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Synergistic Effect of Leaf Extracts of *Cordia sebestena L.* and Iodide Ions on the Corrosion Inhibition of Mild Steel in Sulphuric Acid

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The inhibitive action of leaf extracts of *Cordia sebestena* on corrosion of mild steel in 0.5 M H_2SO_4 solution was studied by weight loss measurement at 303-333K. Results indicate that leaf extracts of *Cordia sebestena* is a good inhibitor for mild steel corrosion in 0.5 M H_2SO_4. The inhibition efficiency was found to increase with increase in extracts concentration. A maximum inhibition efficiency of 95.79% was obtained for 50%v/v at 303K, which increased to 99.09% in the presence of 5mM KI. Temperature studies revealed a decrease in inhibition efficiency with increase in temperature, which suggests physical adsorption mechanism. The adsorption characteristics of leaf extracts of *Cordia sebestena* on mild steel surface obeys Langmuir isotherm. Both kinetic parameters and thermodynamics of adsorption (enthalpy of adsorption, entropy of adsorption and Gibbs free energy) were calculated and discussed. The values of synergism parameter were greater than unity, which suggests synergistic effect between the leaf extracts and KI.

Keywords: Mild steel; Sulphuric acid solution; Weight loss; Acid Inhibitor; Thermodynamic studies; Synergism.

1. INTRODUCTION

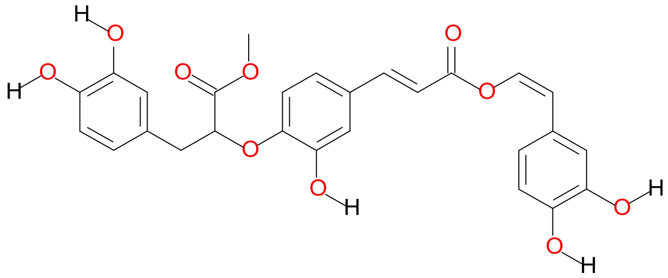
The corrosion behavior of iron and its alloys has been widely investigated in several environments. Significant improvement in the corrosion resistance of metals has been achieved through a number of ways. It includes reduction of the metal impurity content, controlling the pH or ion concentration of the solution, controlling the metal-solution interface, application of several surface modification techniques as well as incorporation of suitable alloying elements [1, 2].

Acid solutions are widely used in industry. Some important fields of application include acid pickling of iron and steel, chemical cleaning and processing, ore production and oil and gas well acidification. Owning to the general aggression of acid solutions, inhibitors are commonly used to reduce the corrosive attack on metallic materials [3]. An inhibitor is a substance that retards the rate of corrosion of metals when added in minute quantity [4]. Most inhibitors are synthesized from cheap raw materials, some are chosen from compounds having heteroatom (N, S, O, P) in their aromatic or long carbon chain [5,6].

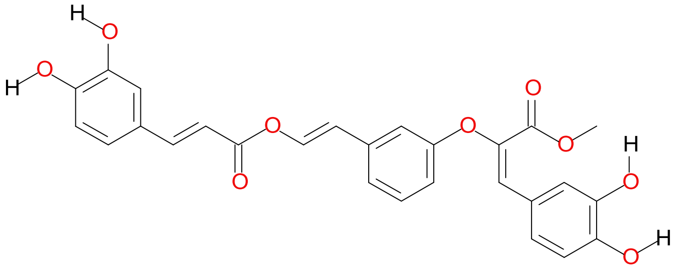
Most organic and inorganic inhibitors have been used for the inhibition of mild steel corrosion in acidic medium but some of these inhibitors are not environmentally friendly [7]. Natural or green corrosion inhibitors are cheap, renewable, biodegradable, ecologically acceptable and do not contain heavy metals or other toxic substances [8]. The successful uses of naturally occurring substances to inhibit the corrosion of metals in various environments have been reported by several researchers [9-19].

Cordia sebestena is a small tropical ornamented tree growing up to a height of 25 feet with evergreen heart shaped leaves. It is commonly called Geiger tree, orange Geiger or scarlet *cordia*. It tolerates drought but not frost and belongs to family Boraginaceae and genus *Cordia*. In traditional medicine, *Cordia sebestena* is used for treatment of urinary incontinence, malaria, catarrh, edema and venereal diseases. The fruits of *Cordia sebestena* have been reported to contain phenylpronoid esters [20]. Sebestenoid A and Sebestenoid B have been isolated and characterized from the leaves and fruits [20].

As a continuation of our current interest on eco-friendly corrosion inhibitors, we report for the first time the inhibitive action of leaf extracts of *Cordia sebestena* on the acid corrosion of mild steel using the weight loss method at 303-333K. The effect of iodide additive on the adsorption behavior of the leaf extracts on the mild steel surface is also reported.



Sebestenoid A



Sebestenoid B

2. EXPERIMENTAL

2.1. Materials

Materials used for the study were mild steel sheet of composition (wt %); Mn (0.6), P (0.36), C (0.15) and Si (0.03) and Fe (98.86). The sheet was mechanically pressed cut into different coupons, each of dimension 5 x 4 x 0.11 cm. A pre-treatment was carried out prior to experiment, in which specimen surface was mechanically grinded with 240, 400, 600, 800 and1000 grades of emery paper, rinsed with bi distilled water, degreased in ethanol and dried at room temperature before use. All reagents used for this study were Analytical grade and were products of Sigma-Aldrich.

2.2. Extraction of plants

Cordia sebestena leaves were collected from Redeemer's University campus and were authenticated at the Herbarium of University of Ibadan, Nigeria. The leaves were air-dried for several weeks, the dried leaves were ground and 40 g soaked in 400 ml of 0.5 M H_2SO_4 solution for 24 hours. After 24 hours, the sample was filtered and the filtrate was collected and stored as stock solution. The stock solution of the leaf extracts so obtained was used for preparing different extracts concentration ranging from 10-50%v/v.

2.3. Weight loss measurements

The gravimetric measurement (weight loss) is probably the most widely used method of inhibition assessment [21-26]. The simplicity and reliability of the measurements offered by the weight loss method is such that the technique forms the baseline method of measurement in many corrosion monitoring programmes [9]. Weight loss measurements were conducted under total immersion using 250 ml capacity beakers containing 200 ml test solution at 303-333 K maintained in a thermostated water bath. The mild steel coupons were weighed and suspended in the beaker with the help of rod and hook. The coupons were retrieved at 2 h interval progressively for 10 h, washed thoroughly in 20% NaOH solution containing 200 g/l of zinc dust [2] with bristle brush, rinsed severally in bi-distilled water, dried in acetone, and re-weighed. The weight loss, in grams, was taken as the difference in the weight of the mild steel coupons before and after immersion in different test solutions. Then the tests were repeated at different temperatures. In order to get good reproducibility, experiments were carried out in triplicate. In this present study, the standard deviation values among parallel triplicate experiments were found to be smaller than 5%, indicating good reproducibility.

The corrosion rate (CR) in g cm^{-2} hr^{-1} was calculated from the following equation [27]:

$$CR = \Delta W/St \tag{1}$$

where ΔW is the average weight loss of the three mild steel coupons after immersion, *S* is the total surface area of the mild steel and *t* is the total time of immersion which is 10 hrs.

The surface coverage was calculated from the corrosion rates in the absence and presence of the inhibitor, using equation 2, which is given as:

$$\text{Surface coverage } (\theta) = \frac{CR_{blank} - CR_{inh}}{CR_{blank}} \qquad (2)$$

The inhibition efficiency was computed using equation:

$$\text{Inhibition efficiency (EI \%)} = \frac{CR_{blank} - CR_{inh}}{CR_{blank}} x100 \qquad (3)$$

Where CR_{blank} and CR_{inh} are the corrosion rates in the absence and presence of the inhibitor, respectively.

3. RESULTS AND DISCUSSION

3.1 Effect of Cordia sebestena leaf extracts on the Corrosion rate.

The corrosion of mild steel in the absence and presence of leaf extracts of *Cordia sebestena* was studied using weight loss method at temperature range of 303-333 K. Figure 1 shows the corrosion rate against system concentration for mild steel corrosion at different temperatures. Corrosion rate was found to decrease with increase in inhibitor concentration. The blank solution (0.5 M H_2SO_4 without inhibitor) gave the highest corrosion rate at all temperature while the solution with 50%v/v of leaf extracts in 0.5 M H_2SO_4 gave the least corrosion rate at all the studied temperatures.

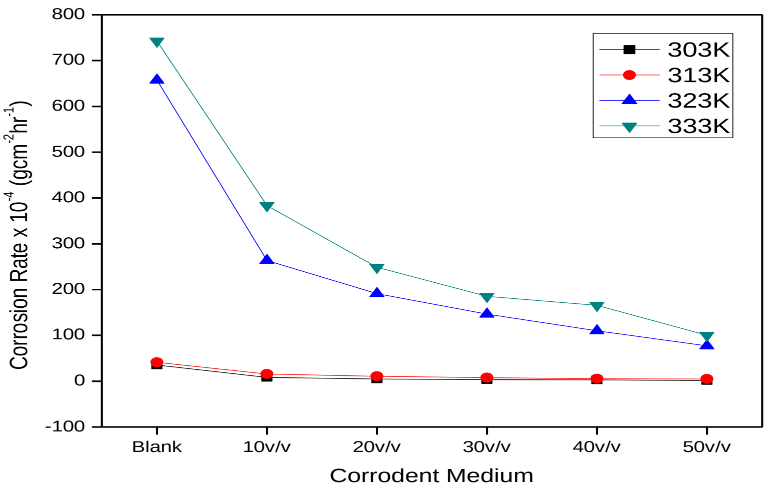


Figure 1. Plot of corrosion rate against concentration at different temperature for mild steel in 0.5M H_2SO_4 solution

This behavior was due to the fact that the amount of coverage of the leaf extracts on mild steel surface increases with inhibitors concentration [28]. Thus, the mild steel surface was efficiently separated from the acid medium [29-32].

Figure 2 shows the relationship between corrosion rate and temperature for mild steel corrosion in 0.5 M H_2SO_4 in the presence and absence of different concentrations of leaf extracts of *Cordia sebestena*. It is obvious from Figure 2 that, the corrosion rate of mild steel in 0.5 M H_2SO_4 increases with increasing temperature both in uninhibited and inhibited solution. This is due to an increase in the rate of diffusion and ionization of the active species in the corrosion process.

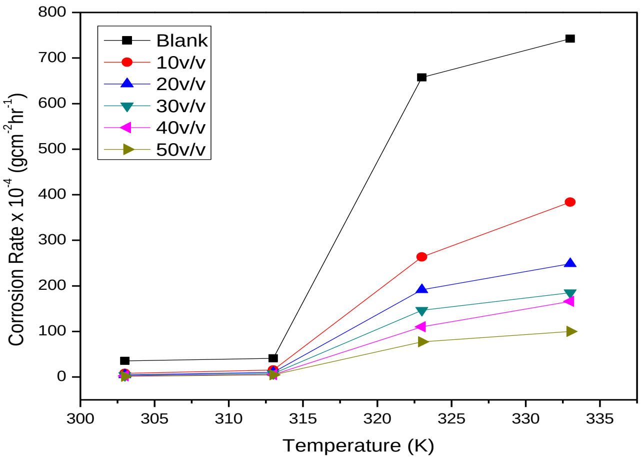


Figure 2. Plot of corrosion rate against temperature for mild steel in 0.5 M H_2SO_4 at various concentrations of leaf extracts of *Cordia sebestena*

3.2 Effect of extracts concentration on inhibition efficiency

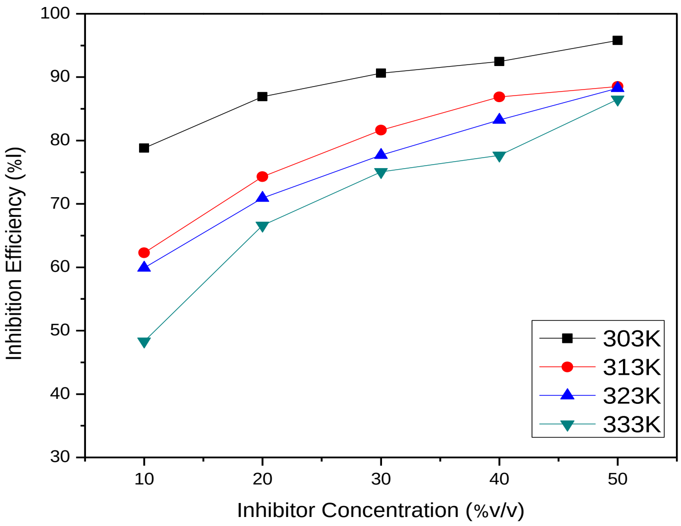


Figure 3. Plot of inhibition efficiency against inhibitor concentration at different temperature for mild steel in 0.5M H_2SO_4 solution

The values of inhibition efficiencies obtained from the weight loss experiment for different inhibitor concentrations in 0.5 M H_2SO_4 and different temperatures were given in Table 1. The results shown in Table 1 and Figure 3 revealed that, inhibition efficiency increased with increased inhibitor concentration. At optimum concentration, the efficiency was 95.79% at 303K which was an indication that the leaf extracts of *Cordia sebestena* is effective inhibitor for mild steel corrosion in 0.5 M H_2SO_4.

Table 1. Calculated values of corrosion rate (CR), surface coverage (θ) and inhibition efficiency (I.E %) for mild steel in 0.5 M H_2SO_4 in the absence and presence of various concentrations of leaf extracts, 5.0mM KI and leaf extracts + 5.0mM KI at different temperatures using weight loss measurement

	CR ($gcm^{-2}h^{-1}$) x 10^{-4}	**θ**	**I.E%**	**CR ($gcm^{-2}h^{-1}$) x 10^{-4}**	**θ**	**I.E%**	**CR ($gcm^{-2}h^{-1}$) x 10^{-4}**	**θ**	**I.E%**	**CR ($gcm^{-2}h^{-1}$) x 10^{-4}**	**θ**	**I.E%**
Blank	35.25	-	-	41.25	-	-	657.6	-	-	742.3	-	-
5.0mM KI	14.20	0.60	59.72	20.20	0.51	51.03	345.50	0.47	47.46	490.20	0.34	33.96
10%v/v	8.18	0.77	78.80	15.56	0.62	62.28	263.5	0.60	59.93	383.6	0.48	48.32
20%v/v	4.62	0.87	86.91	10.60	0.74	74.30	191.3	0.71	70.91	248.6	0.67	66.51
30%v/v	3.31	0.91	90.62	7.57	0.82	81.65	146.6	0.78	77.71	185.2	0.75	75.05
40%v/v	2.66	0.93	92.46	5.41	0.87	86.89	110.2	0.83	83.24	165.8	0.78	77.66
50%v/v	1.48	0.96	95.79	4.73	0.89	88.53	77.19	0.88	88.26	100.2	0.86	86.51
10%v/v + KI	3.12	0.91	91.15	10.20	0.75	75.27	160.2	0.76	75.64	232.4	0.69	68.69
30%v/v + KI	0.82	0.98	97.67	4.83	0.88	88.29	80.96	0.88	87.69	104.6	0.86	85.91
50%v/v + KI	0.32	0.99	99.09	1.50	0.96	96.36	42.57	0.94	93.53	60.2	0.92	91.89

This high inhibition efficiency could be due to the high molecular weight of the photo-chemicals present in the leaf extracts. The phenylpronoid esters, such as sebestenoid A and sebestenoid B [20], which have been reported as present in *Cordia sebestena* leaf extracts, contain the presence of these functional group, namely: C=O, OH and π -electrons of the aromatic moiety, which are electron rich centres. The adsorption of these compounds on the metal surface creates a barrier for charge and mass transfer, leading to a decrease in the interaction between the metal and the corrosive environment, and as a result the corrosion rate of the metal was decreased. According to Patel [33, 34], the inhibition properties of plant extracts may be due to the presence of nitrogen compounds in the extract [35] and tannins [36].

Tannins are complex astringent aromatic glycosides found in various plants. They are made up of polyphenols and heterocyclic derivatives. Polar organic compounds containing N, S, O atoms are good corrosion inhibitors [37]. The polyphenols and heterocyclic derivatives may have been responsible for the formation of an oriented film layer which essentially blocks the discharge of H^+ and dissolution of metal ions.

3.3 Effect of temperature on inhibition efficiency

Thermodynamic and activation parameters played important role in understanding the inhibitive mechanism. The weight loss measurements were conducted in the temperature range of 303-333K at an interval of 10 K, in the absence and presence of different concentrations of leaf extracts of *Cordia sebestena* in 0.5 M H_2SO_4. Figure 4a shows that inhibition efficiency decreases with the experimental temperature.

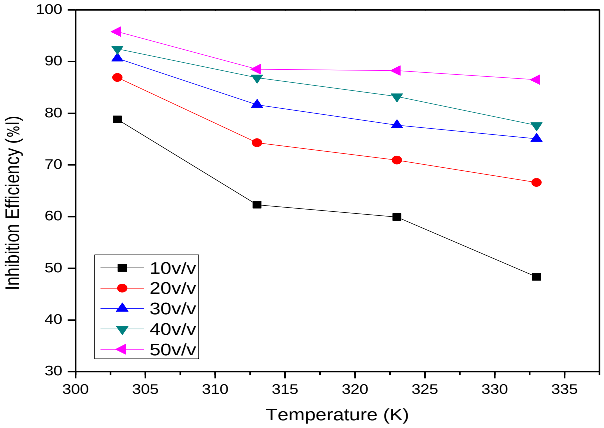


Figure 4a. Plot of inhibition efficiency against temperature for mild steel in 0.5 M H_2SO_4 at various concentrations of leaf extracts of *Cordia sebestena*

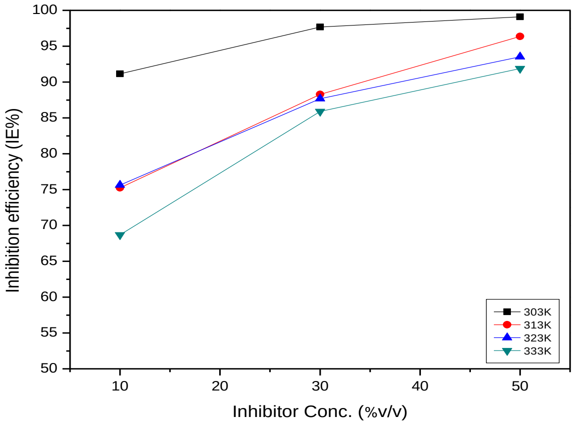


Figure 4b. Plot of inhibition efficiency against inhibitor concentration for mild steel in 0.5M H_2SO_4 in the presence of 5mM KI at different temperatures

This can be attributed to the fact that at higher temperature, desorption of the extracts on the mild steel surface might take place. This suggests that the mode of adsorption of leaf extracts of *Cordia sebestena* on the mild steel surface could be physical adsorption rather than chemical adsorption [38, 39].

The dependence of corrosion rate (CR) of mild steel in acid media on temperature (T) can be expressed by Arrhenius equation [40,41].

$$\log CR = \log A - \frac{E_a}{2.303RT} \qquad (4)$$

where *CR* is the corrosion rate, E_a is the apparent activation energy, *R* is the molar gas constant (8.314 J K^{-1} mol^{-1}), *T* is the absolute temperature, and *A* is the frequency factor. The plot of *log CR* against *1/T* for mild steel corrosion in 0.5 M H_2SO_4 in the absence and presence of different concentrations of the leaf extracts is presented in Figure 5.

Table 2. Activation parameters for the dissolution of mild steel in 0.5 M H_2SO_4 solution in absence and presence of various concentrations of leaf extracts of *Cordia sebestena*

Conc.(%v/v)	Ea* (kJmol^{-1})	ΔH* (kJmol^{-1})	ΔS* (Jmol^{-1}K^{-1})	log A(gcm^{-1}hr^{-1})
Blank	99.87	97.23	26.42	14.64
10	120.64	118.00	83.49	17.62
20	124.79	122.15	93.01	18.11
30	126.38	123.74	95.44	18.24
40	129.36	126.72	102.87	18.63
50	129.90	127.27	101.27	18.54

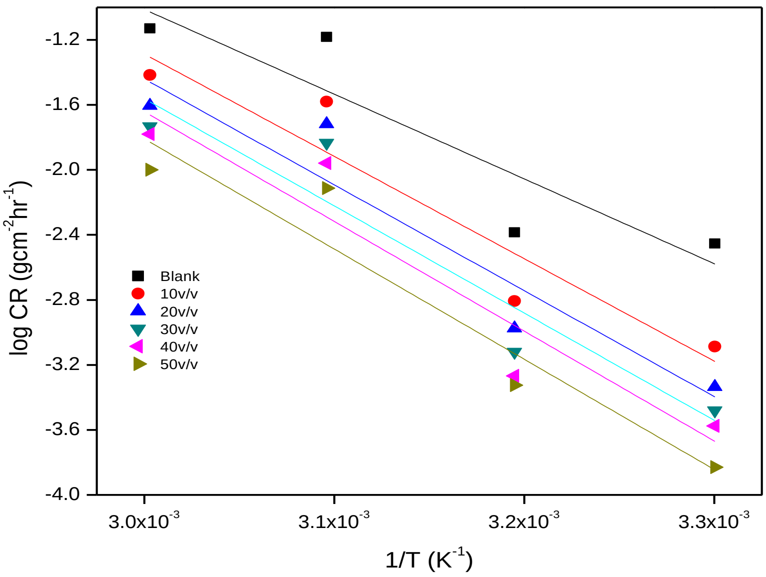


Figure 5. Arrenhuis plot for the dissolution of mild steel in 0.5 M H_2SO_4 in absence and presence of different concentrations of leaf extracts of *Cordia sebestena*

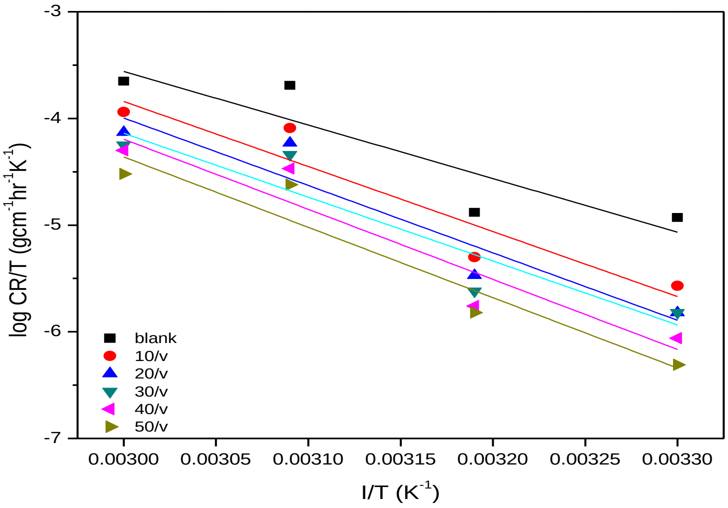


Figure 6. Transition state plot for the dissolution of mild steel in 0.5 M H_2SO_4 in absence and presence of different concentrations of leaf extracts of *Cordia sebestena*

Activation energy value, E_a^* was calculated from the slope of the plots of Figure 5 and were given in Table 2. The activation energies calculated from equation 3 were found to range from 120.64kJmol^{-1} to 129.90kJmol^{-1} for the inhibited solutions. These values were higher than 99.87kJmol^{-1} obtained for the blank; this indicated that the leaf extracts retarded the corrosion of mild steel in 0.5 M H_2SO_4. These results suggested that the adsorption of the leaf extracts on mild steel surface obeys the mechanism of physical adsorption [42].

To calculate the enthalpy of the activation process ΔH^* and the entropy of activation ΔS^*, Equation 5 called the transition state equation was employed.

$$CR = (RT/Nh) \exp (\Delta S^*/R) \exp (-\Delta H^*/RT) \qquad (5)$$

Where CR is the corrosion rate, R is the molar gas constant, T is the absolute temperature, h is the Planck's constant (6.626176 x 10^{-34}Js), and N is the Avogadro's number (6.02252 x 10^{23}mol^{-1}). Plots of $\log CR/T$ against $1/T$ (Figure 6) gave straight lines with slope of $(-\Delta H^*/2.303R)$ and intercept of $(\log R/Nh + \Delta S^*/2.303R)$ from which the values of ΔH^* and ΔS^* listed in Table 2 were calculated. Table 2 revealed that ΔH^* gave positive values which reflect the endothermic nature of the dissolution of mild steel in 0.5 M H_2SO_4 [42]. The negative values of ΔS^* indicate that the activation complex in the rate determining step represents association rather than dissociation. This implies a decrease in disorder on going from reactants to the activated complex [43].

3.4 Adsorption considerations

The adsorption of inhibitor molecules from aqueous solutions can be regarded as a quasi-substitution process between the organic compound in the aqueous phase Org (aq) and water molecules at the electrode surface, $H_2O(s)$.

$$\text{Org (aq)} + x\ \text{H}_2\text{O (s)} \rightarrow \text{Org (s)} + x\ \text{H}_2\text{O (aq)} \qquad (6)$$

where x, the size factor, is the number of water molecules displaced by one molecule of organic inhibitor. Since the corrosion process is based on the adsorption of the leaf extracts on the metal surface, it is essential to know the mode of adsorption and the adsorption isotherm that fits the experimental results. The most frequently used isotherms are Langmiur, Frumkin, Freundlich, Hill de Boer, Parsons, Temkin, and Bockris-Swinkel [44-48]. Plots of the experimental data for each isotherm showed that the best-fitted straight line was for the plot of C/θ against C (Figure 7a and 7b). The correlation coefficient (R^2) was used to choose the isotherm that best fit the experimental data. It was found that the adsorption of leaf extracts of *Cordia sebestena* on mild steel surface obeyed Langmuir adsorption isotherm.

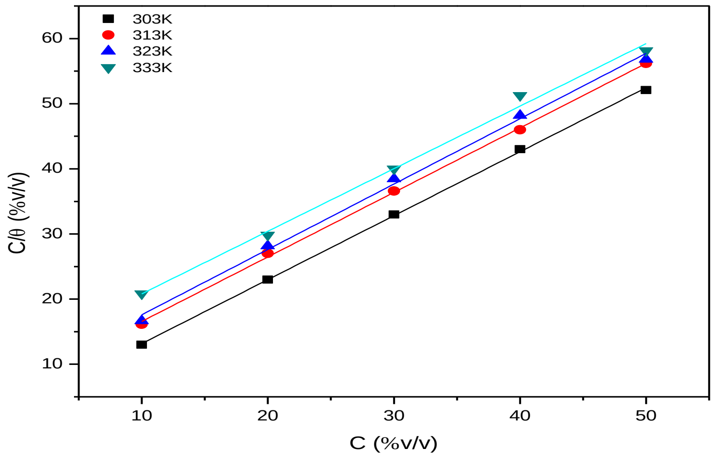


Figure 7a. Langmuir plot for mild steel in 0.5 M H_2SO_4 at different temperatures in various concentrations of *Cordia sebestena* leaf extracts

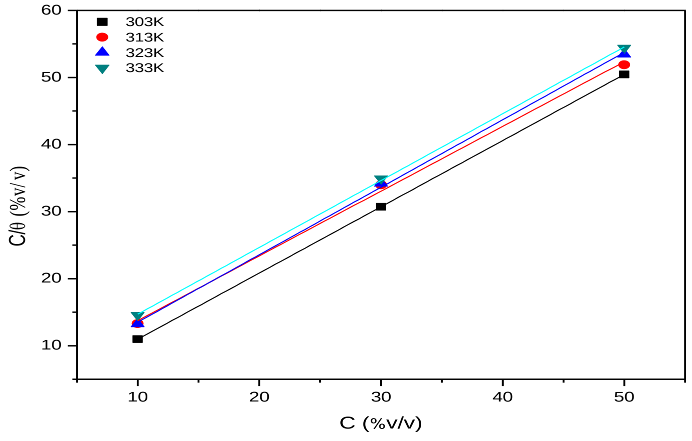


Figure 7b. Langmuir plot for mild steel in 0.5 M H_2SO_4 at different temperatures in various concentrations of *Cordia sebestena* leaf extracts + 5.0mM KI

The Langmuir adsorption isotherm model has been used extensively in the literature for various metal, inhibitor and acid solution systems [9,12,23,28]. The plot of C/θ against C (Figure 7a and 7b), using equation (7), yielded a straight line with $R^2 = 0.999$.

$$C_{inh}/\theta = 1/K_{ads} + C_{inh} \qquad (7)$$

Where C_{inh} is the inhibitor concentration and K_{ads} is the equilibrium constant for the adsorption or desorption process. The values of adsorption constant, slope, and linear correlation coefficient (R^2) can be obtained from the regressions between C/θ and C, and the results were listed in Table 3.

Table 3. Calculated parameters from Langmuir isotherm plot for mild steel in 0.5 M H_2SO_4 in the presence of (a) leaf extracts (b) leaf extracts + 5.0mM KI

	(a)				(b)			
Temp. (K)	Slope	K_{ads} (M)	R^2	ΔG^o_{ads} (kJ/mol)	Slope	K_{ads} (M)	R^2	ΔG^o_{ads} (kJ/mol)
303	0.982	0.30	0.999	-7.09	0.987	0.91	1.000	-9.64
313	0.990	0.16	0.999	-5.60	0.965	0.24	0.998	-6.78
323	1.003	0.13	0.997	-5.31	1.006	0.28	0.999	-7.46
333	0.960	0.09	0.995	-4.41	0.996	0.21	0.999	-6.81

The result showed that all the linear correlation coefficients and all the slopes were close to one and this confirmed that the adsorption of leaf extracts on mild steel surface in 0.5 M H_2SO_4 followed Langmuir adsorption isotherm. However, it can be noticed that the slope deviated slightly from unity; this deviation could be explained on the basis of interaction between species already adsorbed on the surface of the metal. Langmuir isotherm equation postulated that adsorbed molecules do not interact with one another, but this is not possible or true for large organic molecules having polar atoms or groups which can adsorbed on the cathodic and anodic sites of the metal surface. The adsorbed species interact either by mutual repulsion or attraction therefore; the deviation from unity could be due to the adsorption of the leaf extracts on the anodic and cathodic sites. Similar observation was reported by Ebenso and Obot [27].

The calculated value of K_{ads}, is related to the standard free energy of adsorption ΔG_{ads}, by equation 8, given as: [25].

$$\Delta G^o_{ads} = -2.303RT \log (55.5 \times K_{ads}) \qquad (8)$$

Where R is the molar gas constant, T is the system temperature measured in (K) and 55.5 is the molar concentration of water in solution expressed in mol/lit.

Calculated values of free energies (ΔG^o_{ads}) were listed in Table 3; the negative values of ΔG^o_{ads} indicated spontaneous adsorption of the leaf extracts onto the mild steel surface [49] and strong interactions between inhibitor molecules and the metal surface [35]. Generally, values of ΔG^o_{ads} up to -20 kJmol^{-1} are consistent with physisorption, while those around -40 kJmol^{-1} or higher are associated with chemisorption, which is as a result of sharing or transfer of electrons from organic molecules to the metal surface to form a coordinate bond [9]. In this study, the calculated values of ΔG^o_{ads} were less than -20kJmol^{-1} which was an indication that the adsorption mechanism of the leaf extracts on mild steel in 0.5 M H_2SO_4 solution at the studied temperatures was basically physisorption.

In this study, the thermodynamic parameters such as enthalpy of adsorption ΔH^o_{ads} and entropy of adsorption ΔS^o_{ads} were deduced from the integrated version of the van't Hoff equation expressed by [49]:

$$InK_{ads} = \Delta H^o_{ads} /T \ + \Delta S^o_{ads}/R + In\ 55.5^{-1} \qquad (9)$$

The plot of lnK_{ads} versus $1/T$ shown in Figure 8, gave straight lines with slope of $(-\Delta H^o_{ads} /R)$ and intercept of $(\Delta S^o_{ads} /R + In\ 55.5^{-1})$ The calculated values of ΔH^o_{ads} and ΔS^o_{ads} from the van't Hoff equation were -32.16 kJmol^{-1} and -83.43 Jmol^{-1}K^{-1} respectively.

Gibb's-Helmholtz equation was further used to calculate the enthalpy of adsorption ΔH^o_{ads}. The re-arranged form of Gibb's-Helmholtz equation is given in equation 10 below [50, 51].

$$\Delta G^o_{ads}/ T = \Delta H^o_{ads}/ T + k \qquad (10)$$

The relationship between $\Delta G^o_{ads} /T$ and $1/T$ presented in Figure 9, gave a straight line graph with the slope equal to ΔH^o_{ads}. The calculated value of ΔH^o_{ads} was -32.34 kJmol^{-1}, which agreed with the value of ΔH^o_{ads} obtained from van't Hoff equation.

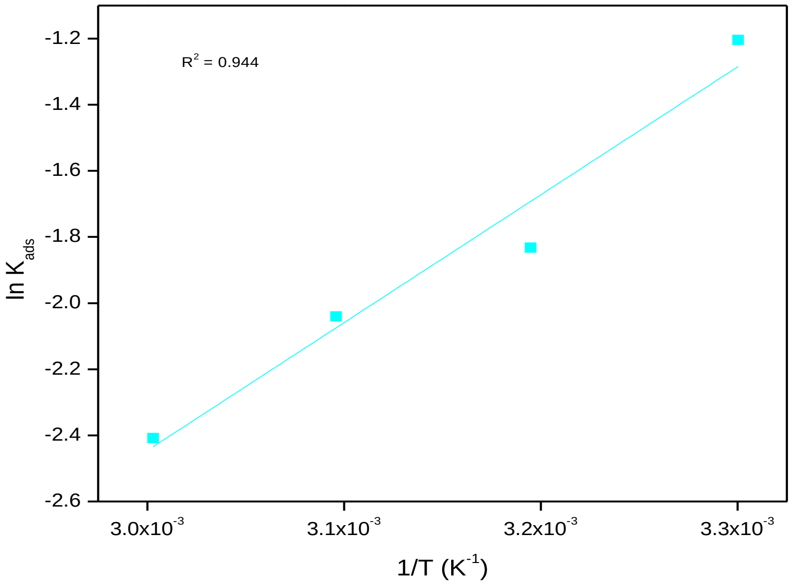


Figure 8. Plot of $In\ K_{ads}$ against $1/T$

Finally, the basic thermodynamic equation which shows the relationship between change in Gibb's free energy ΔG^o_{ads}, change in enthalpy ΔH^o_{ads}, change in entropy ΔS^o_{ads} and temperature T was used to further determine the enthalpy of adsorption and entropy of adsorption.

$$\Delta G^o_{ads} = \Delta H^o_{ads} - T\Delta S^o_{ads} \qquad (11)$$

A plot of ΔG^o_{ads} versus T (Figure 10), gave a linear graph with slope of ΔS^o_{ads} and intercept of ΔH^o_{ads}. The enthalpy of adsorption ΔH^o_{ads} and the entropy of adsorption ΔS^o_{ads} obtained were -32.09kJmol^{-1} and -83.30Jmol^{-1}K^{-1}, respectively.

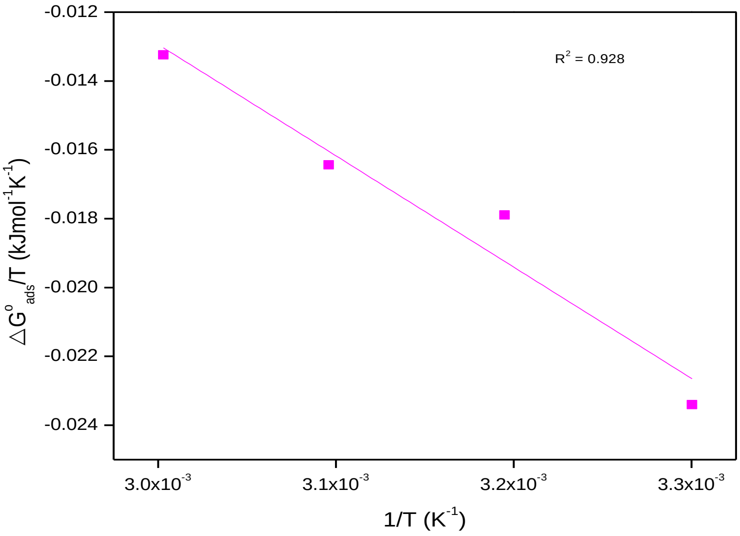


Figure 9. Plot of $\Delta G^o_{ads} / T$ against $1/T$

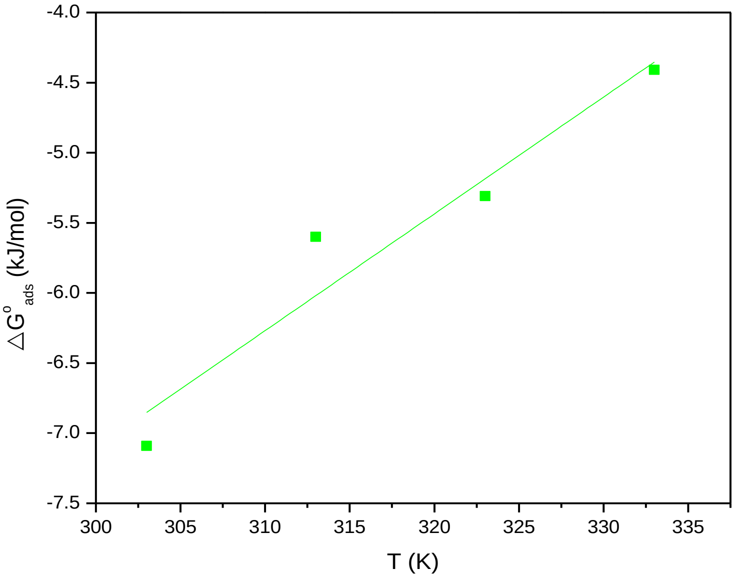


Figure 10. Plot of ΔG^o_{ads} against T

Inspection revealed that the values of enthalpy of adsorption obtained by the van’t Hoff equation, Gibb’s-Helmholtz equation and basic thermodynamic equation were in good agreement (-32.16kJmol^{-1}, -32.34kJmol^{-1} and -32.09 kJ/mol^{-1}). Similarly, the values of entropy of adsorption ΔS^{o}_{ads} obtained by van’t Hoff equation and the basic thermodynamic equation were also in good agreement (-83.43Jmol^{-1}K^{-1} and -83.30Jmol^{-1}K^{-1}).

The negative value of ΔH^{o}_{ads} suggested that the adsorption of leaf extracts of *Cordia sebestena* on the mild steel surface was an exothermic process. In an exothermic process, physisorption is distinguished from chemisorption by considering the absolute value of ΔH^{o}_{ads}. For physisorption process, the enthalpy of adsorption is lower than 40kJmol^{-1} while that for chemisorption approaches 100kJmol^{-1} [52].

In this study, the values of ΔH^{o}_{ads} were lower than 40kJmol^{-1} which further confirmed that the adsorption of leaf extracts of *Cordia sebestena* on mild steel surface was by physical adsorption mechanism. Similar results were reported elsewhere [53, 54]. The entropy of adsorption ΔS^{o}_{ads} was negative because inhibitor molecules freely moving in the bulk solution were adsorbed in orderly fashion onto the mild steel, resulting in a decrease in entropy [55].

3.5 Synergism considerations

Experimental results obtained in this study indicated that the addition of iodide ions to the solution of leaf extracts of *Cordia sebestena* increased the inhibition efficiency and the degree of surface coverage (Table 1 and Figure 11). This behavior can be attributed to the synergistic effect between iodide ions and the photochemical compositions of the leaf extracts. The anions improved the adsorption of organic cations in solution by forming intermediate bridges between the metal surface and the positive end of the organic inhibitor [56-58].

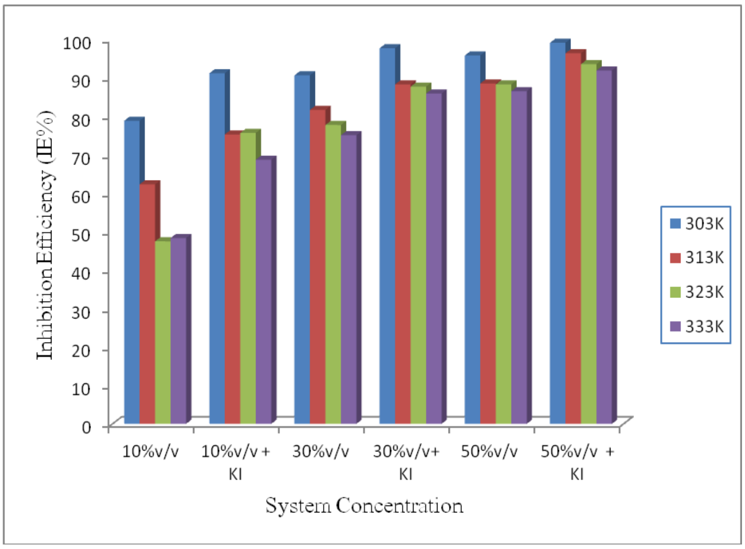


Figure 11. Plot of inhibition efficiency against inhibitor concentration for mild steel in 0.5M H_2SO_4 in the presence of different concentration of *Cordia sebestena* extracts and 5mM KI at different temperatures

Corrosion inhibition synergism thus results from increased surface coverage arising from ion-pair interactions between the organic cations and the anions. The synergistic parameters were calculated using the relationship initially given by Aramaki and Hackerman and reported elsewhere [59]:

$$s_1 = \frac{1 - I_{1+2}}{1 - I'_{1+2}} \qquad (12)$$

Where $I_{1+2} = I_1 + I_2$; I_1 is inhibition efficiency of the iodide ions, I_2 is the inhibition efficiency of the leaf extracts and I'_{1+2} is measured inhibition efficiency for the leaf extracts in combination with iodide ions. The value of s_1 is equal to 1 if the leaf extracts of *Cordia sebestena* and iodide ions have no effect on each other and were adsorbed at the metal/solution interface independently. Alternatively, synergistic effects manifest when $s_1 > 1$ and antagonistic effects prevails when $s_1 < 1$ [9]. The calculated values of synergism parameter were shown in Table 4.

Table 4. Synergistic parameter s_1 for 5.0mM KI in different concentrations of *Cordia sebestena* leaf extracts at various temperatures

Conc. (v/v)	Synergism Parameter (s_1)			
	300K	313K	323K	333K
10	1.53	1.51	1.43	1.20
30	1.55	1.50	1.43	1.27
50	1.58	1.45	1.46	1.32

From the Table, we observed that the values of s_1 for all the concentrations were more than unity, thereby suggesting that the enhanced inhibition efficiency caused by the addition of iodide ions to the leaf extracts was only due to synergistic effect and the effect was more pronounced at higher temperatures (Table 1). Murakawa *et al*. [60] proposed three possible models for inhibitor adsorption with halide ions. (i) The adsorption of the halide ions which then attract the inhibitor molecules to the metal surface (ii) exchange of adsorption site by halide ions and organic ions (competitive adsorption) and (iii) co-adsorption of inhibitor and halide ions. From the results obtained in this study, it can be suggested that iodide ions (I^-) were initially adsorbed on the metal surface and the components of leaf extracts of *Cordia sebestena* in the form of cations were then adsorbed by electrostatic attraction on the top of already chemisorbed layer of iodide ions, thus provide greater surface coverage and enhanced inhibition efficiency.

4. CONCLUSIONS

The following conclusion can be drawn based on the above results:

1. *Cordia sebestena* leaf extracts effectively inhibit the corrosion of mild steel corrosion in 0.5 M H_2SO_4 solution.
2. The inhibition efficiencies increase with increase in inhibitor concentration but decrease with increase in temperature.
3. The corrosion inhibition is due to the adsorption of the photochemical constituents of the leaf extracts on the mild steel surface, blocking the active sites by phenomenon of physical adsorption.
4. The data obtained from this study fits well into the Langmuir adsorption isotherm. From thermodynamic point of view, the adsorption process is spontaneous, exothermic and accompanied with a decrease in entropy of the system.
5. The thermodynamic parameters (enthalpy of adsorption, entropy of adsorption and Gibb's free energy of adsorption) obtained through different equations were in good agreement.
6. Inhibition efficiency was significantly increased by addition of KI. The synergistic effect of KI results from increased adsorption of the positive component of the extracts by electrostatic attraction with iodide ion already adsorbed on the mild steel surface.

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