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Surface Equilibrium and Thermodynamics Implications of the Corrosion Inhibition of Mild Steel in Acid Medium Using Quinine Inhibitor

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Abstract

One problem faced by industries is the degradation of their metal pipes and machine parts which are exposed to chemically aggressive media. This has necessitated the search for cheap and non-toxic substances that can limit corrosion. The inhibition potential of quinine against the corroding of mild steel in 1M HCl medium was tested under varied concentration of quinine and temperature, using gravimetric method. The results showed that corrosion rate and weight loss decreased with increasing concentration of quinine and temperature up to 40 °C, while surface coverage, θ, and inhibition efficiency IE, increased as the concentration and temperature increased. Surface equilibrium studies showed that the inhibition action followed the Freundlich isotherm with value of adsorption intensity that suggests a cooperative adsorption mechanism in heterogeneous sites while thermodynamic analysis implied that the process of inhibition was endothermic having a positive value of ΔH (17.384 kJ mol^{-1}), enthalpy-driven with a negative ΔS (-64.434 kJ mol^{-1}K^{-1}) and occurred by a physisorption mechanism. Positive ΔG obtained at the studied temperatures suggests that the corrosion process was rendered passive and unfeasible. These findings project quinine as a promising inhibitor for chemical degradation of mild steel in hydrochloric acid medium.

Keywords: Quinine, Freundlich isotherm, inhibition, degradation.

INTRODUCTION

Corrosion is an unavoidable natural process whereby the metallic properties of certain alloys and metals are degraded, making them unsuitable for specific use. It is a major challenge to

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industries that make use of mild steel and other alloys for industrial pipes because some industrial activities necessitate exposure of metal pipes or alloys to an aggressive basic, acidic or salt medium (Rajendran and Karthikeyan, 2012). This leads to corrosion. Several measures have been adopted to limit the menace of corrosion in industrial fittings and using corrosion inhibitors appears to be top among the available options for shielding metal surfaces from corrosion.

The use of certain inhibitors has been criticised for their environmental toxic effect. Among the different types of inhibitors, organic compounds are advantageous as inhibitors because their structures contain heteroatoms and multiple bonds (Karthikeyan *et al.,* 2021).

However, drugs are recently being projected as being efficient, cheap and non-toxic inhibitors (Eddy and Odoemelam, 2009). Hence, it is suggested for replacing the toxic traditional inhibitors of corrosion (Mahdi, 2014). Drugs such as sulpha drugs, antibacterials, antifungals, and muscle relaxants, among others, have been reported to impact inhibitive effects on metals in acidic environments. (El-Naggar, 2007; Abdallah, 2004; Eddy *et al.*, 2018; Obot and Obi-Egbedi, 2010).

Akpan and Offiong (2013), investigated Ciprofloxacin and found it promising for inhibiting the corroding of mild steel in an acid environment. Its inhibitory performance was reported as being enhanced by an increase in its concentration and the process obeyed the first-order kinetics and complied with Langmuir isotherm. Pathak (2014) carried out a similar investigation using Trichloroethylene (TCE) as an inhibitor. The result portrayed TCE as being suitable for preventing mild steel from corroding while in an acid solution. The performance efficiency was 90.37 % as optimum and the process was compliant with the Langmuir, Flory-Huggins and Temkin adsorption isotherms. Also, the modazar drug was examined and reported 92.3 % efficient for inhibiting carbon steel from corroding in HCl acid while obeying the Langmuir isotherm. Again, the drug performance was enhanced when its concentration was increased; On the other hand, increasing the temperature of the system, reduced the inhibition efficiency.

In this work, quinine ($C_{20}H_{24}N_2O_2$), a popular but rather obsolete drug for malaria treatment and ingredient in tonic water that impacts a notable bitter taste (Olmsted and Williams, 1997), was tested for its inhibitory potential against the degradation of mild steel in HCl. Some research on corrosion inhibition using quinine as inhibitor has been reported, most of which only focused on kinetics and isotherm analysis of the process but not the thermodynamic implications. Therefore, this study is geared towards assessing quinine application in corrosion inhibition by analysing the thermodynamic implications as well as the adsorption mechanism through isotherm studies.

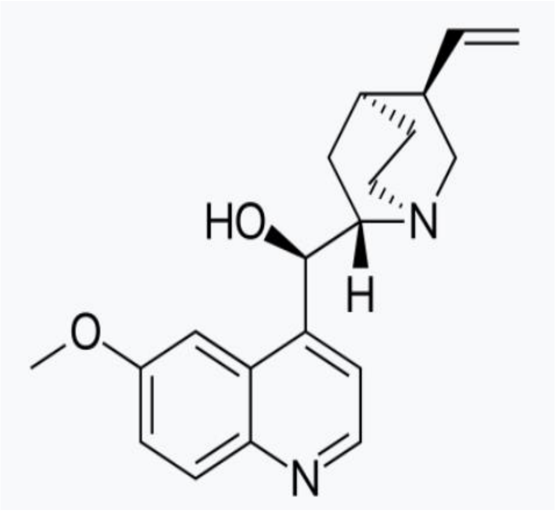

Fig. 1 Structural representation of quinine

MATERIALS AND METHODS

The equipment/apparatus used are: desiccators, wash bottles, conical flasks, thermometer, digital weighing balance, spatula, beaker, oven, tongs, mortar and pestle, measuring cylinder, and crucible. The reagents used were of analytical grade and include acetone, sodium hydroxide, hydrochloric acid and ethanol.

Preparation of the mild steel

Mild steel (MS) was obtained in a regular market in Abraka, a small town in Delta State, Nigeria. The sheets of metal were mechanically cut into different dimensions ranging from 4.5(±0.4) cm x 4.5 (±0.3) cm x 0.056 cm. A thread was tied through a small hole which was made on each coupon, by which the coupons could be held and suspended in the corrosive medium. The coupons were scrubbed with abrasive paper to remove surface contaminants. The surfaces were thereafter cleaned with absolute ethanol, washed with double-distilled water, degreased with acetone, and kept in desiccators before use.

Experimental procedures

Experimental procedures were carefully executed to ascertain how the quinine concentration and temperature affect the mild steel's weight loss, corrosion rate, surface coverage and inhibition efficiency, as follows:

Effect of inhibitor concentration

The weights of the prepared coupons were recorded after which they were immersed in 120 cm^3 of a 0.1 M HCl acid medium containing varying amounts (10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 mg) of quinine as the inhibitor, for 72 hours. The coupons were weighed again after washing and drying them. For the whole set of concentrations studied, there was a control (mild steel and acid without inhibitor) and a virgin (mild steel only, no inhibitor, no acid medium)

Effect of temperature

Weighed coupons were immersed in 120 cm^3 of the 0.1M HCl acid medium containing a fixed amount of the quinine and contacted for 6 hours in an incubator at varied temperatures of 15, 30, 35, 40, and 45 ^oC. The final weights were then recorded after washing and drying. For each temperature under study, there was a virgin, control, and duplicate sample.

Weight loss measurement and estimation of corrosion rate, surface coverage, and inhibition efficiency

The loss of weight in each case was gotten from the difference between the final and initial weights of the specimens thus:

$$\Delta W = W_i - W_f \text{……………………………………………………………(1)}$$

where ΔW is the weight loss, W_i is the initial weight and W_f is the final weight.
The corrosion rate was estimated from the equation (Akpan and Offiong, 2013);

$$CR = \frac{\Delta W}{A \times T} \text{…………………………………………………………………… (2)}$$

where CR is the corrosion rate ($gcm^{-2}\,hr^{-1}$), A is the area of the coupon in cm^2, and T, the time in hours (hr). The Surface coverage achieved by quinine was estimated as follows:

$$Surface\ coverage, \theta = \frac{CR_{blank} - CR_{inh}}{CR_{blank}} \text{ …………………………………….. (3)}$$

where CR_{inh} and CR_{blank} are the corrosion rates with and without inhibitor respectively.
Inhibition efficiency was estimated (Akpan and Offiong, 2013; Kumar and Karthikeyan (2012) as:

$$\text{Inhibition Efficiency} = \frac{CR_{blank} - CR_{inh}}{CR_{blank}} \times 100 \text{ … … … … … … … … … … … … … … …. (4)}$$

Adsorption Isotherm analysis

Adsorption isotherm analysis was done to identify the mechanism by which the quinine molecules were adsorbed at the MS surface, by fitting the extent of surface coverage, θ values, accordingly on the Langmuir and Freundlich isotherms to see which one best describes the adsorption mechanism. The model which has a correlation coefficient closest to unity would be the ideal applicable model.

Langmuir Isotherm

This isotherm can be represented as:

$$\frac{C}{\theta} = \frac{1}{K_L} + C \text{ -- (5)}$$

where C is the quinine concentration (gL^{-1}), θ the surface coverage, K_L, the Langmuir constant of the adsorption process. This model is expressed by the plot of C/θ vs C and the intercept is the reciprocal of K_L.

Freundlich Isotherm

The fitting of reversible and non-ideal adsorption, not restricted to monolayer formation can be done using the Freundlich isotherm as given in the equations below (Yaro *et al.*, 2013):

$$\theta = KC^n \text{ --- (6)}$$

$$\text{Log } \theta = \text{Log}K_f + n_f \text{Log } C \text{ -- (7)}$$

where K_f is the Freundlich equilibrium constant and n is the adsorption intensity. The K_f and n were obtained from the intercept and gradient respectively, of the plot of Log θ against Log C.

Thermodynamic parameters

Thermodynamic parameters including the activation energy, E_a, the heat of adsorption (ΔH), free energy change, (ΔG), and the entropy change (ΔS) are important in elucidating the inhibition thermodynamics. The activation energy E_a is obtained using the Arrhenius equation (10):

$$\text{Log CR} = \text{Log A} - \frac{\text{Ea}}{2.303RT} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (10)$$

where Ea is the apparent activation energy, R is the gas constant, T, the absolute temperature, and A, the frequency factor. A graph of Log CR vs 1/T is linear and its slope is equal to Ea/2.303R.

The Transition state equation may be used to obtain the ΔH and ΔS values (equation 11):

$$\text{Log}\left(\frac{CR}{T}\right) = \left[\text{Log}\left(\frac{R}{Nh}\right) + \frac{\Delta S^{o}}{2.303R}\right] - \frac{\Delta H^{o}}{2.303RT} \text{----------------------------------} \quad (11)$$

where h, N and R are Planck's constant (6.626176×10^{-34} Js), Avogadro's number (6.02×10^{23}), and gas constant (8.314 J $K^{-1}mol^{-1}$) respectively.

Plotting the Log of CR/T vs 1/T should be linear with a slope of $\frac{\Delta H^{o}}{2.303R}$ and intercept, [Log ($\frac{R}{Nh}$) +$\frac{\Delta S^{o}}{2.303R}$] from which, ΔH and ΔS can be estimated appropriately using the equation of the linear regression. Finally, the ΔG at all the temperatures studied may be calculated using the equation:

$$\Delta G^{0}_{ads} = \Delta H_{ads} - T\Delta S^{\circ}_{ads.} \text{---} \quad (12)$$

RESULT AND DISCUSSIONS

Surface Characteristics of the mild steel (MS)

SEM analysis was employed to observe any differences in the surfaces of the virgin MS, the MS contacted in HCl only and MS after contact with a mixture of 1 M HCl and 100 mg quinine inhibitor for six hours. The SEM micrographs are presented in Figure 2a-c. It is noticeable that the MS surface after contact with HCl only (Fig. 1b) was more corroded than that of the MS in HCl mixed with the inhibitor (1c). This confirms the fact that the quinine formed a layer of protection on the MS surface.

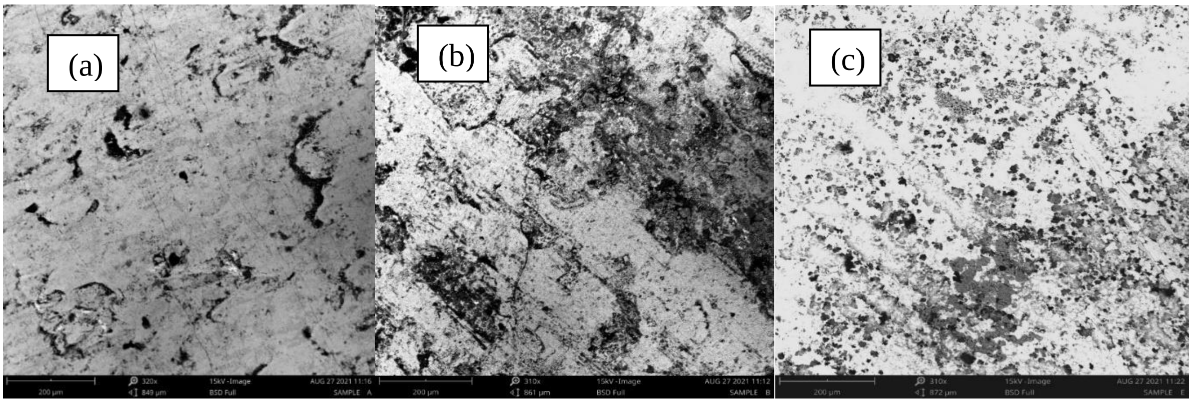

Fig. 2 SEM micrographs of (a) virgin mild steel (b) mild steel in 1M HCl acid (c) mild steel treated with quinine in 1 M HCl

Effect of quinine concentration on weight loss, corrosion rate, inhibitor efficiency, and surface coverage

The impact of quinine concentration on weight loss, corrosion rate, inhibitor efficiency, and surface coverage is displayed in Figures 3 a-d.

The inhibitor concentration was seen to impart a similar effect on weight loss and corrosion rate as seen in Figures 3 a and b. As the quinine concentration increased, the weight loss and corrosion rate declined. This shows that increasing inhibitor concentration, allowed more of the MS surface area to be protected from the attack of acid by the inhibitor. Hence, the decline in weight loss and corrosion rate. A similar trend is reported by Odewole *et al.*, 2021 and other researchers, which confirms that the concentration of inhibitor is crucial to the process. Increasing the inhibitor concentration also increased the surface coverage and inhibitor efficiency as shown in Figures 3 c and d. This suggests that the greater the amount of inhibitor present, the greater the surface coverage attained and the higher the inhibition efficiency. This aligns with the findings of Odewole *et al.*, (2021) and Karthikeyan *et al.*, (2021) who have studied the performances of drug inhibitors against MS corrosion in an acid medium.

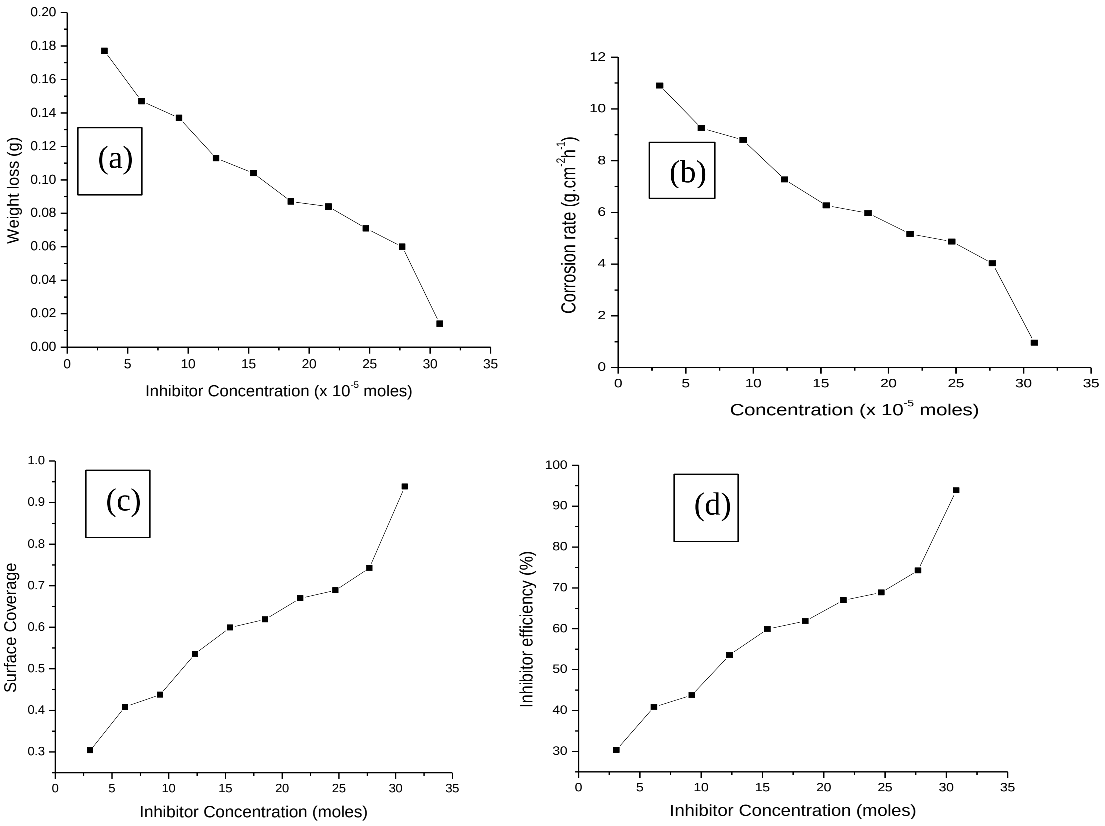

Fig. 3: The effect of quinine concentration on (a) weight loss (b) corrosion rate (c) surface coverage and (d) inhibition efficiency

Effect of temperature on corrosion rate (CR), inhibitor efficiency (IE), and surface coverage

The effect of temperature on the rate of corrosion of MS and inhibitor performance is very significant because bond rupture, decomposition or rearrangement of inhibitor molecules, surface etching and desorption may occur. (Ejikeme *et al.,* 2014; Mobin and Khan, 2013). At a constant concentration of an adsorptive inhibitor, varying the temperature will affect the level of metal dissolution. The CR and IE for MS alone and MS in acid at 15, 30, 35, 40 and 45 °C in the absence and presence of quinine inhibitor are summarized in Figure 4.

From Figure 4, CR in the virgin sample (MS alone without corrosive medium and inhibitor) is the least amongst the three test cases. However, the CR in the inhibited sample is less when compared with that of the blank (uninhibited). This is an indication that the quinine effectively protected the MS surface from absolute contact with the acid, thereby reducing the metal dissolution into the acid and consequently inhibiting the corrosion process.

From Figure 5, the IE increased as the temperature also increased from 15 °C to 40 °C and then declined when the temperature was further increased above 40 °C. This is likely because the temperature raise from 10 °C to 40 °C, increased the IE and is still within the optimum temperature range for the drug's activity. However, a further raise in temperature probably destroyed some of the quinine molecules or facilitated their dissolution into the acid hence the reduction of the fraction of the surface covered and consequently, reduced the efficiency of the inhibitor. This agrees with the report of Chukwueze *et al.,* 2020 and Odewole *et al.,* 2021 amongst others.

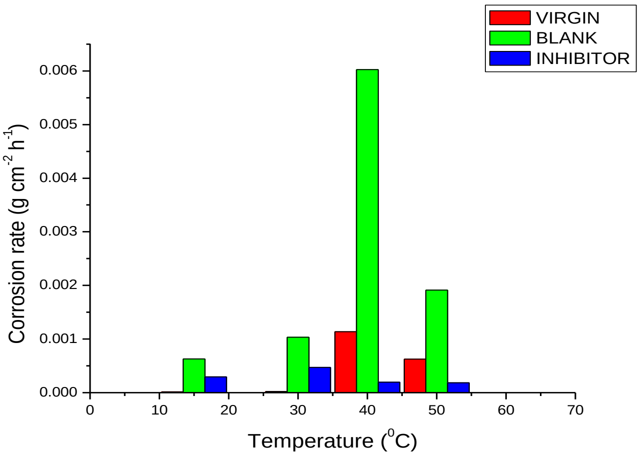

Fig. 4 Effect of temperature on the corrosion rate of virgin MS and MS without and with inhibitor

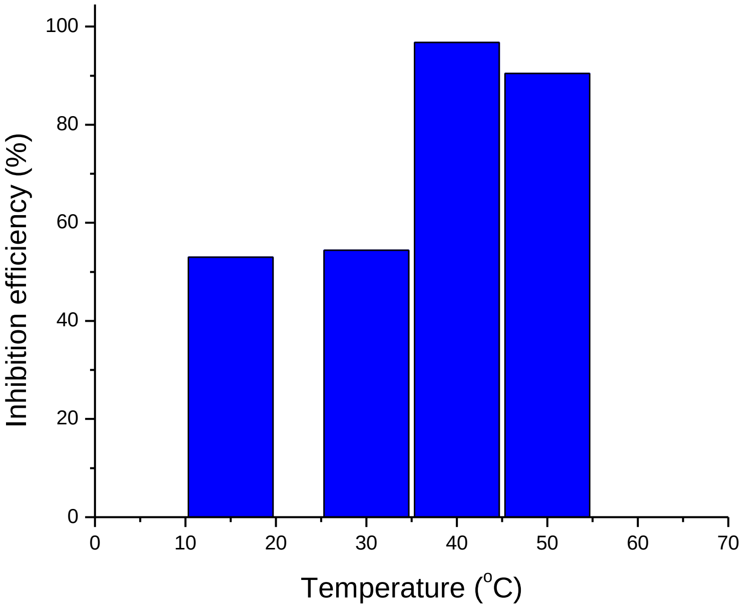

Fig. 5 Effect of temperature on the inhibition efficiency of quinine on mild steel degradation in HCl.

Adsorption Isotherm

Adsorption isotherms which were applied, to quantitatively express, the fraction of quinine molecules on the MS surface and those remaining in solution by fitting the degree of surface coverage (θ) values, are the Langmuir and the Freundlich isotherms.

The Langmuir Isotherm

A graph of C/θ vs C, was made and the correlation coefficient, R^2 of 0.94823 (Figure 6) indicates that this isotherm does not provide a very good description for the adsorption of quinine on MS. The implication of this is that the corrosion inhibition of MS in HCl by quinine is not exclusively monolayer as assumed by the Langmuir model. Therefore no further consideration was given to this model.

Freundlich Isotherm

The graph of log θ versus log C (Figure 7), shows an R^2 value of 0.97963 as an indicator that the Freundlich model gave a better fit than the Langmuir isotherm (R^2 value of 0.94823). This is consistent with the report of Odewole *et al.,* 2021. This infers that the inhibitor adsorbed on the MS must have been multi-layered and occurred in heterogeneous sites or sites that are exponentially different in energy.

The Freundlich constants Kf and n were estimated from the intercept and gradient respectively, of the plot of log θ versus log C (Figure 7) as 27.86 and 0.4386. The value of 1/n being greater than 1 infers that the inhibitor adsorption mechanism is that of a cooperative adsorption.

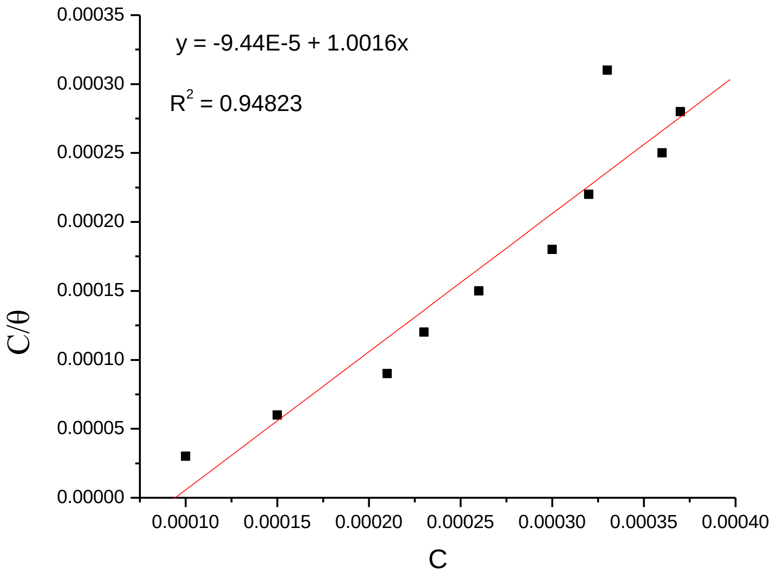

Fig. 6 Langmuir isotherm for corrosion inhibition of mild steel in 1M of HCl using quinine as inhibitor

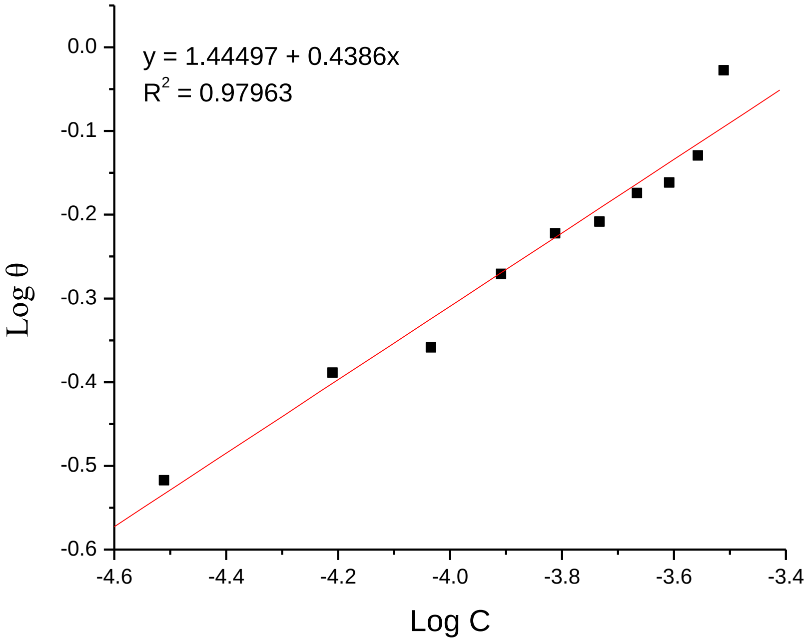

Fig. 7 Freundlich adsorption isotherm for inhibition of mild steel degradation in 1 M of HCl using quinine as an inhibitor

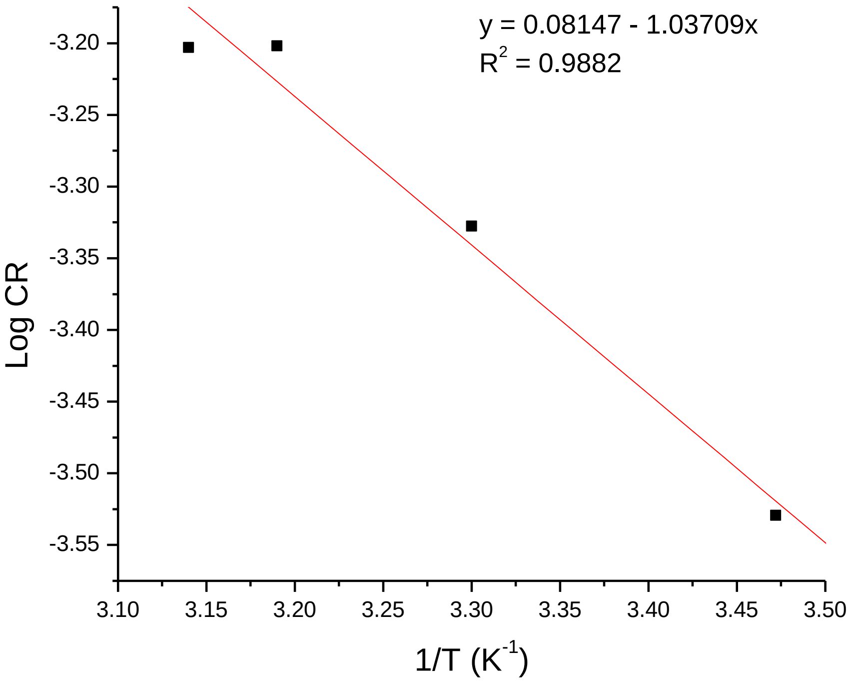

Fig. 8 Arrhenius plot for the inhibition of mild steel degradation in HCl with quinine as inhibitor

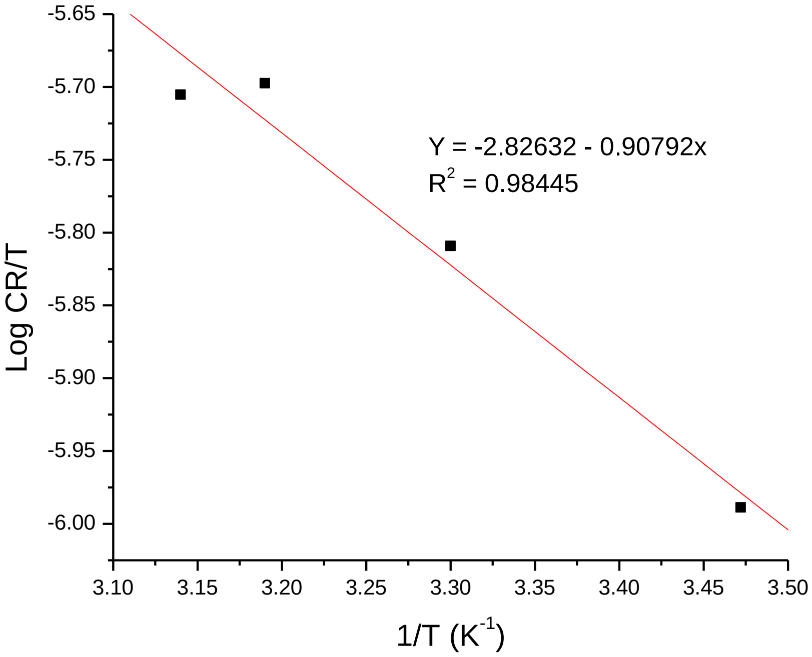

Fig. 9 Transition State plot for the inhibition of mild steel degradation in acid with 100 mg of quinine as the inhibitor

Thermodynamic implication for the process

Thermodynamic parameters (ΔH, E_a, ΔS and ΔG) were estimated to fully describe the thermodynamic implications of the inhibition process. The activation energy, E_a was calculated to be 19.86 kJ mol^{-1}, from the gradient of the graph of log CR against 1/T (Figure 8) as earlier described. Also, the value of enthalpy change, ΔH of 17.384 kJ mol^{-1} was estimated from the gradient of the plot of log CR/T against 1/T (Figure 9). This depicts an endothermic inhibition process whereby heat is absorbed from the surroundings to form new bonds between the quinine and the acid to render it passive and protect the MS surface from acid attack. It is interesting to note that while corrosion is generally exothermic, the inhibition of the degradation of MS in HCl by quinine inhibitor is endothermic. Furthermore, ΔH value shows that the mechanism is that of physisorption. Generally, when the value of ΔH is ≤20 kJ/mol, then electrostatic interaction (physisorption) between the quinine molecules and the charged metal is suspected (Odewole *et al.*, 2021 and Solmaz, 2014). However, when ΔH is ≥40 kJ/mol, it is likely a chemisorption mechanism where an electron is shared or transferred from the inhibitor (quinine) molecules to the metal surface forming a coordinate bond.

A negative entropy change, ΔS (-64.434 kJ mol^{-1}K^{-1}) gotten from the intercept of log CR/T vs 1/T, in accordance with the method described earlier, suggests a decline in the randomness of the corrosion process itself, which is another indicator that the quinine effectively inhibited the corrosion.

The positive values of ΔG (Table 1) suggest that the process of corrosion has been rendered non-spontaneous and thermodynamically unfavourable. Therefore, the inhibition process would need energy to happen since it is endergonic.

Table 1. Thermodynamic parameters for inhibition of MS corrosion in HCl medium.

T (K)	ΔS (kJ $mol^{-1}K^{-1}$)	ΔH (kJ/mol)	ΔG (kJ/mol)
288	-64.434	17.384	18574.376
303			19540.886
313			20185.226
323			20507.396

CONCLUSION

This study has proved quinine, a suitable inhibitor against mild steel degradation in an acid environment. The process was influenced by temperature and quinine concentration. The inhibition potential increased when the inhibitor (quinine) concentration was increased from 10 mg to 100 mg, and when the temperature was raised from 10 °C to 40 °C. The isotherm studies revealed the Freundlich isotherm as being suitable to describe the mode of the quinine, while thermodynamic studies implied an endothermic process, non-spontaneity of the corrosion with a low positive value of heat of adsorption which is suggestive of a physisorption mechanism.

Conflict of interest

The authors herein declare no conflicting interests.

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