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Methanol extract of *Canarium Sweinfurthii* as a green inhibitor for the corrosion of mild steel in HCl: adsorption, kinetic, thermodynamic and synergistic studies

G.A. Ijuo[1], M. A. Orokpo[2,3*], N. Surma[1,4], P.N Tor[3]

[1,2,3,4] *Department of Chemistry, Federal Universisty of Agriculture, PMB, 2373, Makurdi, Benue State, Nigeria*

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ijuogodwin@gmail.com ;
Phone: +2348131837423

Abstract

Weight loss and electrochemical linear polarization measurements were employed in the investigation of corrosion inhibitive properties of *methanolic stem extract of Canarium sweinfarthii* (CS) on mild steel in 1.0 M HCl. The stem extract inhibited the corrosion of the mild steel in the acid medium. The inhibition efficiency (%IE) of the plant extract increased with increasing concentration but decreased with increase in temperature. Inhibition efficiency of the stem extract was also enhanced in the presence of iodide ions. Linear polarization analysis shows that the plant extract function as a mixed inhibitor. The adsorption of the stem extract on the mild steel surface obeyed both Langmiur and Freundlich adsorption isotherm models. The values of E_a obtained suggests that the adsorption mechanism was physisorption. The values of enthalpy (ΔH^0) and entropy of activation, (ΔS^0) obtained signified that the plant extract adsorbed endothermically on the metal surface and the adsorption follows a dissociation mechanism.

1. Introduction

Construction materials are commonly assessed for their performance based on their strength, weight, thermal and electrical conductivity but other important attributes such as corrosion resistance and environmental compatibility receive far less attention. Without adequate analysis and provision to mitigate corrosion, the materials develop problems after they are put into use. To remedy corrosion during the lifecycle of a material can be very expensive. In some cases it may be impossible to return the system to its original state without replacing problematic components or structures at great expense. Therefore, the need to protect these materials in aggressive environments have become very expedient.

The corrosion of metals/alloys in aggressive environments can be mitigated by a large number of organic compounds especially those containing nitrogen, oxygen and sulphur with a hydrocarbon part attached to the polar group [1-2]. These organic compounds are predominantly plant components. Phytochemical screening and anticorrosion properties of some plants have shown that secondary metabolites like alkaloids, saponins, flavonoids, cardiac glycosides and especially tanines are responsible for the corrosion inhibitive properties of these plants [3-6].

The phytochemical study of Canarium sweinfurthil leaves has been reported and shown to contain secondary metabolites such as saponins, tannins, cardiac glycosides, steroids and flavonoids [7]. Another report showed that the phytochemical screening of the matured seed methanolic extracts contains tannins, resins, saponins, flavonoids, terpenoids, steroids, alkaloids, protein, glycosides, carbohydrates and fixed fat and oils, while the stem bark contains various secondary metabolites such as the anthocyanins, flavonoids, tannins, quinones, saponins, alkaloids, steroids, terpenoids and leuco-anthocyanins [8-9].

Since plant materials have proven to demonstrate great corrosion inhibition potentials and considering the fact that they are eco-friendly, inexpensive, readily available and renewable sources of materials, this present work attempts to investigate the use of Canarium swenfurthii stem extract as an inhibitor for the corrosion of mild steel in 1.0 M HCl.

2. Material and Methods

2.1. Plant material

The sheet of mild steel used for this study was obtained commercially from modern market Makurdi in Benue State, Nigeria. The sheet was 0.14 cm thick and was mechanically press cut into 3.0 × 2.0 cm coupons. These coupons were wet-polished with silicon carbide abrasive paper (from grade #400 to #1000), rinsed with distilled water, dried in acetone and warm air, weighed and stored in a moisture-free desiccator before use.

2.2 Preparation of plant extracts

The stem barks of Canarium sweinfurthii were collected from IpinuIgede forest in Oyinyi-Iyeche, Oju Local Government Area of Benue State. The plant specimen was identified in the Department of forestry and wildlife, Federal University of Agriculture Makurdi. The fresh stem bark was air dried for six weeks, then pulverized with a pestle and mortar. The finely powdered sample was stored in a polyethylene bag until needed for analysis. The aggressive solution was 1.0 M HCl, prepared from analytical grade reagents. Each dry pulverized sample was defatted using 60-80% n-hexane for 48 hours. Each sample was further extracted using methanol and filtered. The filtrate was dried at room temperature. The inhibitor test solutions of the stem extract were dissolved in 250 mL 1.0 M HCl to obtain inhibitor test solutions of 0.2 g/L - 1.0 g/L concentrations. The inhibitive effect of the stem extract was also investigated in the presence of 0.05 M KI.

2.3 Gravimetric measurements

The effect of immersion time and the temperature was carried out using weight loss measurement. The effect of temperature was carried out at 303, 313, 323 and 333 K. Weight loss measurement was conducted on the pre-cleaned and weighed coupons suspended in beakers (maintained at 303, 313, 323 and 333K respectively) containing the test solutions using glass hooks and rods. Tests were conducted under total immersion conditions in 250 mL of the aerated and unstirred test solutions. The coupons were weighed after 3 hours of immersion in the test solution. To determine weight loss with respect to time, the coupons were immersed in 20% NaOH solution containing 250 g/L of zinc dust, scrubbed with a bristle brush, washed, dried and weighed then immersed in beakers containing 250 mL test solutions using glass hooks and rods and retrieved at 24-h intervals for 168 h. The weight loss was taken to be the difference between the weight of the coupons at a given time and its initial weight. The experiment was run in duplicates to obtain good reproducible data. Average values for each experiment was obtained and used in subsequent calculations. The percentage inhibition efficiency (%IE $_{exp}$), the degree of surface coverage (θ) and the corrosion rate (CR) of mild steel were calculated using equations (1) – (3);

$$\%IE_{exp} = \left(1 - \frac{W_{(1)}}{W_{(0)}}\right) \times 100 \qquad 1$$

$$\theta = 1 - \frac{W_1}{W_0} \text{ Or } \frac{IE_{exp}}{100} 2$$

$$CR(gh^{-1}cm^{-2} = \frac{\Delta W}{At} 3$$

where W_1 and W_o are the weight losses (g) for mild steel in the presence and absence of the inhibitor, θ is the degree of surface coverage of the inhibitor, A is the area of the metal coupon (in cm^2), t is the period of immersion (in hours) and $\Delta W = W_1 - W_0$ is the weight loss of mild steel after time, t [10].

2.4 Electrochemical Measurements

The coupons were sealed with epoxy resin in such a way that only one square surface was left uncovered. The exposed surface was degreased in acetone, rinsed with distilled water and dried in warm air. The electrochemical linear polarization experiments were conducted at room temperature (27±2 °C) using 100 mL of test solution in a conventional three-electrode cell voltammeter. The mild steel coupons were used as working electrodes, platinum (Pt) electrode and saturated calomel electrode (SCE) which served as auxiliary and

reference electrodes, respectively. Before the linear polarization experiment, the electrode was allowed to corrode freely and its Open Circuit Potential (OCP) was recorded as a function of time up to 30 min. AC impedance measurements were carried out at the corrosion potential (E_{corr}) with a frequency range from 100,000 to 0.1 Hz at an amplitude of 10 mV and a scan rate of 10 points per decade. The %IE was calculated from the charge transfer resistance (Rct) values by using the equation

$$\%IE = \frac{R_{ct(1)} - R_{ct(0)}}{R_{ct(1)}} \times 1004$$

where, $Rct_{(0)}$ is the charge transfer resistance of the mild steel without inhibitor and $R_{ct(1)}$ is the charge transfer resistance of mild steel with inhibitor. The Tafel polarization curves were recorded by scanning the electrode potential from -300 mV to 300 mV vs (SCE) with a scanning rate of 1 mV/s. The linear Tafel segments of the anodic and cathodic curves were extrapolated to corrosion potential to obtain the corrosion current densities (Icorr). The %IE was obtained from the equation below

$$\%IE = \frac{Icorr(i) - Icorr(o)}{Icorr(i)} \times 1005$$

where$I_{corr(0)}$ is the corrosion current densities of mild steel without inhibitor and $I_{corr(i)}$ is the corrosion current densities of mild steel with inhibitor [11].

3. Results and discussion

3.1 Effect of concentration on corrosion rate of mild steel

The effect of Canarium sweinfurthiistem extract concentration on the corrosion rate of the mild steel coupon at 303 K is shown in Figure 1.

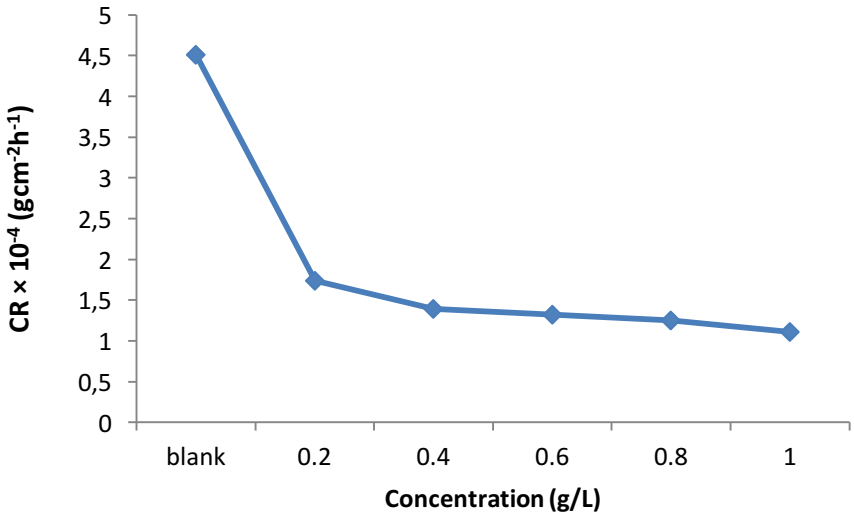


Figure 1:Effect of various concentrations (g/L) of Canarium sweinfurthii stem extract on the corrosion rate ($g/cm^{-2}h^{-1}$) of mild steel in 1.0 M HCl at 303 K.

From the plot (Figure 1), it is evident that the corrosion rate of mild steel coupons in 1.0 M HCl decreased with increasing concentration of the plant extract. This suggests that the surface coverage of the adsorbed extracts on the mild steel increased with increasing concentration providing a barrier that prevented further corrosion, [12].

The corresponding values of corrosion rates of mild steel in 1.0 M HCl and inhibition efficiencies, %IE of various concentrations of Canarium sweinfurthii stem extract obtained from the plots are presented in Table 1. The inhibition efficiencies increased with increasing plant concentrations. This as well may be due to increase in the fraction of the mild steel covered by the adsorbed constituent of the extract.

Table 1 : Corrosion Rates of mild steel and inhibition efficiencies of *Canarium sweinfurthii* stem extract in 1.0 M HCl at 303 K and 24 hrs immersion.

Concentration (g/L)	Corrosion rate ($gcm^{-2}hr^{-1}$) x 10^{-4}	Inhibition efficiency (%IE)	Surface coverage (θ)
Blank	4.51		
0.2	1.46	61.54	0.6154
0.4	1.40	66.15	0.6615
0.6	1.26	70.77	0.7077
0.8	1.11	73.85	0.7385
1.0	0.97	75.39	0.7539

3.2Effect of Immersion Time

Figure 2 shows the effect of immersion time on the weight loss of mild steel in 1.0 M HCl at 303 K in the absence and presence of the extracts. From the plots, it can be deduced that the weight loss of mild steel generally increased with time. Effect of immersion time on the inhibition efficiency, %IE of different concentrations of Canarium sweinfurthii stem extract is shown in Figure 3.

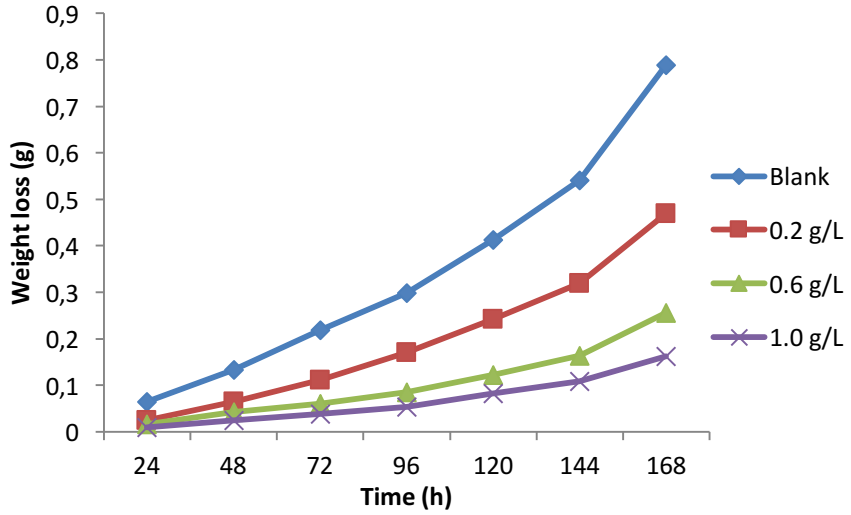


Figure 2: Effect of immersion time on weight loss of mild steel in 1.0 M HCl in the absence and presence of *Canarium sweinfurthii stem extract*.

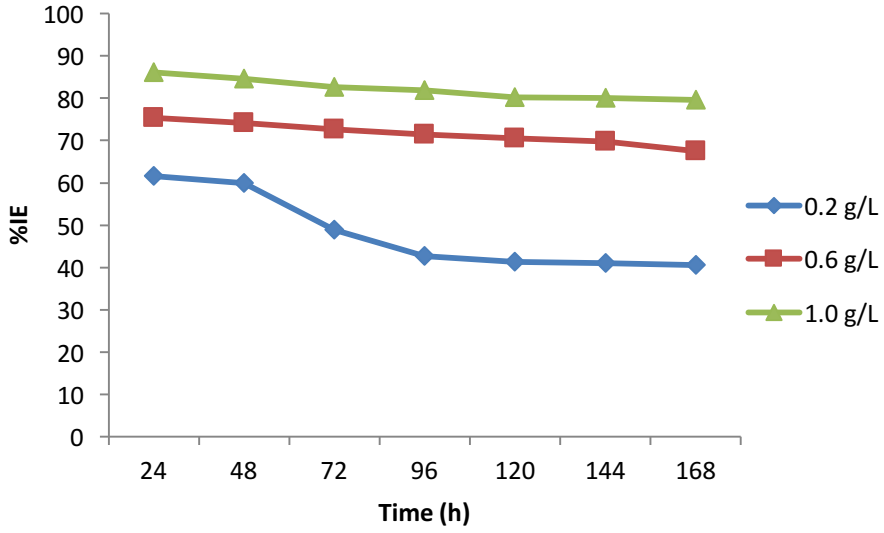


Figure 3: Effect of immersion time (hrs) on inhibition efficiency (%IE) of *Canarium sweinfurthii* stem extract on the corrosion of mild steel in 1.0 M HCl

The inhibition efficiencies of the extract at all concentrations of study were quite high but decreased gradually with time, with IE > 60 % at 0.6 g/L and 1.0 g/L concentrations for 168 hrs. This could be due to the fact that the aggressive action of the chloride ions in the acid medium reduced the integrity of the adsorbed stem extract resulting in the decrease observed in inhibition efficiency at longer immersion time [13]. Since inhibition efficiencies, %IE of the stem extract stayed above 60% for 168 hrs at 0.6 g/L and 1.0 g/L concentrations, it can be deduced from Figure 3 that Canarium schweinfurthii stem extract is a good inhibitor.

3.3 Effect of Temperature

The variation of corrosion rate of mild steel in 1.0 M HCl in the absence and presence of various concentration of the extract was investigated at 303-33 K for three hours. Figure 4 shows that corrosion rate of mild steel in 1.0 M HCl increased with temperature. This is expected because energetically, as temperature increases, the rate of corrosion of the mild steel also increases due to increase in the average kinetic energy of the reacting molecules [14]. The rate of corrosion of mild steel was however reduced in the presence of the plant extract. Figure 5 shows that the inhibition efficiencies of Canarium sweinfurthii stem extract decreased with increasing temperature (303-333 K). This may be as a result of increasing solubility of the adsorbed protective inhibitor films on the mild steel surface, thereby increasing the vulnerability of the mild steel coupons to acidic attack in HCl [15].

Table 2 : Inhibition efficiencies (%IE) of Canarium sweinfurthii stem extract and corrosion rates of mild steel in the absence and presence of various concentrations of the extract at 303-333 K.

System	Corrosion rate × 10^{-4} ($gcm^{-2}hr^{-1}$)				Inhibition efficiency (%)			
	303 K	313 K	323 K	333 K	303 K	313 K	323 K	333 K
Blank	4.444	11.67	20.56	48.49	-	-	-	-
0.2 g/L	2.222	7.778	15.00	24.44	50.00	33.33	27.07	50.00
0.6 g/L	1.667	6.667	13.33	19.44	62.50	42.86	35.15	60.23
1.0 g/L	1.111	5.000	10.56	14.44	75.00	57.14	48.65	70.55

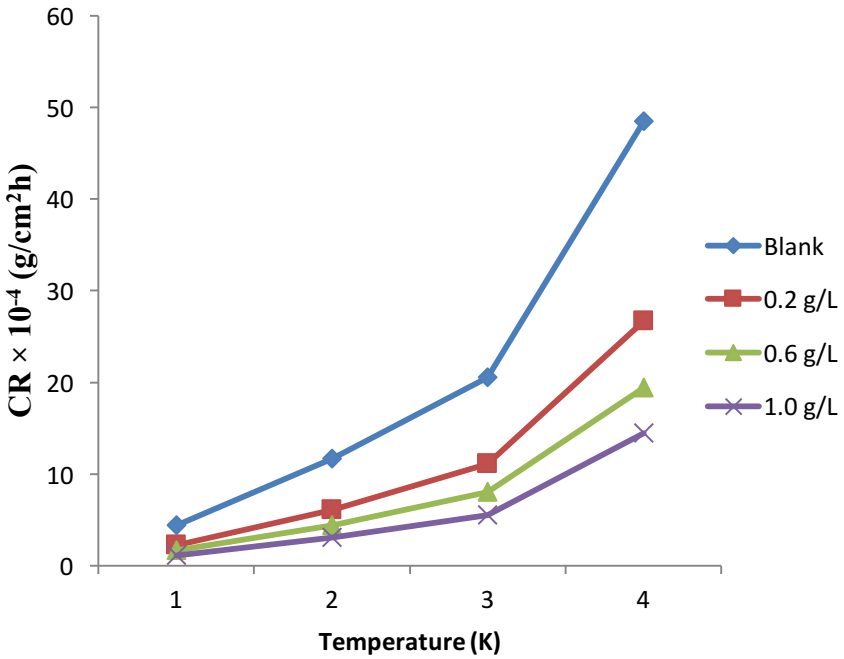


Figure 4: Effect of temperature (K) on the corrosion rate of mild steel in 1.0 M HCl in the absence and presence ofCanarium sweinfurthii stem extract.

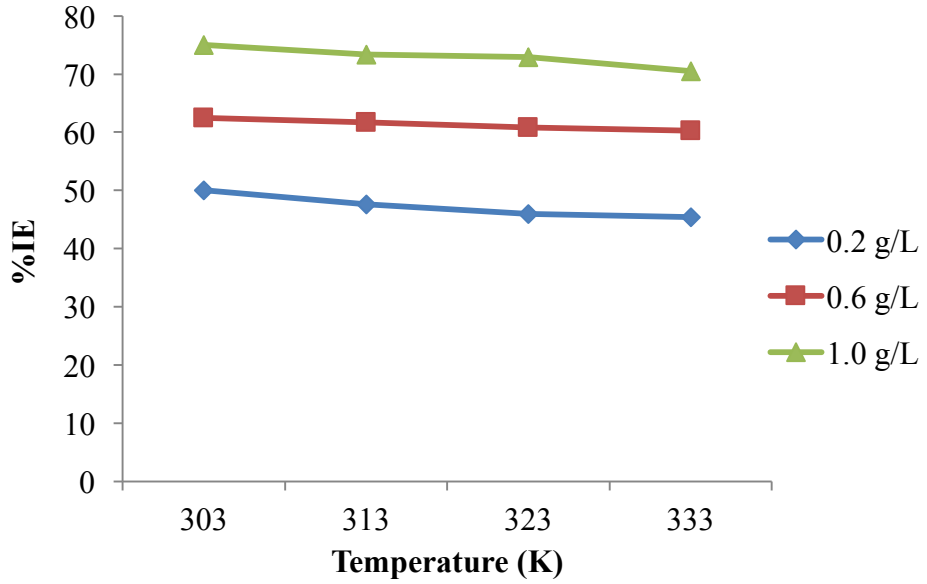


Figure 5: Effect of temperature (K) on inhibition efficiency (%IE) of Canarium sweinfurthii stem extract on corrosion of mild steel in 1.0 M HCl.

3.4 Synergistic Effect

The combination of the total action of a compound greater than its individual effects is referred to as synergism. It is the result of the electrostatic attraction of the inhibitor into the helmholtz electrical double layer by the adsorbed ions leading to synergistic adsorption and subsequent increase in the degree of surface coverage [16]. Figure 6 shows the inhibition efficiency of Canarium sweinfurthii stem extract in the presence of iodide ions. %IE is higher in the presence of the iodide ions than those for only the stem extract. This result agrees with the findings of other researchers [17].

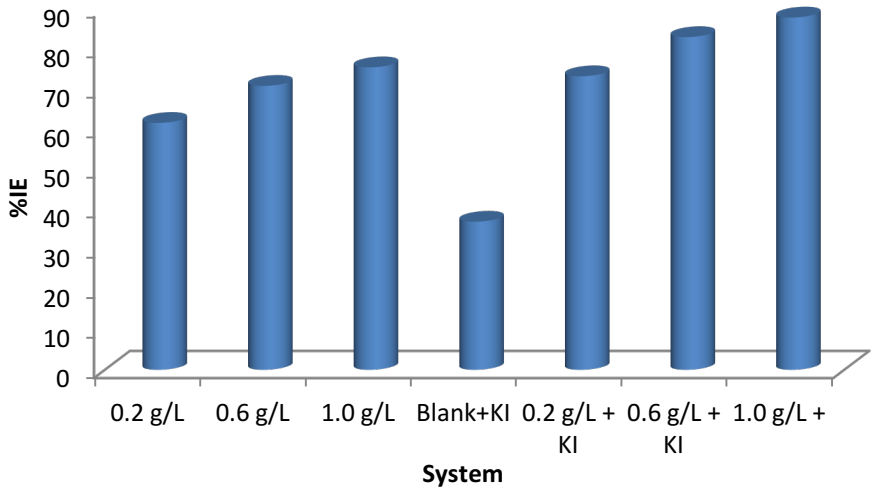


Fig 6: Effect of the addition of 0.05 M KI on the inhibition efficiency of Canarium sweinfurthii stem extract on the corrosion of mild steel at 303 K.

Synergism results in the enhancement of the inhibitor's inhibitive force, decrease in the amount of inhibitor usage as well as diversification of the inhibitors application in acidic media. The influence of the iodide ion is

usually greater than other halide ions due to its large ionic radius, high hydrophobicity, and low electronegativity [18].

3.5 Adsorption Characteristics

Basic information on the interaction between the inhibitors and the metal/alloy surface can be provided by the adsorption isotherm. In order to obtain the isotherm, the surface coverage values ($\boldsymbol{\theta}$) for various concentrations of the plant extract were tested by fitting into several adsorption isotherms including Temkin, Frumkin, Freundlich and Langmuir adsorption isotherms. This was to verify the nature of interactions between the inhibitors and mild steel surface. The linear regression coefficients (R^2) obtained from lines of best fit proved that Langmuir and Freundlich adsorption isotherms best characterized the adsorption behaviour because r^2 values were close to unity for both isotherms. It has already been established that the plot of $\mathbf{C/\theta}$ **vs C** is linear for Langmuir adsorption isotherm and this is shown to be the case as shown in Figure 7. It can therefore be inferred that the solid surface contains a fixed number of adsorption sites and each site holds adsorbed specie [19]. A linear plot of log θ against log C also shows that the adsorption of inhibitors on mild steel surface in the aqueous medium follows Feundlich isotherm. Hence, the adsorption sites can be assumed to be distributed exponentially with respect to energy of adsorption and that the surface sites are subdivided into several types, each possessing a characteristic heat of adsorption [20-21].

Table 3: Parameters of various adsorption isotherms for the adsorption of Canarium sweinfurthii stem extract on mild steel surface at 303 and 333 K.

Isotherm	Temperature (K)	Intercept	Slope	K_{ads} (M^{-1})	R^2
Langmuir					
	303 K	0.035	0.465	28.57	0.989
	333 K	0.080	0.510	12.50	0.990
Freundlich					
	303 K	-0.883	0.200	0.131	0.996
	333 K	-0.856	0.170	0.139	0.973

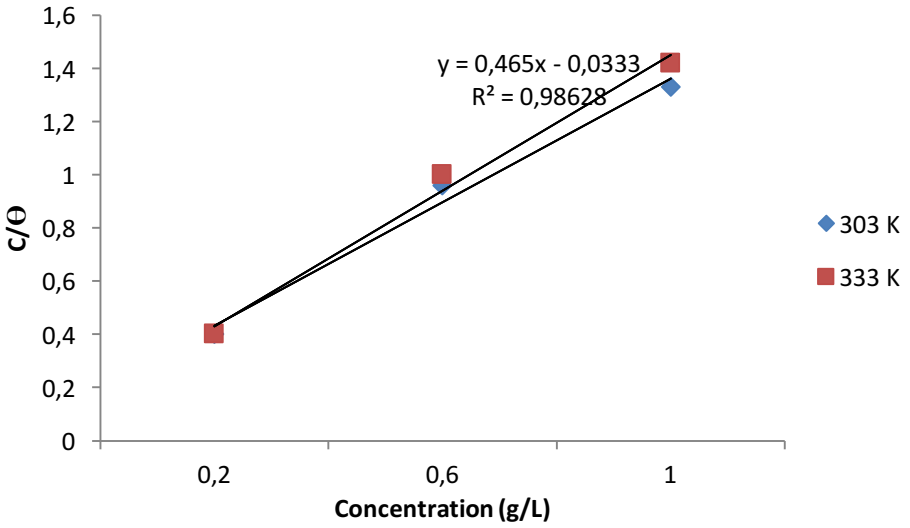


Figure 7: Langmuir adsorption isotherm for the adsorption of Canarium sweinfurthii stem extract on mild steel surface.

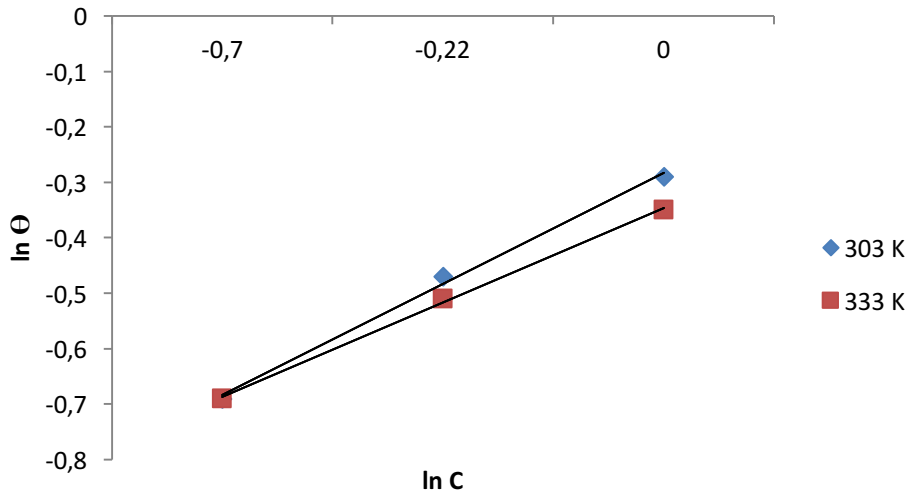


Figure 8: Freundlich isotherm for the adsorption of Canarium sweinfurthii stem extract on mild steel surface.

Values of k_{ads} shows strength between adsorbate and adsorbent, hence large values of k_{ads} signifies greater adsorption and as well as better inhibition efficiency and vice versa. Table 3, clearly shows fairly large k_{ads} values indicating strong attraction between extract and mild steel surface [22-23].

3.6Thermodynamics

The Arrhenius equation (equation) expresses the dependence of corrosion rate on temperature.

$$CR = Aexp^{-Ea/RT} \quad 6$$

$$\text{Log CR} = \log A - \frac{Ea}{2.303RT} \quad 7$$

$$\text{Log}\left(\frac{CR2}{CR1}\right) = \frac{Ea}{2.303R}\left(\frac{1}{T1} - \frac{1}{T2}\right) \quad 8$$

where CR is the corrosion rate of the metal, CR_1 and CR_2 are the corrosion rates of the mild steel at two temperatures, T_1(303 K) and T_2 are (333 K) respectively, A is the Arrhenius constant, E_a is the activation energy, R is the universal gas constant and T (K) is the absolute temperature.

Estimated values of Ea for the corrosion of mild steel in the presence of the plant extract are listed on Table 4. The data showed that Ea value for the corrosion of mild steel in the presence of the extract is higher (67.27-71.74 kJ mol^{-1}) than that in the free acid solution (67.16 kJ mol^{-1}). This infers that the adsorbed organic matter provided a physical barrier to the charge and mass transfer, leading to reduction in corrosion rate hence supporting the mechanism of physical adsorption. For physical adsorption, it is expected that the value of activated energies should be less than 80.00 kJ mol^{-1}. The values of enthalpy of activation, ΔHand entropy of activation ΔS were obtained from the transition state equation [26].

$$\log\left(\frac{CR}{T}\right) = \log\left(\frac{R}{Nh}\right) + \left(\frac{\Delta S_{ads}}{2.303R}\right) - \left(\frac{\Delta H_{ads}}{2.303RT}\right) \quad \mathbf{9}$$

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.

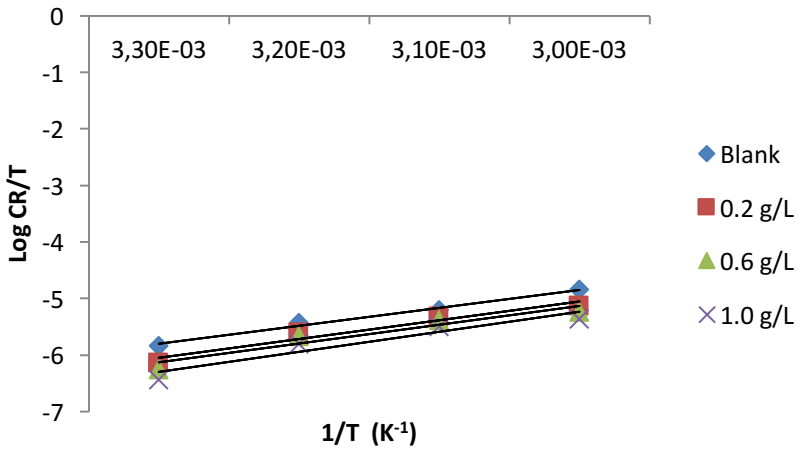


Figure 9: Transition state plots for the corrosion of mild steel in the absence and presence of Canarium sweinfurthii stem extract.

Table 4: Thermodynamic activation parameters for the corrosion of mild steel in the absence and presence of Canarium sweinfurthii stem extract.

Concentration (g/L)	E_a (kJ mol^{-1})	ΔH^0 (J mol^{-1})	ΔS^0 (kJ mol^{-1})
Blank	67.16	6.13	-0.315
0.2	67.27	7.54	-0.322
0.6	68.70	7.74	-0.322
1.0	71.74	8.46	-0.325

The evaluated values of ΔH and ΔS obtained from the plot of logCR/T vs 1/T in Figure 9 is presented on Table 4. The results showed that the enthalpy of activation, ΔH^0 for the plant extract is positive. This implies that the dissolution process of the mild steel is an endothermic process. Also, the values of entropy of activation, ΔS^0 were negative for all the extract concentrations studied. This indicates that the activation complex in the rate determining step representing dissociation, signifying that a decrease in disorder took place on going from reactants to the activated complex [27-29].

3.6 Linear Polarization Measurements

The electrochemical parameters from the polarization curves and inhibitor efficiency values are summarized in Table (5). The values of corrosion current densities in the absence ($Icorr_{bl}$) and presence of inhibitor ($Icorr_{inh}$) were used to estimmate the inhibition efficiencies (%IE) from polarization data using equation 5.The data displayed shows that the addition of the plant decreased the corrosion current density in the acid medium. The shape of the polarization curve suggests the presences of reducing species at the interface. Addition of the inhibitor is seen to affect both anodic and cathodic half reactions, shifting the corrosion potential (Ecorr) slightly towards more positive (anodic) value and reducing the anodic and cathodic current densities. This shows that the inhibitors not only inhibited corrosion of mild steel in HCl but also functioned as a mixed type inhibitor.

Table 5: Linear polarisation data for mild steel in 1.0 M HCl in the absence and presence of Canarium sweinfurthii stem extract.

System	Ecorr (mV)	Jcorr (μA/cm²)	βa (V/dec)	βc (V/dec)	CR (mm/year)	%IE
Blank	-1.5772	1.4050	0.1633	0.0635	16.324	-
0.2 g/L	-0.9648	0.0929	0.0464	0.0784	1.0797	93.390
0.6 g/L	-0.8559	0.0927	0.3002	0.0411	1.0775	93.400
1.0 g/L	-0.9018	0.0539	0.0986	0.0349	0.6263	96.160

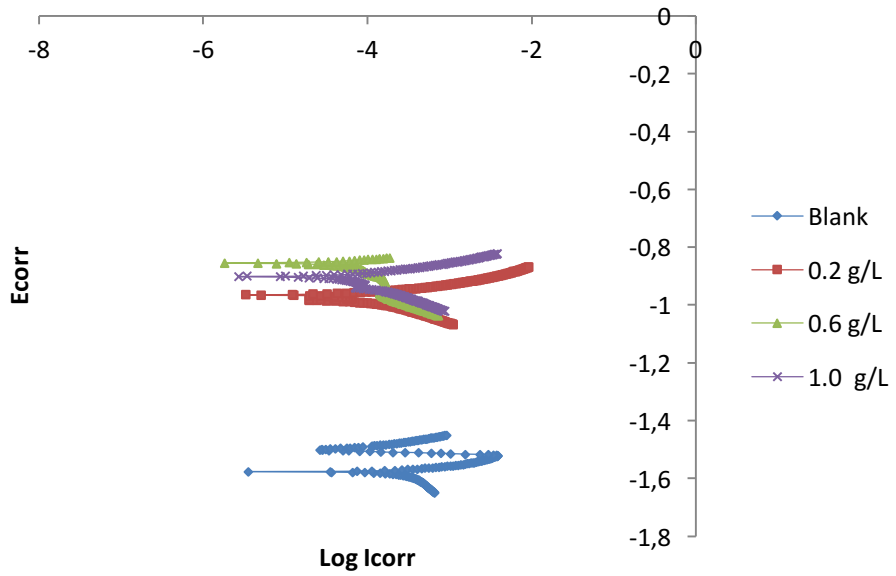
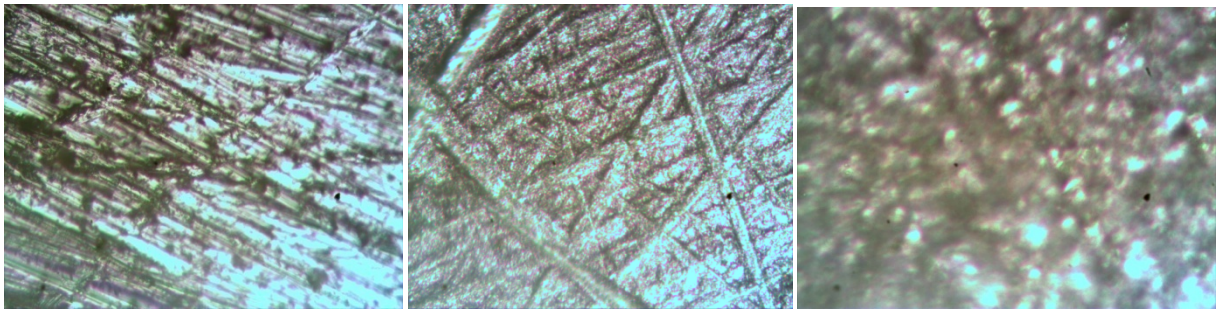


Figure 10: Linear polarisation curve for mild steel in 1.0 M HCl in the absence and presence of Canariumsweinfurthii stem extract.

3.7 Surface Morphology

Surface morphology of MS was studied by optical microscopy after 24 h immersion in 1.0 M HCl at 2048 x 1536 resolution.



(a) (b) (c)

Figure 11: (a) Polished MS, (b) MS in 1.0 M HCl and (c) MS in the presence of 1.0 g/L CS

Figure 11(a) is a micrograph of polished MS that is not immersed in aggressive medium, Figure 11(b) showed strongly damaged MS surface due to the formation of corrosion products after immersion in 1.0 M HCl solution. The micrograph of MS surface after immersion in 1.0 M HCl with 1.0 g/L CS is shown in Figure 11(c). It could be seen that no pits and cracks are observed in the micrographs after immersion of MS in 1.0 M HCl in the presence of the inhibitor except polishing lines. Thus, it revealed the presence of a good protective film upon adsorption of inhibitor molecules onto the MS surface, which was responsible for the inhibition of corrosion.

Conclusion

The study reveals that *Canariumsweinfurthii* stem extract inhibited the corrosion of mild steel in 1.0 M HCl, with its inhibition efficiency increasing with concentration. The presence of KI increased the inhibition efficiency of the plant extract. The linear polarization studies revealed that the plant extract is a mixed type inhibitor, hence having effect on both the cathodic and anodic processes. The values of activation energies (Ea) obtained showed that the plantextract adsorbed on the mild steel surface through the mechanism of physisorption. The positive values of enthalpy of activation ($\Delta \boldsymbol{H^0}$) obtained from the study signified that the plant extract adsorbed endothermically on the metal surface while the negative values of entropy of activation, ΔS^0 obtained indicates that the activation complex is the rate determining step representing dissociation

mechanism. The adsorption characteristics of the plant extract gave best fit with Langmuir and Freundlich isotherms.

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