Journal of Advanced Electrochemistry 2(4) (2016) 130–135

ISSN: 2455-0205

Contents List available at JACS Directory

Journal of Advanced Electrochemistry

journal homepage: http://www.jacsdirectory.com/jaec

Corrosion Inhibitive Properties, Adsorption Behaviour and Synergistic Effect of Methanolic Extract of *Crysophyllum albidum* on Mild Steel Corrosion in HCl

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ARTICLE DETAILS

Article history:
Received 12 October 2016
Accepted 03 November 2016
Available online 13 November 2016

Keywords:
Adsorption Isotherm
Crysophyllum albidum
Corrosion Inhibition
Physisorption
Synergism

ABSTRACT

The adsorption of *Chrysophyllum albidum* stem extract and corrosion inhibition properties on mild steel in 1.0 M HCl was investigated using weight loss and electrochemical linear polarization measurements. Inhibiton efficiencies of the plant extracts increased with increasing concentration but decreased with increasing time and temperature rise. The adsorption of the inhibitor on the mild steel surfaces was spontaneous and agrees with Langmuir and Freundlich adsorption isotherms. The values of activation energy of adsorbtion (E_a) and free energy of adsorbtion (ΔG^0) obtained and other thermodynamic parameters shows that the adsorption mechanisms was a physical adsorption. FTIR analysis revealed the presence of phenolic compounds suspected to be Tannins and Phenolic acid. Micrographs from optical microscopy revealed that the extracts inhibited corrosion of mild steel in 1.0 M HCl. The addition of 0.05 M KI enhanced inhibiton efficiency of the plant extract. The inhibitory properties of stem bark extract of *Chrysophyllum albidum* (CA) on the corrosion of mild steel in 1.0 M HCl was investigated using weight loss and electrochemical linear polarization measurements. The plant inhibited the corrosion of the mild steel in the acid medium. The inhibition efficiencies of the inhibitor increased with increasing concentration but decreased with increasing temperature and immersion time. The adsorbtion of the inhibitor unto the surface of the mild steel was found to agree with both Langmiur and Freundlich adsorbtion Isotherms. The values of E_a was found to increase with increasing concentration of the inhibitor but decreased with increasing temperature, indicative of physisorption mechanism. All ΔG^0 values obtained were negative and less than 80 kJmol^{-1}, suggestive of a spontaneous adsorption. ΔH values obtained were all positive, indicative of an endothermic process. The kinetic study showed that the reaction followed a pseudo first order kinetics and the FTIR analysis revealed the presence of phenolic compounds suspected to be phenolic acid and tannins. Optical microscopy analysis revealed the presence of protective film upon adsorption of inhibitor onto the mild surface, which is responsible for the inhibition of corrosion. The inhibition efficiencies of the the various concentrations of the inhibitor was generally observed to increase by an average of 10% with the addition of 0.05 M KI, implying a positive synergistic effect between the extract and KI.

1. Introduction

One of the most damaging redox phenomenon is corrosion, defined as an irreversible interfacial reaction of a material (metal, ceramic, polymer) with its environment which results in consumption of the material or in dissolution into the material of a component of the environment (IUPAC 2014). In addition to its multibillion dollar annual costs due to destruction of equipment and structures, corrosion has ravaged and impeded efforts to facilitate technological advancement and effective usage of metallic materials. Consequently, the emphasis of most institutions that depends on metallic workability have been unavoidably channeled from plans, research and strategies that brings about advancement in technology resulting to economic gain to incessant expenditure in control and prevention of corrosion. According to Loto [1], corrosion phenomenon, control and prevention have become unavoidable major scientific issue that must be addressed as far as there are increasing needs of metallic materials in all facets of technological development.

Many synthetic compounds especially nitrogen, oxygen and sulphur containing inhibitors have shown anticorrosion activity, however most of them are highly toxic to both humans and the environment, consequently, necessity is laid on researchers and scientists to leverage upon available, non-toxic and effective natural products that equally demonstrate sufficient capacity and proficiency in preventing corrosion.

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In recent years, a lot of research efforts have gone into the search for non-toxic naturally occurring substances for use as metal corrosion inhibitors. In this regard, a number of amino acids as well as extracts from leaves, roots and stem barks of plant (biomass) and even fruits or fruit peels have been reported as effective inhibitors of metal corrosion [2-4]. The crucial property of the plant extracts is the presence of phytochemical compounds in their composition including alkaloids, tannins, flavonoids, saponins, amino acids, ascorbic acid, phenolic acids, pigments, resins, triterpenoids, with molecular electronic structures akin to conventional corrosion inhibitors. *Chrysophyllium albidum,* a 36.5 m tall plant, is popularly known in South-western Nigeria as “agbalumo” and referred to as “udara” in South-eastern Nigeria and Ombi by Igede people of Benue state have been reported to have these metabolites [5]. Thus serve as sources of non-toxic and inexpensive corrosion inhibiting additives.

Inhibition effectiveness however depends largely on the chemical, electrical, and structural characteristics of the adsorbed inhibitor layer, which in turn depends on a set of factors which includes the nature of the metal surface including the population of potential adsorption sites and the inhibitor structure and concentration and as well as the temperature and composition of the aggressive environment [6]. Because corrosion process can be complex and includes specificity of action of most inhibitors, combinations of inhibiting additives have proven to be more effective and practical means for corrosion control. Halide ion combination with some organic inhibitors for instance has been reported to enhance inhibition efficiency [6]. The tendency of halide ions been specifically adsorbed on a corroding metal surface has been long established. The adsorbed ions usually attract the inhibitor electrostatically into the Helmholtz electrical double layer, leading to

Cite this Article as: M.A. Orokpo, H.F. Chahul, J.I. Ona, Corrosion inhibitive properties, adsorption behaviour and synergistic effect of methanolic extract of *Crysophyllum albidum* on mild steel corrosion in HCl, J. Adv. Electrochem. 2(4) (2016) 130–135.

synergistic adsorption resulting to an increase in the degree of surface coverage [7]. Most such studies, however, often assume that the characteristics of the additives remain chemically unaltered on adsorption.

This investigation will serve as a positive contribution to this evolving research area. In the present work, an experimental study on the effects of *Chrysophyllum albidum* (CA) extracts on the corrosion of Mild steel (MS) in 1.0 M HCl using gravimetric and electrochemical measurement will be presented.

2. Experimental Methods

2.1 Materials

Pulverized stem bark extract of *Chrysophyllum albidum* was used as inhibitor. 1.0 M analytical grade HCl used as aggressive solution, N-Hexane used to defat, methanol used to extract, acetone used as drying agent and distilled water used for preparing all the solutions were all obtained from Emole scientific Makurdi. Analytical digital weighing balance (Acculab startorius group) was used. Potentiostat/Galvanostat (NOVA AUTOLAB PGSTAT 302N VERSION 1.10.1.9) was used for Linear Polarization measurement at Ahmadu Bello University Zaria. FTIR-8400S was used for Infrared Spectrophotometer at National Research Institute, Zaria. TSView Digital Metallurgical Microscope model TUCSEN 0923502 was used at Mechanical Engineering Department, University of Agriculture, Makurdi.

2.2 Material Preparation

The sheet of mild steel used for this study was obtained commercially from modern market in Makurdi, Benue State, Nigeria. The sheet was 0.14 cm thick and was mechanically cut into 3.0 × 2.0 cm coupons at the mechanical engineering department, university of Agriculture, Makurdi. 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 and weighed and used for weight loss studies while 1.0 cm long stem (isolated with epoxy resin) to provide an exposure surface area of 1.0 cm^2 was used.

2.3 Preparation of Plant Extracts

The stem bark of *Chrysophyllium albidum* was collected from Ipinu forest in Oju Local Government Area of Benue State and was air dried for six weeks, then pulverized with a pestle and mortar. The corrosion experiment was performed on Mild Steel (MS). The dry pulverized sample was defatted using 60-80% n-Hexane for 48 hours and further extracted using methanol and filtered and the filtrate was dried at room temperature. Stock solution of the methanolic extract was prepared and from the stock solution, inhibitor test solutions were prepared in the desired concentration range and dissolved in the aggressive solution while 0.05 MKI was added for synergistic studies.

2.4 Gravimetric Experiment

Weight loss measurements was conducted at 303-333 K on test coupons using the method of [8]. The pre-cleaned and weighed coupons were suspended in beakers (respectively maintained at 303-333 K) containing the test solutions using glass hooks and rods. Tests were conducted under total immersion conditions in 200 mL of the aerated and unstirred test solutions. To determine weight loss with respect to time, the coupons were retrieved at 24 hrs intervals progressively for 168 hrs from the test solution and washed, dried and weighed. The weight loss (at a given time) was taken to be the difference between the initial weight (in the 1.0 M HCl with and without addition of inhibitor of different concentration at room temperature) and the weight of the coupons at the given time. All tests were run in duplicate to obtain good reproducible data. Average values for each experiment were obtained and used in subsequent calculations. This process was also carried out for the temperature studies for 30 mins and 303-333 K. The percentage inhibition efficiency (IE_{exp}), the degree of surface coverage (θ) and the corrosion rate (CR) of mild steel were calculated using equations,

$$IE_{\exp} = \left(1 - \frac{W_{(1)}}{W_{(b)}}\right) x100 \quad (1)$$

where, $W_{(b)}$ is the weight loss of the mild steel without inhibitor and $W_{(i)}$ is the weight loss of mild steel with inhibitor.

$$\theta = 1 - \frac{W_{(1)}}{W_{(b)}} \text{ Or } \frac{IE_{\exp}}{100} \quad (2)$$

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

where, W_i and W_b are the weight loss (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 $\Delta W = W_1 - W_b$ is the weight loss of mild steel after time, t.

2.5 Electrochemical Measurements

The test coupons were sealed with epoxy resin ensuring that only one square surface was left uncovered. The exposed surface was degreased in acetone, rinsed with distilled water and dried in warm air. Electrochemical experiments were performed in a conventional three-electrode cell voltammeter. Mild steel specimens were used as a working electrode, platinum (Pt) electrode as auxiliary electrode and saturated calomel electrode (SCE) served as reference electrodes. All electrochemical experiments were conducted at room temperature (27±2 °C) using 100 mL of test solution. Before the linear polarization (Tafel) 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 was carried out at the corrosion potential (Ecorr) with frequency range from 100,000 to 0.1 Hz at an amplitude of 10 mV and scan rate of 10 points per decade. The impedance diagram is given in Nyquist representation. The %IE was calculated from the charge transfer resistance (R_{ct}) values by using the equation,

$$\%IE = \frac{R_{ct(1)} - R_{ct(0)}}{R_{ct(1)}} \times 100 \quad (4)$$

where, $R_{ct(0)}$ is the charge transfer resistance of MS without inhibitor and $R_{ct(1)}$ is the charge transfer resistance of MS 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 (I_{corr}). The %IE was obtained from the equation below,

$$\%IE = \frac{\mathrm{Icorr(i)} - \mathrm{Icorr(o)}}{\mathrm{Icorr(i)}} \times 100 \quad (5)$$

where, $I_{corr(0)}$ is the corrosion current densities of MS without inhibitor and $I_{corr(i)}$ is the corrosion current densities of MS with inhibitor.

2.6 Infrared (IR) Spectroscopy

For the IR analysis, the plant extract was analysed and the coupon was dipped in 200 mL of 1.0 M HCl (in the presence and absence of plant extract) for 5 days and the adsorbed layer on the coupon was dried, scraped off and used for analysis. The analysis was done by scanning the sample through a wave number range of 400-4000 cm^{-1}.

2.7 Optical Microscopy

Optical microscopy was employed to observe the surface morphologis of the metals in the absence and in the presence of the plant extracts. Surface morphology of mild steel was studied by optical microscopy before and after 24 hrs immersion in 1.0 M HCl (in the presence and absence of inhibitor). Micrograph was taken for the polished coupon before and after immersion in 1.0 M HCl. Micrographs were also taken for polished coupons after 24 hrs immersion in 1.0 g/L *Crysophyllum albidum*.

3. Results and Discussion

3.1 Weight Loss Measurement

3.1.1 Effect of Concentration

Figs. 1 and 2 respectively shows the effect of *Crysophyllum albidum* stem extract concentration on the corrosion rate and inhibition efficiency at 303 K for the corrosion inhibition of mild steel in the absence and presence of various concentrations of plant extract.

From the plot (Fig. 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 prevents further corrosion. This result is in perfect agreement with [9]. Also, the inhibition efficiency of the extract as shown in Fig. 2 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 below presents the corresponding values of corrosion rates of mild steel and inhibition efficiencies, %IE, of various concentrations of *Crysophyllum albidum* stem extract in 1.0 M HCl as shown by the plots.

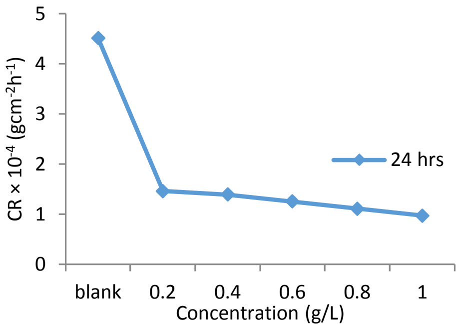

Fig. 1 Variation of corrosion rate (g/cm^{-2}h^{-1}) of mild steel against various concentrations of *Crysophyllum albidum* stem extract in 1.0 M HCl at 303 K

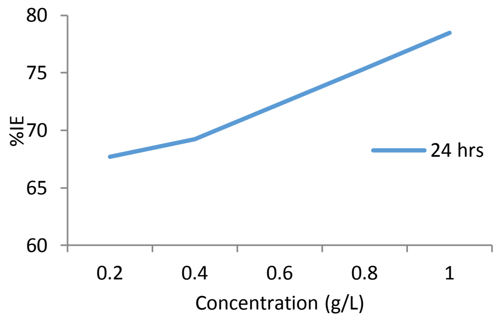

Fig. 2 Effect of Concentration on corrosion inhibition efficiency (%IE) of mild steel in 1.0 M HCl in the presence of CA

Table 1 Corrosion rates of mild steel and inhibition efficiencies of *Crysophyllum albidum* stem extract in 1.0 M HCl at 303 K and 24 hrs immersion

Concentration (g/L)	Corrosion rate (gcm^{-2}hr^{-1})	Inhibition efficiency (%IE)	Surface coverage (θ)
Blank	0.000451	-	-
0.2	0.000146	67.69	0.6769
0.4	0.000139	68.45	0.6845
0.6	0.000125	72.31	0.7231
0.8	0.000111	75.87	0.7587
1.0	0.000097	78.46	0.7846

3.1.2 Effect of Immersion Time

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 0.2, 0.6 and 1.0 g/L concentrations of the extracts as shown in Fig. 3 reveals that though weight loss of mild steel increase with increasing time , the corrosion rate decreased with increasing concentrations.

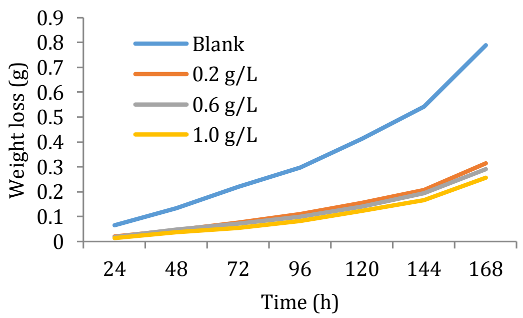

Fig. 3 Gravimetric data for the effect of immersion time on the corrosion inhibition of mild steel in 1.0 M HCl in the absence and presence of CA

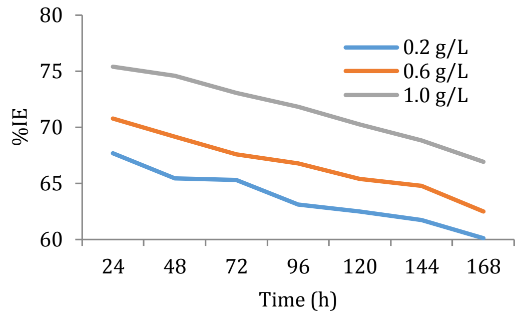

Fig. 4 Effect of immersion time on the corrosion inhibition efficiency (%IE) of mild steel in 1.0 M HCl in the absence and presence of CS

Fig. 4 depicts the effect of immersion time on the inhibition efficiency for different concentrations of *Crysophyllum albidum* stem extract in 1.0 M HCl from which it can be observed that the extracts actually inhibited the corrosion of mild steel. The inhibition efficiencies of all the concentrations stayed above 60% for 168 hrs indicative of the fact that the extract is a good inhibitor, however the inhibition efficiencies reduced progressively this could be due to the fact that the aggressive action of the chloride ion in the acid medium reduced the integrity of the adsorbed stem extract resulting in reduced inhibition efficiency with longer immersion time [8, 9].

3.1.3 Effect of Temperature

The variation of corrosion rate of mild steel in 1.0 M HCl in the absence and presence of 0.2, 0.6 and 1.0 g/L of CA was studied at 303 K between 24-168 hours and at 303-333K for three hours respectively. Fig. 5 and results of Table 2 reveals that corrosion rate of mild steel in 1.0 M HCl increased with temperature. This suggests that, as the temperature increases, the hydrogen evolution over potential decreases as is the case with corrosion in acidic medium (hydrogen depolarization) [9,10]. Corrosion rate can also be said to have increased due to increase in the kinetic energy [10].

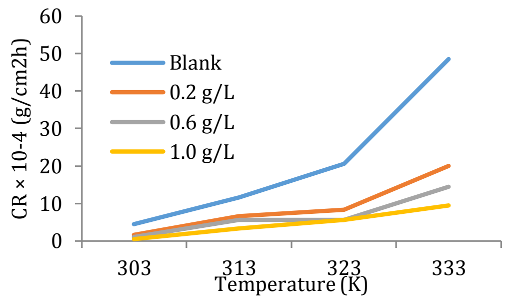

Fig. 5 Effect of temperature on the corrosion rate of mild steel in 1.0 M HCl in the absence and presence of CA

Table 2 Inhibition efficiencies (%IE) and corrosion rates for the corrosion of mild steel in the absence and presence of various concentrations of the extract in 1.0 M HCl 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	1.667	4.444	8.333	20.00	62.50	61.91	59.46	59.00
0.6 g/L	1.111	3.056	5.556	14.44	75.00	73.81	72.13	70.46
1.0 g/L	0.833	2.778	5.000	14.44	81.25	76.19	75.68	70.46

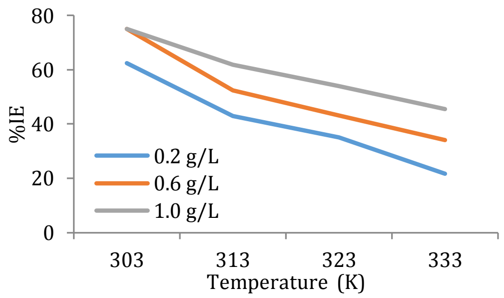

Fig. 6 Effect of temperature (K) on corrosion inhibition efficiency (%IE) of mild steel in 1.0 M HCl in the presence of CA

Table 3 below shows the inhibition efficiency of 5.0 mM KI and extract-iodide mixtures at 303 K

System	%IE
5.0 mMKI	36.93
0.2 g/L CA + 5.0 mMKI	80.49
0.6 g/L CA + 5.0 mMKI	85.37
1.0 g/L CA + 5.0 mMKI	92.68

The inhibition efficiency of mild steel exposed to various concentrations of CA in 1.0 M HCl is shown in Fig. 6 and Table 3. The inhibition efficiencies of the inhibitors 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, thereby increasing the susceptibility of the coupons in the acid medium [9].

3.2 Synergistic Effect

The combined total action of a compound greater than the sum of its individual effects is referred to as synergism. It improves the inhibitive force of inhibitor, resulting to decrease in the amount of inhibitor usage and to subsequent diversification of the inhibitorsapplication in acidic media. Synergism usually occurs when the adsorbed ions attracts the inhibitor electrostatically into the Helmholtz electrical double layer, leading to synergistic adsorption resulting to an increases in the degree of surface coverage [11].

The iodide ion usually has a greater influence and this is due to its high hydrophobicity, large ionic radius, and low electronegativity, compared to the other halide ions [11].

The inhibition efficiency in the presence of the iodide is higher than those for only CA in 1.0 M HCl. This result is in agreement with the report by [9]. Fig. 7 illustrates the relationship between the inhibition efficiency and the respective concentration of the inhibitor in the presence of 5.0 mM KI.

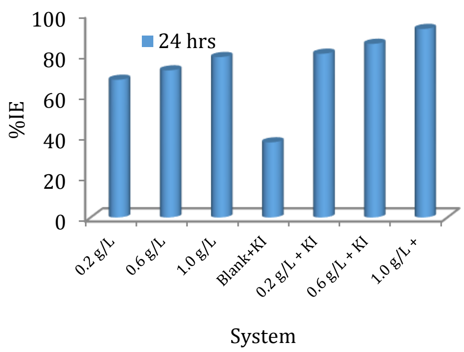

Fig. 7 The Effect of 5.0 mM potassium iodide (KI) on inhibition efficiencies of various concentrations of *Crysophyllum albidum* (CA) extract for the corrosion of mild steel in 1.0 M HCl at room temperature using weight loss measurements

3.3 Adsorption Characteristics

Basic information on the interaction between the inhibitors and the MS surface can be provided by the adsorption isotherm. In order to obtain the isotherm, the surface coverage values (θ) for different concentrations of CA was tested by fitting into several adsorption isotherms including Temkin, Frumkin, Freundlich and Langmuir adsorption isotherms 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 since their r^2 values were close to unity. It has already been established that the plot of C/θ vs Cis linear for Langmuir adsorption isotherm and this is shown to be the case in Fig. 8.

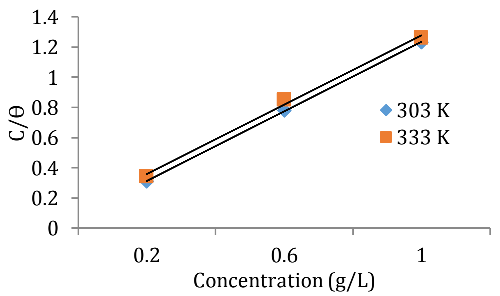

Fig. 8 Langmuir adsorption isotherm for the adsorption of CA onto mild steel surface in 1.0 M HCl at 303 K and 333 K respectively

It can therefore be inferred that the solid surface contains a fixed number of adsorption sites and each site holds adsorbed specie and this is consistent with the view of [6]. 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 (Fig. 9) [18]. 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 [9, 10]. It can therefore be said that the assumptions of either Langmuir or Feundlich can be used to characterize the nature of adsorption.

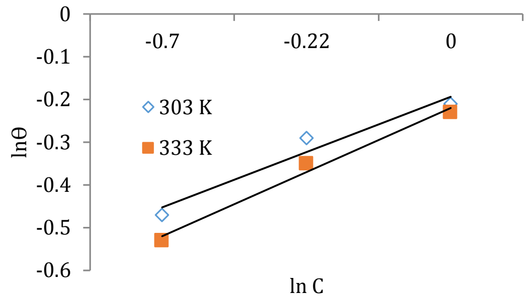

Fig. 9 Freundlich adsorption isotherm for the adsorption of CA onto mild steel surface in 1.0 M HCl at 303 K and 333 K respectively

Table 4 Parameters of various adsorption isotherms for the adsorption of *Crysophyllum albidum* stem extract on mild steel surface at 303 and 333 K

Isotherm	Temp. K)	Intercept	Slope	K_{ads} (M^{-1})	R^2	ΔG ($kJmol^{-1}$)
Langmuir	303 K	0.147	0.460	6.849	0.999	-14.97
	333 K	0.103	0.460	9.709	0.996	-17.41
Freundlich	303 K	-0.583	0.130	0.261	0.953	-6.733
	333 K	-0.670	0.150	0.214	0.986	-6.851

The strength of interaction between adsorbate and adsorbent can be verified from values of K_{ads}, hence large values of K_{ads} signifies greater adsorption and as well better inhibition efficiency and vice versa [7,9,12]. Table 4, clearly shows small K_{ads} values indicating weak attraction between extract and mild steel surface [8, 13].

The relationship between the adsorption equilibrium constant (K_{ads}) obtained from the intercept of the adsorption isotherm and the adsorption free energy is shown below;

$$\text{Log } K_{ads} = -1.744 - \frac{\Delta G ads}{2.303RT} \quad (6)$$

$$\Delta G_{ads} = -2.303 \times RT \text{ Log } (55.5\, K_{ads}) \quad (7)$$

Generally, negative ΔG_{ads} values indicates spontaneity of the adsorption process [20, 21] and ΔG_{ads} values with magnitude < -40 $kJmol^{-1}$ indicates electrostatic interactions between inhibitor molecule and charged metal surface (physisorption), while those with magnitude of 40 $kJmol^{-1}$ are associated with charge transfer from inhibitor molecules to metal surface (chemisorption) [9,10,14].

From Table 4, it can be seen that evaluated values of ΔG_{ads} were negative and < -20 $kJmol^{-1}$and this indicates a spontaneous adsorption process and a physisorption mechanism.

3.4 Thermodynamics

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

$$CR = A\exp^{-Ea/RT} \quad (8)$$

$$\text{LogCR} = \log A - \frac{Ea}{2.303RT} \quad (9)$$

$$\text{Log}\,({}^{CR2}/_{CR1}) = {}^{Ea}/_{2.303R}({}^{1}/_{T1} - {}^{1}/_{T2}) \quad (10)$$

The corrosion rates of the metal at two temperatures, T_1(303 K) and T_2 are (333 K) are respectively known to be CR_1 and CR_2 which is eventually used to calculate the energy of activation.

CR is the corrosion rate of the metalA is the Arrhenius constant, E_a is the activation energy, R is the universal gas constant and T (K) is the absolute temperature.

Table 4 shows a list of the estimated values of Ea for mild steel corrosion in the presence of CA extract in 1.0 M HCl and it can be inferred from the table that the Ea values of the corrosion of mild steel in 1.0 M HCl solution in the presence of the extract is higher than that in the free acid solution. The Ea was found to be 66.84 KJmol^{-1} for 1.0 M HCl and increased with increasing concentration of the inhibitors, with the highest values of 79.94 KJmol^{-1} in the presence of 1.0 g/L of CA. This showed that the adsorbed organic matter has provided a physical barrier to the charge and mass transfer, leading to reduction in corrosion rate [8-10]. Earlier reports also revealed that an Ea threshold value of 80 KJmol^{-1} indicates chemisorption, while less than 80 KJmol^{-1} infers physisorption [9]. On the basis of the experimentally determined Ea values that are all less than 80 KJmol^{-1}, it is evident that the additives were physically adsorbed on the coupons.

The transition state equation is used to calculate thermodynamic parameters for the adsorption of the inhibitors on a metal surface. According to the transition state Eq. (8), the enthalpy and entropy of adsorption of the inhibitor can be related to the corrosion rate of a metal as follows,

$$CR = \frac{RT}{Nh} \exp^{\left(\frac{\Delta S_{ads}}{R}\right)} \exp^{\left(\frac{-\Delta H_{ads}}{RT}\right)} \quad (11)$$

$$\log\left(\frac{CR}{T}\right) = \log\left(\frac{R}{Nh}\right) + \left(\frac{\Delta S_{ads}}{2.303R}\right) - \left(\frac{\Delta H_{ads}}{2.303RT}\right) \quad (12)$$

where CR is the corrosion rate of Mild steel, R is the gas constant, N is the Avogadro's number, h is the Planck's constant, T is the temperature, ΔS_{ads} and ΔH_{ads} are the entropy and enthalpy of adsorption of the inhibitor on a metal, respectively [15].

A straight line is expected from a plot of log(CR/T) versus 1/T with slope and intercept equal to $\Delta H_{ads}/2.303R$ and $(\log(R/Nh) + \Delta S_{ads}/2.303R)$, respectively. The Arrhenius equation can be equated with the transition state equation.

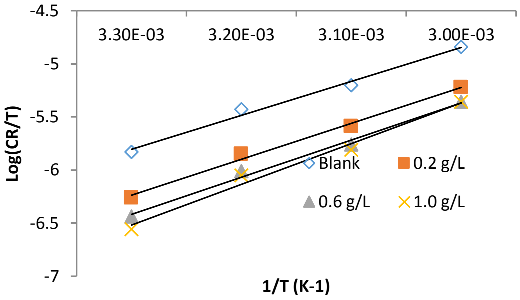

Fig. 10 Transition state plots for the corrosion of mild steel in the absence and presence of CA

Table 5 Thermodynamic activation parameters for the dissolution of mild steel in 1 M HCl in the absence and presence of CA at 303-333 K

System	Concentration (g/L)	E_a (kJmol^{-1})	ΔH (Jmol^{-1})	ΔS (kJmol^{-1})
	Blank	66.84	6.13	-0.322
	0.2	69.49	6.47	-0.331
	0.6	71.73	6.68	-0.332
CA	1.0	79.78	7.35	-0.337

The evaluated values of ΔH and ΔS obtained from the plot of log(CR/T) vs 1/T in Fig. 9 is shown in Table 5. The results showed that all the enthalpy of activation for the inhibitors are positive, implying that the dissolution process of the mild steel is an endothermic process. Also, the entropies of activation energy were negative for the extract, indicating that the activation complex represents association steps and that the reaction was spontaneous and feasible. These results were in excellent agreement with the reports of previous work [9].

3.5 Linear Electrochemical Polarization

The electrochemical parameters derived from the polarization curves (Fig. 11) and inhibitor efficiency values are summarized in Table 6. The values of corrosion current densities in the absence ($Icorr_{bl}$) and presence of inhibitor ($Icorr_{inh}$) were used to estimate the inhibition efficiencies (%IE) from polarization data as follows;

$$\%IE = [(Icorr_{bl} - Icorr_{inh}) / Icorr_{bl}] \times 100 \quad (13)$$

where $Icorr_{bl}$ and $Icorr_{inh}$ are the corrosion current densities in the absence and presence of the inhibitor (CA).

Table 6 Electrochemical polarisation data for mild steel in 1.0 M HCl in the absence and presence of CA at 303 K

System	Ecorr (mV)	jcorr (A/cm^2)	βa (V/dec)	Bc (V/dec)	CR (mm/year)	%IE
Blank	-1.5772	1.4050	0.1633	0.0635	16.324	-
0.2 g/L	-1.0046	0.0847	0.0753	0.0542	0.9843	93.970
0.6 g/L	-0.9493	0.0574	0.0865	0.0384	0.6625	95.940
1.0 g/L	-1.0602	0.0483	0.0721	0.0245	0.5609	96.560

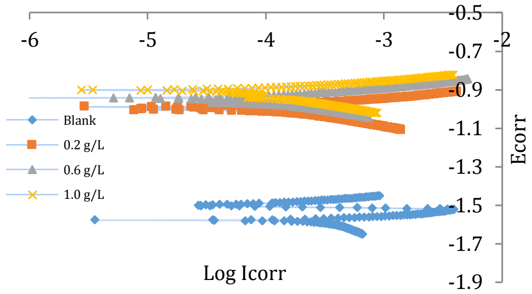

Fig. 11 Electrochemical polarisation curve for mild steel in 1.0 M HCl in the absence and presence of CA at 303 K

The data displayed shows that the addition of the inhibitor 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.

3.6 Fourier Transform Infrared Spectrophotometer

Fig. 12 shows characteristic adsorption peaks at 3406.40; 2941.54; 1641.49; 1495.85; 1144.79 – 1043.83 and 619.17 – 401.21 cm^{-1} for sample CA. The peak at 3406.40 cm^{-1}, is assigned phenolic –OH stretch, 2941.54 cm^{-1} is assigned alkyl C-H stretch,1641.49 cm^{-1} is assigned aromatic ring, 1495.85 cm^{-1}is assigned aromatic C=C bending, 1144.79 – 1043.83 cm^{-1} is assigned C-O stretch and 619.17 – 401.21cm^{-1} aromatic substitution. All this peaks shows characterise adsorption for phenolic and tannins [16].

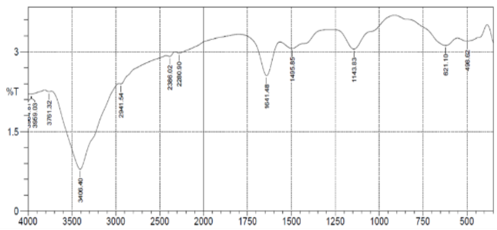

Fig. 12 FTIR spectra for CA

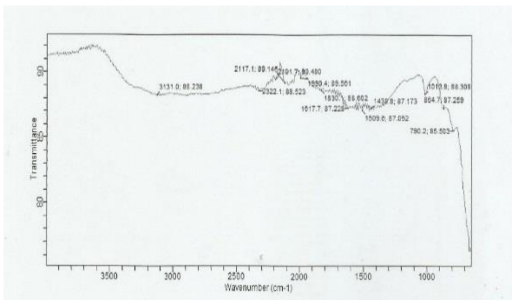

Fig. 13 FTIR spectra for CA on MS

Fig. 13 shows the infrared spectra of CA adsorbed unto the MS surface. The spectra reviews that the characteristic peakat 3406.40 cm^{-1} disappeared, indicating the participation of the oxygen atoms in the adsorption process and this is through its lone pair electrons. All other peaks that indicates the presence of aromatic rings also disappeared, showing that the aromatic rings of the phenolic group actively participated in the adsorption process. The spectra therefore reviews that CA was strongly adsorbed to the metal surface due to donation of oxygen's lone paired electrons to the vacant d-orbitals of the metal leaching to the formation of the metal complexes [13, 16].

3.7 Optical Microscopy

The surface morphology of MS was studied by optical microscopy at 24 hrs immersion in 1.0 M HCl before and after addition of CA inhibitor.

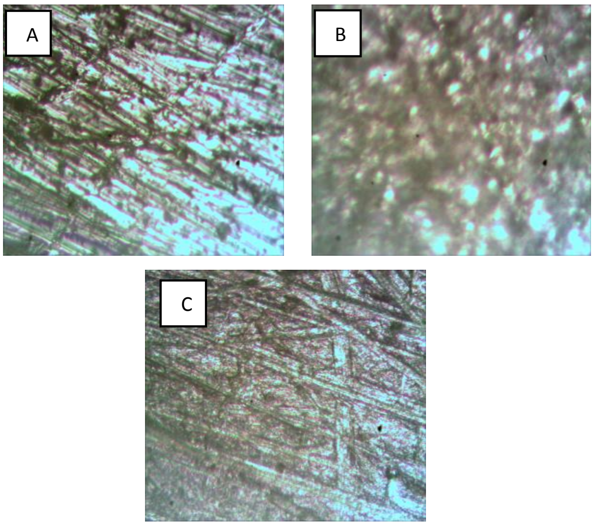

Fig. 14 SEM imgaes of studied MS

The micrograph's obtained from the optical microscopy study of the surface morphology of the MS at 24 hrs immersion in 1.0 M HCl before and after addition of CA inhibitor is shown above (Fig. 14). Plate (A) represents the micrographs obtained from polished MS without exposure to the corrosive environment while plate (B) shows a highly corroded MS surface after immersion in 1.0 M HCl. Plates (C) is a micrograph from 1.0 M HCl with CA. A comparison between plates 'A and B' shows that plate 'B' was highly corroded whereas plates 'C' still retained its polishing lines revealing the presence of a good prtotective film upon adsorption of inhibitor molecule unto the MS surface, which was responsible for the corrosion inhibition.

4. Conclusion

The weight loss studies revealed that the extract of CA is a very good inhibitor for the corrosion of mild steel in 1.0 M HCl, with its inhibition efficiency decreasing with both increasing time and temperature but increasing with increasing concentration. Linear polarization studies revealed that CA is a mixed type inhibitor, hence having effect on both the cathodic and anodic processes.

Adsorption studies revealed that the adsorption of different concentrations of the plant extract CA unto the surface of the mild steel in 1.0 M HCl followed Langmuir and Fruendlich adsorption isotherms. The thermodynamic data obtained from the temperature studies revealed that ΔG was negative and less than 80 KJ/mol, Ea was negative and less than 40 KJ/mol, ΔH was positive. The respective values of ΔG, ΔH and Ea shows that the reaction was spontaneous, endothermic and follows a physisorton mechanism. The adsorption of the plant extracts unto the surface of the mild steel followed pseudo first order rate. FTIR analysis revealed the presence of polyphenolic compounds, which are most likely to be tannin or phenolic acid. The micrographs from the optical microscopy study reassures that the extract is a good corrosion inhibitor. The addition of KI extract-acid medium is also seen to have increased the inhibition efficiency of the plant extract.

Acknowledgement

We thank the department of Chemistry, University of Agriculture, Makurdi for granting us access to the laboratory and its equipment to carry out this research.

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