to the higher dissolution rates of mild steel at elevated temperature and a possible desorption of adsorbed inhibitor due to increase solution agitation resulting from higher corrosion rates, which may also reduce the ability of inhibitor to be adsorbed on the metal surface. Such behaviour as observed in this study, suggests physical adsorption of the exudate gum on the corroding mild steel surface [30, 33]. The highest corrosion rate (11.0 x 10^{-3} mpy) was obtained for the blank at 60 ^{o}C. In the presence of RH and RH-halides mixtures, the corrosion rates was observed to reduce significantly indicating that RH actually inhibited the corrosion of mild steel in acidic environment. The lowest value of the corrosion rate was observed to be 2.0 x 10^{-3} mpy at 30 ^{o}C obtained for RH-KI mixtures.

Table 1. Corrosion parameters for mild steel in 0.1M H_2SO_4 in the absence and presence of *Raphia hookeri* (RH) halides and RH – halides mixtures at different temperatures.

Temperature (^oC)	System/Concentration	CR (mpy) $x10^{-3}$	(%I)	θ
30	Blank	6.2	-	-
	0.06M KCl	3.8	64.9	0.65
	0.06M KBr	3.4	57.0	0.57
	0.06M KI	2.7	60.0	0.60
	Exudate (RH) (0.5g/l)	2.5	70.0	0.72
	RH + 0.06M KCl	2.3	72.0	0.70
	RH + 0.06M KBr	2.2	73.4	0.73
	RH + 0.06M KI	2.0	75.2	0.75
40	Blank	8.8	-	-
	0.06M KCl	5.0	45.2	0.45
	0.06M KBr	4.8	50.4	0.50
	0.06M KI	4.6	58.1	0.58
	Exudate (RH) (0.5g/l)	3.0	69.4	0.69
	RH + 0.06M KCl	2.8	70.3	0.70
	RH + 0.06M KBr	3.0	71.3	0.71
	RH + 0.06M KI	2.7	72.1	0.72
50	Blank	10.2	-	-
	0.06M KCl	7.9	43.4	0.43
	0.06M KBr	7.6	47.9	0.48
	0.06M KI	7.4	57.0	0.57
	Exudate (RH) (0.5g/l)	5.0	67.1	0.67
	RH + 0.06M KCl	5.2	68.5	0.69
	RH + 0.06M KBr	4.9	70.1	0.70
	RH + 0.06M KI	4.5	70.4	0.71
60	Blank	11.0	-	-
	0.06M KCl	8.2	39.1	0.39
	0.06M KBr	8.0	45.6	0.46
	0.06M KI	7.9	56.0	0.56
	Exudate (RH) (0.5g/l)	5.2	58.2	0.58
	RH + 0.06M KCl	5.3	58.5	0.59
	RH + 0.06M KBr	5.1	60.0	0.60
	RH + 0.06M KI	4.6	61.3	0.61

The inhibition efficiency was found to increase with increasing concentration of RH exudate gum up to 5g/l. It was also noted to decrease with rising temperature. Addition of halide ions further increases the inhibition efficiency values. The highest inhibition efficiency of (75.2%) was obtained when RH exudate gum combined with iodide ions at 30 ^oC (Table 1). The synergistic effect also increases on addition of halide ions to the RH exudate gum solution in the order $Cl^- < Br^- < I^-$.

The protection action of organic substances during metal corrosion is based on the adsorption ability of their molecules, where the resulting adsorption film isolates the metal surface from the corrosive medium [34-36]. Consequently, in inhibited solutions, the corrosion rate is indicative of the number of free corrosion sites remaining after some sites have been effectively blocked by inhibitor adsorption.. It is generally accepted that the first step in the adsorption of an organic inhibitor on a metal surface usually involves the replacement of one or more water molecules adsorbed at the metal surface [37].

$$\mathrm{Inh}_{(sol)} + x\mathrm{H_2O} \leftrightarrows \mathrm{Inh}_{(ads)} + x\mathrm{H_2O}_{(sol)} \quad (4)$$

The inhibitor may then combine with freshly generated Fe^{2+} ions on the steel surface, forming metal – inhibitor complexes:

$$\mathrm{Fe} \rightarrow \mathrm{Fe}^{2+} + 2e \quad (5)$$

$$\mathrm{Fe}^{2+} + \mathrm{Inh}_{(ads)} \rightarrow [\mathrm{Fe}-\mathrm{Inh}]^{2+}_{(ads)} \quad (6)$$

The resulting complex could, depending on its relative solubility, either inhibit or catalyze further metal dissolution; hence the integrity depends on the environment capacity to dilute it.

The results obtained so far suggest that the exudate gum from RH exhibited good inhibition efficiency during mild steel corrosion in 0.1M H_2SO_4 solution. Owing to the complex chemical composition of the exudate gum, it is quite difficult to assign the inhibitive effect to a particular constituent. Initial physiochemical analysis of the exudate gum identified the presence of hexuronic acid and neutral sugar residues, volatile monoterpenes, canaric and related triterpene acids, reducing and non-reducing sugars [27]. Mutual adsorptive effects of these compounds and other components present in the exudates gum cannot be ruled out in the adsorption process. The adsorption of these components on the mild steel surface reduces the surface area available for corrosion [29, 30]. Further investigation using surface analytical techniques will enable the characterization of the active materials in the adsorbed layer and identification of the most active species.

3.2 Hydrogen Evolution Measurements

The Hydrogen evolution technique provides a rapid and reliable means of ascertaining any perturbation by the inhibitor with regard to gas evolution at the metal corrodent interphase [38, 39]. Results obtained by this method are corroborated by other well established techniques including weight loss and thermometric [36], potentiostatic polarization [40] and electrochemical impedance spectroscopy [41].

The inhibition efficiency, (%I) was calculated using equation (7):

$$\%I = \left(1 - \frac{V_{Ht}^{1}}{V_{Ht}^{o}}\right) x100 \quad (7)$$

where V_H^1 is the volume of hydrogen evolved at time" t" for inhibited solution and V_H^O for unhibited solution.

The volume of hydrogen evolved, V_H, during the dissolution of mild steel in 1M H_2SO_4 solutions in the absence and presence of RH exudate gum, halides and RH-halides mixtures at 30 °C was measured as a function of time. The results are shown in Fig.2. The presence of exudate gum decreases markedly the volume of H_2 evolved compared to the blank, and therefore inhibited mild steel corrosion in the acidic solution. Further reduction in the volume of H_2 was also observed on the addition of halides at 30 °C. Similar trends were observed at 40-60 C.

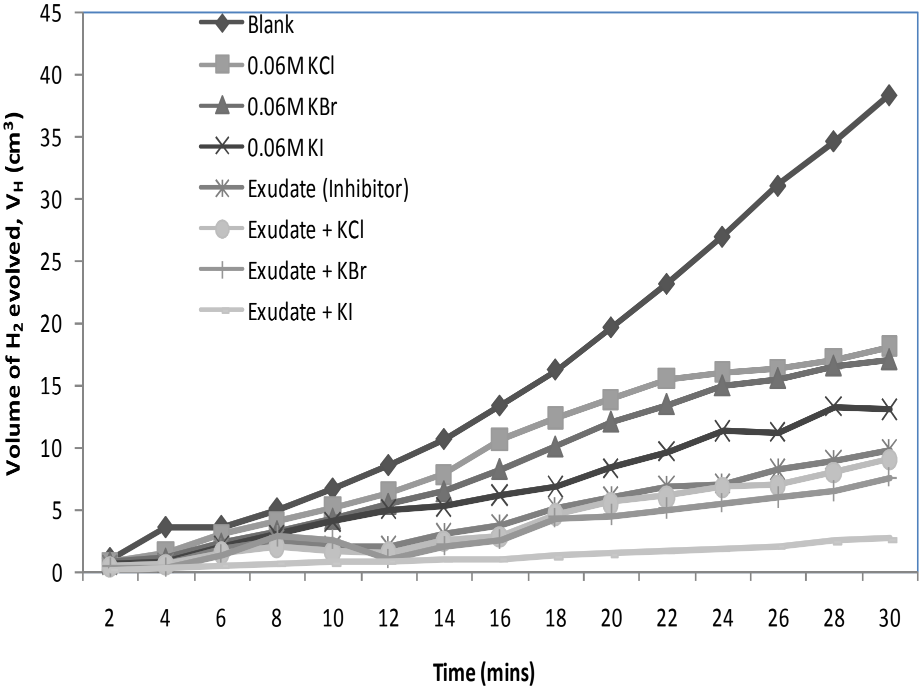

Figure 2. A plot of volume of Hydrogen evolved against time for mild steel corrosion in 0.1M H_2SO_4 devoid and in the presence of exudates gum and exudates gum-halides mixtures at 30 °C

Comparison of inhibition efficiencies calculated from the weight loss and hydrogen evolution methods at 30 °C are given in Table 2. The two techniques give almost similar values of inhibition efficiency but the values of inhibition efficiency obtained from hydrogen evolution method are lower. This may be attributed to the difference in time required to form an adsorbed layer of the inhibitor on the metal surface that can inhibit corrosion [31].

Table 2. Comparison of inhibition efficiency (%I) from weight loss and hydrogen evolution methods at 30° C.

Systems/Concentration	Inhibition efficiency (%I)	
	Weight loss	Hydrogen evolution
Exudate (RH)	70.0	62.0
RH + 0.06M KCl	72.0	69.6
RH + 0.06M KBr	73.4	71.0
RH + 0.06M KI	75.2	72.0

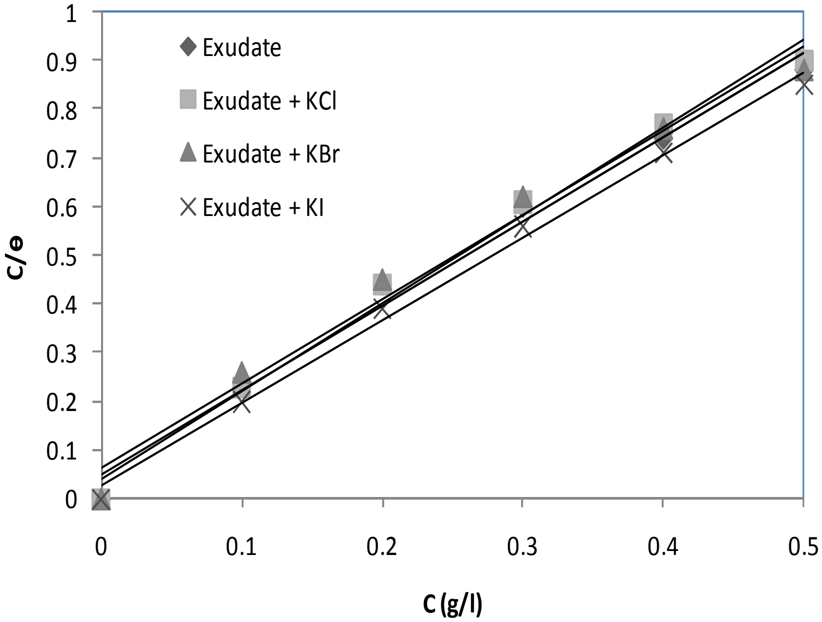

Figure 3. Langmuir adsorption isotherm for mild steel corrosion in 0.1M H_2SO_4 in presence of exudate gum and exudate gum-halides mixtures at 30 ^oC

3.3. Adsorption Isotherms

Adsorption isotherms are very important in determining the mechanism of organo-electrochemical reaction [42]. The most frequently used isotherms are Langmuir, Frumkin, Hill de-Boer, Parsons, Temkin, Flory-Huggin, Freundlich, Dhar-Flory-Huggin, Kinetic/Thermodynamic model of El-Awady et al. and Bockris-Swinkels [43-52]. All these isotherms are of the general form:

$$f(\theta, x)\exp(-2a\theta) = KC \qquad (8)$$

where f(θ, x) is the configurational factor which depends upon the physical model and the assumptions underlying the derivation of the isotherm, θ the surface coverage, C, the inhibitor concentration in the electrolyte, x the size factor ratio, a the molecular interaction parameter and K the equilibrium constant of the adsorption process. In this study, Langmuir adsorption isotherm was found to be suitable for the experimental findings. The isotherm is described by equation (9):

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \qquad (9)$$

with $$\Delta G^o_{ads} = -RT\ln(Kx55.5) \qquad (10)$$

where C is the inhibitor concentration, k_{ads} the adsorption equilibrium constant and ΔG^o_{ads} the standard free energy of adsorption. Though the plot of C/θ versus C was linear (Fig.3) (correlation > 0.9), the deviation of the slopes from unity (Table 3) (for ideal Langmuir isotherm) can be attributed to the molecular interaction among the adsorbed inhibitor species, a factor which was not taken into consideration during the derivation of the Langmuir equation The fit of the experimental data to this isotherm provides evidence for the role of adsorption in the observed inhibitive effect of the exudate gum.

The obtained values of k_{ads} are presented in Table 3. All the values are low which suggest weak interactions (physisorption) of the active constituents present in RH exudate gum and the mild steel surface [33].

Table 3. Adsorption coefficients deduced from Langmuir Isotherm for *Raphia hookeri* and RH – halides mixtures in 0.1M H_2SO_4 on mild steel at 30 ^oC.

Systems/Concentration	Langmuir Isotherms		
	K_{ads}	Slope	R^2
Exudate	8.19	0.173	0.987
RH + 0.06M KCl	7.29	0.179	0.989
RH + 0.06M KBr	8.93	0.173	0.981
RH + 0.06M KI	6.99	0.170	0.995

3.4. Kinetic / Thermodynamic studies

The adsorption of the organic compounds can be described by two main types of interactions: physical adsorption and chemisorptions. They are influenced by the nature of the charge of the metal, the chemical structure of the inhibitor, pH, the type of electrolyte and temperature [54]. Thus in order to further elucidate the inhibitive properties of the inhibitor and the temperature dependence on the corrosion rates, the apparent activation energy (E_a) for the corrosion process in the absence and presence of inhibitor were evaluated from Arrhenius equation:

$$LogCR = LogA - \frac{E_a}{2.303RT} \qquad (11)$$

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. Arrhenius plot for the corrosion rate of mild steel in the absence and presence of RH exudate gum, RH–halides mixtures is given in Fig.4. Straight lines were obtained from the plot of Log CR versus 1/T with slope equal to $\frac{-E_a}{2.303R}$. We note that E_a increased in the presence of the exudates gum and exudate gum-halides mixtures when compared to the blank, hence leading to the reduction in the corrosion rates. It has been suggested that adsorption of an organic inhibitor can affect the corrosion rate by either decreasing the available reaction area (geometric blocking effect) or by modifying the activation energy of the anodic or cathodic reactions occurring in the inhibitor-free surface in the course of the inhibited corrosion process [33,55]. 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 chemisorptions [29]. Additional information on the inhibition mechanism could be obtained from analysis of the adsorbed layer and detailed study of the corrosion morphology.

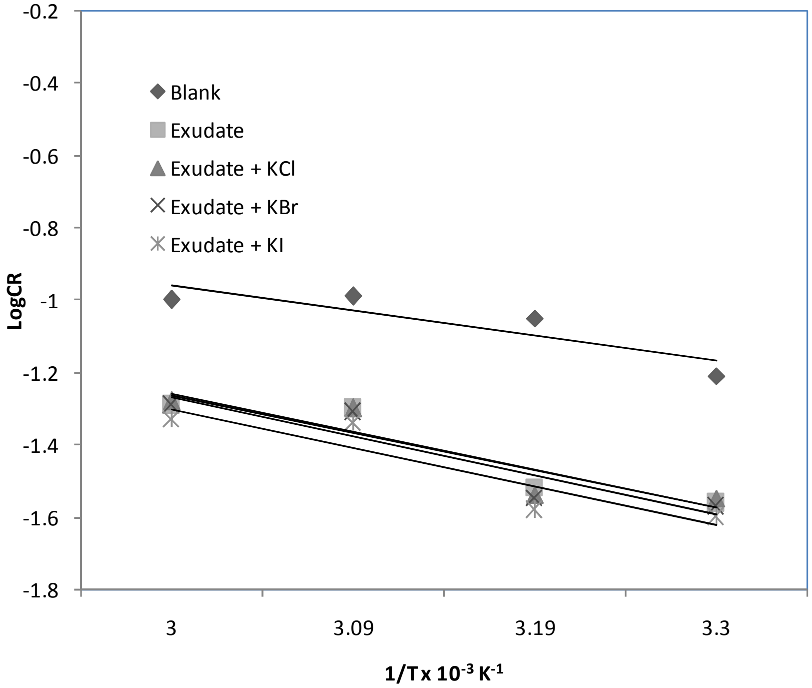

Figure 4. Arrhenius plot for mild steel corrosion in 0.1M H_2SO_4 in the absence and presence of exudate gum and exudate gum-halides mixtures

Other kinetic parameters such as enthalpy (ΔH^o) and entropy (ΔS^o) of activation of corrosion process may be evaluated from the effect of temperature. An alternative formulation of Arrhenius equation also called transition state plot is helpful [56].

$$CR = \left(\frac{RT}{Nh}\right)\exp\left(\frac{\Delta S^o}{R}\right)\exp\left(\frac{-\Delta H^o}{RT}\right) \tag{12}$$

where h is the Planck's constant, N is the Avogadro's number, T is the absolute temperature and R is the universal gas constant. A plot of Log (CR/T) as a function of 1/T was made in the absence and in the presence of RH exudate gum and RH exudate gum-halides mixtures as shown in Fig.5. Similar plots were obtained at 40-60 ^{o}C. Linear plots were obtained. Enthalpy and entropy of activation were obtained from the slope and intercept of the linear plots respectively. The results which are presented in Table 4, show that the enthalpy of activation are all positive. The positive sign of the enthalpy reflects the endothermic nature of the mild steel dissolution process [53]. Also all the entropies of activation were negative. The negative values of entropies imply that the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex [55].

Table 4. Thermodynamics and activation parameters for mild steel in 0.1M H_2SO_4 in the absence and the presence of different concentrations of *Raphia hookeri*, and RH – halides mixtures.

Systems/Concentration	ΔG^o_{ads} (kJmol^{-1})	E_a (kJmol^{-1})	ΔH^o (kJmol^{-1})	ΔS^o(Jmol^{1}K^{-1})
Blank	-	13.20	5.55	-49.78
Exudate	-15.4	19.70	8.42	-64.14
RH + 0.06M KCl	-15.1	20.10	9.40	-62.13
RH + 0.06M KBr	-15.6	19.70	8.42	-64.14
RH + 0.06M KI	-15.0	20.20	9.31	-65.48

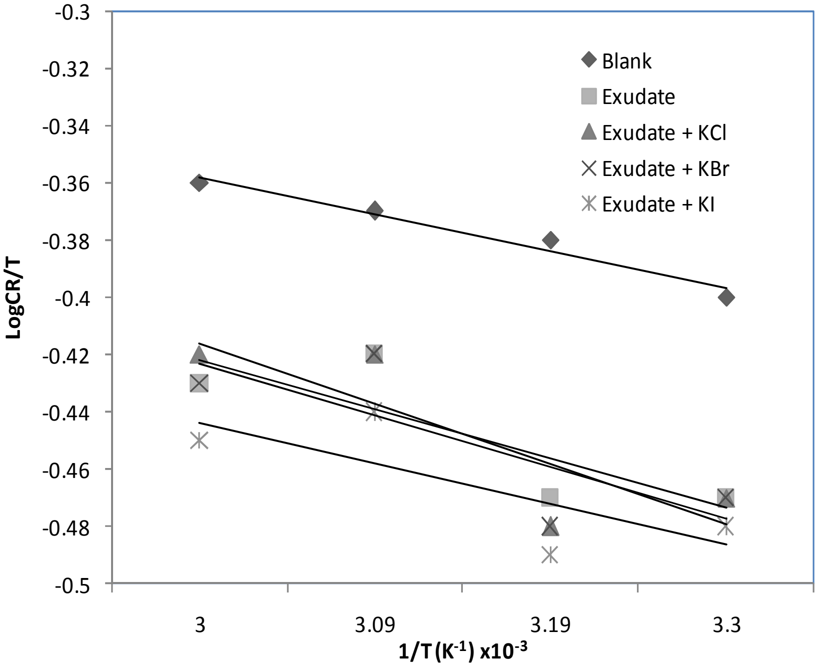

Figure 5. Transition state plot for mild steel corrosion in 0.1M H_2SO_4 in the absence and presence of exudate gum and exudate gum-halides mixtures

The free energy of adsorption values ΔG^o_{ads} , were obtained from equation (9). The values obtained are presented in Table 4. Results obtained indicate that the values of ΔG^o_{ads} are negative in all cases indicating that the exudate gum is strongly adsorbed on the mild steel surface [22]. The value of ΔG^o_{ads}, indicates that the inhibitor function by physically adsorbing on the surface of the mild steel. Generally values of ΔG^o_{ads} up to -20kJmol^{-1} are consistent with electrostatic interaction between charged molecules and a charged metal (which indicates physisorption) while those more negative than -40kJmol^{-1} involves charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of bond (which indicates chemisorptions) [14]. Physical adsorption is as a result of electrostatic attraction between charged metal surface and charged species in the bulk of the solution. Adsorption of negatively 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 [30].

3.5. Effect of halide ions

The increase in the inhibition efficiency of organic compounds in the presence of some anions has been observed by several investigators [23, 31, 58, 59] and was ascribed to synergistic effect. Trials to enhance the performance of *Raphia hookeri* exudates gum by addition of halide salts were carried out in the present study. Table 1 shows the influence of 0.06M KCl, KBr and KI on the inhibition efficiency of 0.5g/l exudate gum for mild steel. It can be seen from the table that the addition of halides generally increase the inhibition efficiency of the exudate gum for the mild steel at the temperatures investigated

Halide ions are normally strongly adsorbed on the surface of a corroding metal and facilitate the adsorption of organic compounds by forming intermediate bridges between the positively charged metal surface and the positive end of the organic molecule. Thus, the inhibitor is not adsorbed directly on the metal itself, but rather by coulombic attraction to the adsorbed halide ions on the metal surface. The process is similar to the so-called phenomenon of anion induced adsorption [60] and may be represented by the highly simplified mechanism:

$$X_s \rightarrow X_{ads} \qquad (13)$$

$$M_s + X_{ads} \rightarrow MX_{ads} \qquad (14)$$

where X_s and M_s designate the halide ion and organic species, respectively, in the bulk solution;

X_{ads} and MX_{ads} refer to the halide ion and ion-pair, respectively, in the adsorbed state. These ion-pair interactions increase the degree of surface coverage thus increasing inhibition efficiency.

The stabilization of adsorbed halide ions by means of electrostatic interactions with the exudate gum according to Gomma [59] leads to greater surface coverage (from Cl^- to I^-) and thereby, greater inhibition. Halide ions are good ligands because they exhibit a low electronegativity (less than 3.5) [31,32]. Electronegativity decreases from Cl^- to I^-, (Cl^- = 3.16 Ǻ, Br^- = 2.96 Ǻ, I^- = 2.66 Ǻ), while the covalent radius increases from Cl^- to I^- (Cl^- = 0.99 Å, Br^- = 1.14 Å, I^- =1.33 Å). Thus steel can form compounds with halide ions. Also, halide ions inhibit corrosion of steel in combination with exudate gum from *Raphia hookeri*. The inhibitive effect increases in the order $Cl^- < Br^- < I^-$, which seems to indicate that the radii of halogen ions may also play a role. With increasing ionic radius of electron cloud, adsorption is facilitated; ie. they are deformed more easily when adsorbed on a steel surface. Therefore I^- (radius 1.33 Ǻ) is more predisposed to adsorption than are Br^- (radius 1.14 Ǻ) and Cl^- (radius 0.99 Ǻ). It has further been reported that strong chemisorption of iodide ions on the metal surface may also be responsible for this trend. The cation (from compounds present in the exudate gum) is then adsorbed by columbic attraction on the metal surface where iodide ions are already adsorbed by chemisorptions [58].

The synergism parameter S_1 was calculated using the relation initially given by Aramaki and Hackermann and reported elsewhere [25,32,59].

$$S_1 = \frac{1 - I_{1+2}}{1 - I_{1+2}^{'}} \qquad (15)$$

where I_{1+2}= (I_1 + I_2); I_1 = inhibition efficiency of the halides; I_2 = inhibition efficiency of exudate gum; I'= measured inhibition efficiency for the exudate gum in combination with anion. This parameter was calculated from the values of inhibition efficiency obtained from weight loss measurements at 30°C and is given in Table 5 for the halides.

Table 5. Synergism parameter S_1 for various halides.

Halides	S_1
KCl	1.88
KBr	1.74
KI	1.73

The S_1 values shown in the table are more than unity and this suggests that the enhanced inhibition efficiency caused by the addition of halide ions to the exudate gum in the order $Cl^- < Br^- < I^-$ is only due to synergistic effect. Similar results have been reported by other authors [37, 61].

4. CONCLUSIONS

Based on the above results, the following conclusion can be drawn:

1. *Raphia hookeri* exudate gum was found to be an efficient inhibitor for mild steel in 0.1M H_2SO_4.

2. Inhibition efficiency increased with an increase in exudate gum content up to 5g/l to reach 70% at 30 °C ,but decreased with rise in temperature.

3. The corrosion process is inhibited by adsorption of the exudate gum on the mild steel surface following the Langmuir adsorption isotherm.

4. Addition of halide salts synergistically increased the inhibition efficiency of the exudate gum in the order KCl < KBr < KI.

5. The presence of the exudate gum increases the activation energy (E_a) of the corrosion process.

6. The negative free energy (ΔG^o_{ads}) of adsorption indicates strong and spontaneous adsorption of the exudate gum on the mild steel surface.

7. The inhibition efficiencies determined by weight loss and hydrogen evolution methods are in reasonable good agreement.

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