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Electrochemical and Adsorption Behaviour of *Diospyros mespiliformis* **on Annealed Carbon steel Corrosion in Hydrochloric Acid**

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Authors' contributions

This work was carried out in collaboration between all authors. Authors AAA, FCE and EEO wrote the protocol, designed and supervised the study. Authors RSO and AMK performed the experimental work, managed literature search and wrote the first draft. All the authors read and approved the final manuscript.

Article Information

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Original Research Article

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ABSTRACT

The interfacial activities of *Diospyros mespiliformis* on annealed carbon steel in 2 M HCl solution was studied by electrochemical methods; polarization and impedance spectroscopy measurements, while weight loss of the carbon steel at varying temperatures and gasometric method was studied. The results of the study revealed that *D. mespiliformis* mitigates the corrosion of carbon steel (FE164531) in HCl solution through adsorption. Results from Tafel plots suggest that *Diospyros mespiliformis* (DM) behaves predominantly as a cathodic inhibitor with highest inhibition efficiency (91%) at 1000 ppm. The Nyquist and Bode plots of the test solutions were similar in both inhibited and free medium and contained capacitive and inductive loops. Thermodynamic parameters suggest that *D. mespiliformis* is adsorbed on carbon steel mainly by physical adsorption. The values of enthalpy and entropy of adsorption suggests that DM adsorption

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on FE164531 surface was spontaneous. A good correlation was obtained following the percentage inhibition efficiencies calculated from all the techniques employed.

Keywords: Annealed carbon steel; Diospyros mespiliformis; corrosion inhibition; adsorption; hydrochloric acid.

1. INTRODUCTION

The significance of corrosion protection of carbon steel in acidic solutions has become necessary due to its propensity to be attacked in acidic media when deployed in services like acid pickling, chemical cleaning of scale in metallurgy, electrochemical systems, oil recovery and also the petrochemical industry. The protection of carbon steel against corrosion in acidic environments can be achieved in various ways using corrosion inhibitors [1-3]. Several research have been carried out on the use of eco-friendly inhibitors to contain corrosion of carbon steel, mild steel, stainless steel, aluminium and many other metals in both acid and alkaline solutions [4-7]. Corrosion inhibitors are commonly added in small quantity to pickling acids, acid stimulation fluids, cooling waters, oil and gas production streams, either continuously or intermittently to control attacks. These inhibitors generally control corrosion by forming various types of films either by adsorption or the formation of bulky precipitates, and/or the formation of a passive layer on the metal surface that modify its corrosivity [8-10]. The mechanism of most corrosion inhibitor on metal oxidization can be explained on the basis of molecular adsorption, which involves forming a thin, invisible film that coat the metal thereby protecting it from attack or a combination of adsorption films and corrosion product forms a passive layer on the metal surface [11]. In aqueous acidic solutions, corrosion inhibitors subsist either as neutral molecules or protonated molecules which adsorb on the metal/acid solution interface through
electrostatic attraction between charged between charged molecules and charged metal or by the interaction of unshared π electrons in the inhibitor molecule with the metal surface [12]. Apart from sea water, hydrochloric acid remains the main source of the aggressive chloride ions in aqueous solutions and occurrences of carbon steel corrosion in environments containing chloride ions are known [13]. Several reports claimed the used of green inhibitor as cheap, effective, renewable and non-toxic for metal corrosion [14-20]. The effectiveness of these bioextracts as metal corrosion inhibitor mainly

depend on its phytocompund functional groups having; steric effects, π-orbital character of donating electrons via adsorption at active sites and electronic density of donor atoms among other variables. *Diospyros mespiliformis* commonly called African ebony is confined to tropical and sub-tropical regions notably in Central and West Africa [21]. Several ethnopharmacological applications have been reported for *D. mespiliformis* which include the use of leaves decoction as extraordinary remedy for fever, whooping cough and for wounds [22,23]. GC-MS analysis of extracts from *Diospyros mespiliformis* yielded components such as triterpenes, carotenoides, saponosides, anthracenosides, anthocyanosides and tannins [21].

In this present work, corrosion study was made using annealed carbon steel immersed in aerated stagnant 2 M HCl solutions with and without addition of ethanolic extract of *D. mespiliformis* leaves, using weight loss, gasometry and electrochemical techniques. The corrosion rate (mpy) of carbon steel and inhibition efficiency of *D. mespiliformis* leaves extract was evaluated with the different methods employed while insight into the adsorption mechanism was assessed through electrochemical impedance spectroscopy (EIS). The experimental data were fitted into Langmuir adsorption isotherm while the effects of temperature gave thermodynamic parameters such as ΔH_{ads} and ΔS_{ads} .

2. EXPERIMENTAL

2.1 Material Preparation

Corrosive solutions were freshly prepared from analytical grade chemical reagents using bidistilled water and were used without further purification for each test run. Annealed carbon steel (FE164531) sheets of 99.5% purity, used for this study has the following typical analysis ppm: C< 1200, Mn< 5000, S< 500, P< 500 which was procured commercially from Advent research materials Ltd, Eynsham Oxford England OX29 4JA. The sheet was mechanically presscut into 40 x 40 x 0.92 mm coupons with a hole of 1mm drilled at the middle of the upper edge of the coupons and then polished successively with metallographic emery paper of increasing fineness of up to 1200 grits. These coupons were degreased in absolute ethanol, dried in acetone, further dried with hot air and stored in moisturefree desiccator prior usage. Dried leaves of *D. mespiliformis* were blended to powder form; 10 g of powdered leaves was refluxed in 100 ml ethanol for 3 h, allowed to cool for 6 h and filtered. The filtrate was concentrated using rotary evaporator and stored in an oven at 40°C. From the concentrate, inhibitor test solutions were prepared in concentrations of 10 ppm, 100 ppm and 1000 ppm.

2.2 Weight Loss

In gravimetric measurements, FE164531 coupons were weighed before total immersion in a 250 ml beaker containing 200 ml test solutions, being suspended by suitable hooks at 1 cm below the solution surface. The beakers were placed in a freely aerated thermostated water bath maintained at constant temperature at 303, 313, 323 and 333±0.5 K. The coupons were retrieved after 3 hours, scrubbed with brush under running bidistilled water, dried as before and weighed [13]. The difference in weight of the coupons before and after immersion in different test solutions was taken as the weight loss. The corrosion rate of the carbon steel and inhibition efficiency of the inhibitor $(E_W %)$ was calculated using the following equations 1 and 2 respectively [10].

$$
CR (mpy) = \frac{534 \text{ \Delta W}}{\text{pAT}}
$$
 (1)

$$
E_W \% = \frac{CR^0 - CR}{CR^0} \tag{2}
$$

where $ΔW$ is weight loss in mg, $ρ$ is the density of carbon, A the area of the coupon in inches, T is the immersion time in hours, CR and $CR⁰$ are the corrosion rate in the presence and absence of inhibitors respectively.

2.3 Gasometric

Fifty milliliters of test solutions poured into a reaction vessel was used in the gasometric method. Upon introduction of the metal coupon, the vessel was quickly corked and the initial volumes of air in the burette, taken against that of the paraffin oil were recorded. The decrease in volume of the paraffin oil in the burette due to hydrogen gas evolution was noted after every five minutes till the last volume of paraffin oil in the burette. The volume of hydrogen gas evolved was used to evaluate inhibition efficiency of the test inhibitors using equation 3 [24].

$$
E_{\rm H}\% = 1 - \frac{c_{\rm R}_{\rm H}}{c_{\rm R}_{\rm H}^0} \tag{3}
$$

where $\text{CR}_{\rm H}$ and $\text{CR}^0_{\rm H}$ are corrosion rates got from total volume of gas evolved in the presence and absence of test inhibitors respectively.

2.4 Polarization Technique

The electrochemical experiments were carried out in a three-electrode electrochemical cylindrical Pyrex glass cell with a graphite rod counter electrode and saturated calomel electrode (SCE) as reference. Annealed carbon steel having an exposed area of 1cm^2 was used as working electrode. Before recording the polarization curves, the working electrode was kept at its open circuit value in aerated stagnant 2 M HCl solution without and with inhibitor for 30 min. All electrochemical experiments were performed at room temperature (27±1°C) using a Versa STAT 3 electrochemical System. The potentiodynamic polarization curves were obtained by scanning the potential of working electrode from -0.25 V to 1.7 V vs. SCE at a scan rate of 1 mV/s [8], while impedance spectroscopy experiments (EIS) was scanned at the opencircuit potential at frequencies from 100 kHz to 0.1 Hz with AC signal amplitude of 5 mV peak-topeak along phase shifts between AC voltage and current. The Nyquist and bode plots were acquired using ZSimpWin Version 3.20. The values of E_{corr} , i_{corr} , R_t and C_{dl} were obtained from the electrochemical measurements. The electrochemical measurements. inhibition efficiencies were determined using equations below:

$$
E_i\% = \frac{i_{corr}^* - i_{corr}}{i_{corr}^*}
$$
 (4)

$$
E_R\% = 1 - \frac{R_{\rm ct}^0}{R_{\rm ct}} \times 100
$$
 (5)

Where i_{corr} and i_{corr} is corrosion current densities for inhibited and uninhibited solutions respectively, while R_t and R_t^0 is charge transfer resistance in the presence and absence of inhibitor molecules respectively.

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3. RESULTS AND DISCUSSION

3.1 Polarization Measurements

Fig. 1 shows the anodic and cathodic polarization
curves for FE164531 while calculated $curves$ for FE164531 electrochemical parameters such as, corrosion potential (*Ecorr*), corrosion current density (*icorr*), degree of surface coverage of the inhibitor (*θ*), the inhibition efficiency of the inhibitor (*Ei %*) and linear polarization resistance (R_p) values are listed in Table 1. As can be seen from Fig. 1, the polarization curves showed features of spontaneous passivation in all test media. Addition of *D. mespiliformis* leaves extracts at varying concentrations did not visibly alter the polarization behavior of the metal in the active metal dissolution region at the anode but however, a decrease in current density was observed. This suggests that *D. mespiliformis* did not interfere with the corrosion mechanism of FE164531 carbon steel, however the inhibitor additives caused a decrease in both cathodic and anodic currents proposing a reduction in anodic dissolution and retardation of hydrogen evolution reaction [5,8]. The cathodic polarization curves exhibit active behaviour with increasing inhibitor concentration with a shift towards lower current density region. The anodic polarization curves are almost identical irrespective of the concentration of test inhibitor. The lower values of corrosion current density facilitate slow electron transfer in the redox process, hence the rate of corrosion reaction becomes reduced. The decrease of current density indicate the fact that *D. mespiliformis* molecules gets adsorbed on pure carbon steel surface and hence retards the corrosion reaction of electrode with concurrent replacement of electrolyte solution at the metal/electrolyte interface [25]. Fig. 1 also reveal a decrease in both corrosion current and potential in the cathodic region with a cathodic shift was observed in the *Ecorr* indicating that *D. mespiliformis* is a probable cathodic inhibitor. A spontaneous passivation in the anodic region was seen with a decrease in the corrosion potential as the inhibitor was introduced. This decrease is observed at the initial anodic – active dissolution of FE164531 which is an indication of the stability of the film formation comprising of γ- $Fe₂O₃/Fe₃O₄$ on FE164531 surface [3,26]. As the potential becomes more passive, the rates of anodic reactions increase while that of cathodic reactions decreases. This observation is an indication that the formation of γ -Fe₂O₃/Fe₃O₄ films gradually spreading over the surface of FE164531. Usually a low current density and

long anodization time presents a very good protection against corrosion due to the diminution of the porosity of the anodic films formed. The corrosion reaction of carbon steel in solutions containing chloride ions occur via these mechanisms as reported by Sherif [27];

$$
Fe_{(s)} + 2Cl_{(aq)}^- \to FeCl_{2(s)} + 2e^-
$$
 (6)

$$
\text{FeCl}_{2(s)} \rightarrow \text{FeCl}_{2(\text{interface})} \rightarrow \text{FeCl}_{2(aq)} \tag{7}
$$

$$
\text{FeCl}_{2(s)} + \text{Cl}^{-}_{(aq)} \rightarrow \text{FeCl}_{3(s)} + e^{-}
$$
 (8)

$$
\text{FeCl}_{3(s)} \rightarrow \text{FeCl}_{3(\text{interface})} \rightarrow \text{FeCl}_{3(aq)} \tag{9}
$$

The mechanism show that the film formed on the carbon steel surface is a mixed porous film of a precipitated ferrous chloride, $FeCl₂$ and f erric chloride, FeCl₃ compounds. Considering concentration gradients, the ferrous and ferric chloride specie at metal/electrolyte interface diffuse through the porous film and the diffusion boundary layer and then into the bulk solution through convection currents. This results in continuous uniform and pitting corrosion of FE164531 by attack of the chloride ions. The introduction of inhibitor molecules controlled the corrosion current with a maximum of 91% inhibition efficiency at 1000 ppm concentration. This can be explained on the bases that *D. mespiliformis* at this concentration strongly inhibit and block the corrosion sites on the carbon steel surface and retards uniform corrosion and prevents formation of pits. Table 1 show that the corrosion potential exhibiting a decrease with increasing concentration could be attributed to the passage of metal ions through the adsorbed film occuring slowly and the corrosion current due to metal ion transportation becoming reduced.

The inhibition efficiency results of the inhibitor were calculated from the corrosion current (i_{corr}) values according to equation 4 and the values are presented in Table 1. The linear polarization resistance (*Rp*) was found to increases from 0.496 to 1.497 Ω which results in increase in corrosion current resistance on addition of *D. mespiliformis* to 2 M HCl. On increasing the inhibitor concentration, E_{corr} values were shifted
more negative. This proposes that D. negative. This proposes that *D*. *mespiliformis* behaves predominantly as cathodic inhibitor. The increase of polarization resistance with increasing inhibitor concentration is mainly due to its adsorption on FE164531 surface. The value of R_p is a measure of electron transfer across the surface and it increases with an increase in corrosion rate. The values of R_p in Table 1 showed a steady increase following

increased inhibitor concentration from 10 ppm to 1000 ppm. This increase as compared to the blank value indicates a reduction in FE164531 carbon steel corrosion rate through the formation of adsorbed protective film against corrosion attack at the metal/electrolyte interface [28,29].

3.2 Impedance Spectroscopy Measurements

To determine kinetic parameters for electron transfer reactions at the carbon steel/electrolyte interface. electrochemical impedance spectroscopy experiment was carried out at open circuit potential in the absence and presence of *D. mespiliformis*. Typical Nyquist and Bode plots were obtained at the metal/electrolyte interface for all test solutions. Fig. 2 shows the Nyquist plot of one capacitive loop exhibiting an extended semicircle in the complex impedance plane both in uninhibited and inhibited solutions, an indication that corrosion rate is controlled by charge transfer resistance. The impedance diagrams obtained were not perfect semicircles, and increases in diameter as inhibitor concentration increases indicating that the presence of inhibitor molecules strengthens the inhibitive film and/or the Faradic processes occurring through defects of this film with increase in *D. mespiliformis* concentration. The impedance data obtained are analyzed by simple

equivalent Randles circuit which sufficiently explains EIS data for liquid and steam-treated samples [8,30]. Fig. 3 shows typical Randles circuit consisting of solution resistance *Rs* in series with a component composed of transfer resistance R_t and parallel film capacitance C_{dl} . The obtained values for the charge transfer resistance and parallel film capacitance are listed in Table 2. As seen from Table 2 that the value of *Rt* increases in the concentrations of the inhibitor. Fig. 4 shows the Bode plots for FE164531 in 2 M HCl with and without different concentrations of *D. mespiliformis* inhibitor. The capacitance of parallel film (C_{d}) was calculated from equation 7.

$$
C_{dl} = \frac{1}{2\pi f_{max} R_{ct}} \tag{10}
$$

Table 2 shows that C_{dl} values decreased when the concentration of the inhibitor molecules increased. The decrease in C_{dl} might arise from a decrease in local dielectric constant and/or an increase of the electrical double layer thickness which might arise from substitution of preadsorbed water molecules on the metal/electrolyte interface by adsorbed organic constituents of *D. mespiliformis* leaves extract whose dielectric constant is lower, suggesting that inhibitor molecules function by adsorption at the metal/solution interface [30].

Fig. 1. Anodic and cathodic polarization curves for FE164531 electrode in aerated solution of 2 M HCl in the absence and presence of different concentrations of *D. mespiliformis* **leaves extracts**

Solution	Parameters							
	i_{corr} (µA cm ⁻²)	$-E_{corr}$ (mV vs SCE)		E, %	$R_o(\Omega)$			
blank	5465.8	357.28	$- -$	$- -$	0.496			
10 ppm	2715.03	427.01	0.5033	50	1.272			
100 ppm	1342.04	436.27	0.7545	76	1.338			
1000 ppm	517.01	443.08	0.9054	91	1.497			

Table 1. Corrosion parameters obtained from polarization curves for FE164531 carbon steel in 2 M HCl solution in the absence and presence of *D. mespiliformis* **leaves extracts**

Fig. 2. FE164531 carbon steel in 2 M HCl solutions with and without different concentrations of *D. mespiliformis* **leaves extract**

Fig. 3. Electrical equivalent circuit used to fit the impendence data

Fig. 4. FE164531 carbon steel in 2 M HCl solutions with and without different concentrations of *D. mespiliformis* **leaves extract**

Solution	Parameters						
	$R_t(\Omega \text{ cm}^2)$	C_{dl} (µ cm ²)		E_R %	-∆S Jmol ⁻¹ .K	ΔH KJmol ⁻¹	
blank	34.2	294.8	$- -$	$- -$	52.632	44.0076	
10 ppm					47.224	45.8647	
100 ppm	185.4	104.1	0.8156	82	36.063	49.5686	
1000 ppm	267.6	91.7	0.8718	87	16.04	56.3511	

Table 2. EIS data and adsorption parameters for FE164531 carbon steel in 2 M HCl solutions in the absence and presence of *D. mespiliformis* **leaves extract**

As the adsorption of the inhibitors at the metal/electrolyte interface increases, there was a gradual decrease in the parallel film capacitance (C_{dl}) and corrosion current values decreased indicating a decrease in local dielectric constant of the electrical double layer [8,31-33]. The inhibitor decreased the C_{d} values by replacing water molecules present at the electrode surface [34].

The low frequency impedance in the Bode plot continue to increase as the frequency drops, indicating a strong resistance to the flow of ions and electrons through the adsorbed film, hence preventing corrosion reaction. A capacitive behavior is indicated from medium to low frequencies by phase angles approaching 9°, suggesting that a weak adsorbed film is formed on FE164531 carbon steel in the 2 M HCl solutions which is consistent with physical adsorption.

3.3 Gasometric Technique

The gasometric measurement is based on the idea that the rate of hydrogen gas evolution in a corrosion reaction is directly proportional to the corrosion rate of the metal. This technique, apart from its experimental rapidity, ensures a more sensitive monitoring in situ of any perturbation by the inhibitor vis-a-vis hydrogen gas evolution on the metal-corrodent interphase [24]. The volume of H_2 evolved was observed to appreciably reduce in the presence of test inhibitors as compared to the free acid solution. Further reduction in the volume of $H₂$ evolved was observed as concentration of test inhibitor molecules increased. Fig. 5 reveals that the most remarkable reduction in the volume of H_2 evolved was observed with *D. mespiliformis* molecules at 1000 ppm with inhibition efficiency of the inhibitor at 83%. The inhibition efficiency of the inhibitor obtained from the hydrogen gas evolution measurements also increased with increase in inhibitor molecules concentration. The results obtained in the gasometric experiments are in

agreement with the trend reported for weight loss and electrochemical measurements [19]. When the surface coverage of the adsorbed inhibitor species increases, lateral reactions between inhibitor molecules may arise, thereby influencing inhibition efficiency. Attractive lateral interactions usually give rise to stronger adsorption hence higher inhibition efficiency [35]. This effect has been shown in cases of compounds containing long chain hydrocarbon because of attractive Van der Waals forces.

3.4 Weight Loss

FE164531 was found to corrode at an appreciable rate in 2 M HCl solution. Results obtained clearly show that ethanolic extract of *D. mespiliformis* leaves effectively retards corrosion rate of FE164531 carbon steel in 2 M HCl solution, indicating inhibition of the corrosion reaction. The weight loss data reveal the dependence of inhibition efficiency of *D. mespiliformis* on concentration and temperature. Fig. 6 shows variation of FE164531 corrosion rate with temperature in the absence and presence of *D. mespiliformis* molecules. Corrosion rate increased linearly with increase in temperature but decreased with increasing *D. mespiliformis* concentration in the acid solution. Fig. 7 shows inhibition efficiency (*EW%*) of *D. mespiliformis* leaves extract on FE164531 carbon steel in 2 M HCl solution. It is clear from the figure that increase in concentration of *D. mespiliformis* molecules for all tests performed at varying temperatures result a decrease in corrosion reaction rate indicating geometric blocking effect of *D. mespiliformis* extract at active corrosion sites [36]. The extract inhibits corrosion by controlling the redox reactions. In most of the cases, the nitrogen/oxygen atom present in the inhibitor molecules is easily protonated in acidic solution and converted into quaternary/oxonium ions [37]. These protonated species get adsorbed on the cathodic sites of the metal surface and decrease the hydrogen evolution hence retard metal dissolution.

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Inhibition efficiency of *D. mespiliformis* leaves extract depends on various factors including but not limited to corrosive strength of the environment, concentration of inhibitor molecules, any synergetic effects with other molecules present in the environment and flow effects [14,38]. Inhibition efficiency trend observed for FE164531 in 2 M HCl using *D. mespiliformis* at varying temperature is an indication of physical adsorption. The evaluated

inhibition efficiency had the optimum inhibition efficiency obtained at 68% for 303 K temperature with 1000 ppm inhibitor concentration. The fact that inhibition efficiency decreased with increasing temperature $(303 - 313K)$ signifies that the inhibitors function effectively at lower temperatures. It also indicates that the time lag for the adsorption and desorption of the inhibitor molecules on FE164531 surfaces become shorter at higher temperature.

Fig. 5. Variation of the volume of H₂ gas evolved with time for FE164531 carbon steel **corrosion in 2 M HCl solutions with and without different concentrations of** *D. mespiliformis* **leaves extract**

Fig. 6. Linear plot of FE164531 corrosion rate as a function of temperature in the absence and presence of *D. mespiliformis* **leaves extract**

Fig. 7. Inhibition efficiency as a function of *D. mespiliformis* **concentration for FE164531 carbon steel in 2 M HCl solutions at varying temperature obtained from weight loss results**

3.5 Effect of Temperature and Adsorption Consideration

Temperature investigation allows the determination of thermodynamic functions of annealed carbon steel in 2 M HCl with and without inhibitor. The obtained data were applied Langmuir adsorption isotherm which assumes that percentage area covered by the inhibitor is directly related to decrease in corrosion rate. The Langmuir adsorption isotherm was obtained from equation 11 [14].

$$
log\left(\frac{\theta}{1-\theta}\right) = logA + logC - \left(\frac{\Delta H_{ads}}{2.303RT}\right) \tag{11}
$$

herein, θ is the surface covered by inhibitor, *A* the temperature dependant constant, *C* is the bulk concentration of inhibitor, *∆Hads* the heat of adsorption. The heat of adsorption was calculated from slope of the plot of $log\left(\frac{\theta}{1-\theta}\right)$ vs $\frac{1}{T}$. Fig. 8 shows heat of adsorption plot for *D*. *mespiliformis* on carbon steel in 2 M HCl while *∆Hads* values are listed in Table 2. It can be observed from concentration at 1000 ppm has most positive value and 10 ppm has the least value of heat of adsorption supporting the fact that increase in concentration implies more stabilized adsorbed inhibitor molecule on the surface of FE164531. This could indicate that there was an increase in the adsorbable inhibitors on the metal surface as

concentration increased. It is clearly seen in Fig. 7 that increase in temperature undermined the integrity of the inhibitor which results to a decrease in inhibition efficiency. This decrease in *EW*% with temperature rise is due to desorption of the inhibitor molecules from the surface of FE164531, thus it can be said that the inhibitor molecules were physically adsorbed on the metal surface. The low positive value of ΔH_{ads} reveal that the process of adsorption of *D. mespiliformis* on carbon steel surface is an endothermic multilayer adsorption process.

The adsorption parameters are given in Table 2. The values of ΔH_{ads} increased with increasing inhibitor concentration indicating that the energy barrier of corrosion process increased and the activated complex is higher than that formed in the uninhibited solution. The positive sign of ΔH_{ads} show the endothermic nature of adsorption of *D. mespiliformis* on FE164531 carbon steel surface. The negative values of ΔS_{ads} pointed to a greater order produced during the process of activation. From Table 2, corrosion reaction control could be seen as cooperative effective, that is, ΔH_{ads} and ΔS_{ads} having opposite signs. These two variables could be additive in which the two variables are opposed but the enthalpy values which are larger results an enthalpycontrolled reaction effect [39]. The values of $\Delta S_{\rm ads}$ are higher for inhibited solutions than those for the uninhibited solution reflecting an increase in randomness on going from reactants to the

Fig. 8. Heat of adsorption plots as a function of temperature

activated complex. The increase in values of ∆S by the adsorption of *D. mespiliformis* on FE164531 carbon steel surface could be regarded as quasisubstitution between the inhibitors molecules in the aqueous phase and water molecules on electrode surface [40]. However, the adsorption of *D. mespiliformis* desorbs water molecules from the electrode surface, hence decreasing the surface reactivity of FE164531 carbon steel.

4. CONCLUSION

The presence of *D. mespiliformis* leaves extract in 2 M HCl solutions for FE164531 carbon steel corrosion inhibition remarkably shifted the values of E_{corr} to the less negative directions and decreased the values of *icorr*, while the values of *Rp* increased with increasing inhibitor molecule concentration. This effect is due to the fact that *D. mespiliformis* molecules decrease the severity of HCl solutions and increase the corrosion resistance of FE164531 carbon steel surface by adsorption. The increasing values of IE% obtained with increasing inhibitor concentration is attributed to greater adsorption of inhibitor molecules at active sites on FE164531 carbon steel surface, hence prevention of carbon steel oxides and chlorides formation. This was also confirmed by the agreement between the results gotten from the various methods employed. It is worth noting that the change in the concentration of inhibitor did not alter the profile of the impedance behavior suggesting similar

mechanism for the corrosion inhibition of pure carbon steel by inhibitor at various concentrations.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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