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Research paper

Corrosion inhibition of carbon steel in perchloric acid by potassium iodide

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Abstract

Corrosion processes are responsible for numerous losses mainly in the industrial scope. It is clear that the best way to combat it is prevention. The effect of temperature on the corrosion behavior of carbon steel was studied by mass loss measurements in the temperature range 293–333 K. The inhibition efficiency increases with increasing temperature. The inhibitor showed 97.98 % inhibition efficiency at 1.10^{-3} M concentration of iodide potassium in 1 M perchloric acid solutions. The values of activation energy (E_a), enthalpy of activation (ΔH_a) and entropy of activation (ΔS_a), free energy of adsorption (ΔG_{ads}), enthalpy of adsorption (ΔH_{ads}) and entropy of adsorption (ΔS_{ads}) were calculated. The adsorption of this inhibitor on carbon steel surface obeys Langmuir adsorption isotherm.

Keywords: *Corrosion Inhibition; Carbon Steel; Potassium Iodide; Weight Loss; Adsorption Isotherm*.

1. Introduction

Carbon steels are the most commonly used construction materials and corrosion phenomena has become important particularly in acidic media because its employability are increased. Strong acids are widely used in industries for many purposes, especially in cleaning, descaling, pickling procedures, Oil Well acidizing and other applications isotherm (Abd El–Maksoud 2008). Therefore, protective measures should be required to reduce the corrosion rate in acids by using chemical and other means, among the different methods use of inhibitors is most commonly and economical (Al-Otaibi et al. 2014). A corrosion inhibitor is a chemical substance which, when added in small concentrations to an environment, minimizes or prevents corrosion (Riggs 1973; Uhlig et al. 1985). Inhibitors had great acceptance in the industries due to excellent anti-corrosive proprieties. The inhibition efficiency depends on the various parameters, corrosive medium, pH, temperature, duration of immersion, metal composition and on the nature of the inhibitor (Loto et al. 2012; Attar et al. 2014). Adsorption isotherms provide information about the interaction of the adsorbed molecules with the electrode surface (Bereket et al. 2002; attar et al. 2014). The adsorption of the inhibitors can be described by two main types of interaction: Physisorption and/or chemisorption (Xiumei et al. 2012; Zarrok et al. 2012): One is physical adsorption, which involves electrostatic forces between ionic charges or dipoles on the adsorbed species and the electric charge at the metal/solution interface. The heat of adsorption is low and therefore this type of adsorption is stable only at relatively low temperatures. The other is chemical adsorption, which involves charge transfer or sharing from the inhibitor molecules to the metal surface to form a coordinate type bond. This type of adsorption is known to have much stronger adsorption energy compared to the other mode of adsorption. Thus, such bond is more stable at higher temperatures. The weight loss method (gravimetric) is known to be the most widely used method of monitoring inhibition efficiency (Obot et al. 2010).
The aim of the present work is to study the inhibition efficiency of iodide potassium for the corrosion of carbon steel in perchloric acid medium 1M and to evaluate thermodynamic parameters of corrosion inhibition process for the adsorption of inhibitor on carbon steel metal surface.

2. Experimental

2.1. Material preparation

The test solutions of 1 M of Perchloric acid were prepared by the dilution of analytical grade 72% $HClO_4$ with bi-distilled water in 50 mL. Steel XC38 containing in wt. %: 0.37 C, 0.68 Mn, 0.077 Cr, 0.059 Ni, 0.023 Si, 0.016 S, 0.011 Ti, 0.009 Co, 0.16 Cu, and iron is the remainder. The electrode was polished using different grades of emery papers after be polished, degreased and weighed. Each specimen was weighed using an analytical balance of 0.0001 g accuracy. All experiments are in triplicates and illustrated data are mean values of obtained results.

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3. Results and discussion

3.1. Effect of immersion time

The weight loss measurements were performed in 1 M $HClO_4$ in absence and presence of KI at 10^{-3} M concentration for 30 min to 24 h immersion time at temperature of 303 K.
The inhibition efficiency (IE%) of potassium iodide was calculated using the formula (1).

$$IE(\%)=100*(W_{corr}-W_{inh})/W_{corr} \quad (1)$$

Where W_{corr} and W_{inh} are the corrosion rates of carbon steel samples in the absence and presence of potassium iodide compound, respectively.
The corrosion rate (w) was calculated from the formula (2):

$$W = (m_1-m_2)/S.t \quad (2)$$

Where m_1 is the mass of the specimen before corrosion, m_2 the mass of the specimen after immersion in solution, S the total area of the specimen and t the corrosion.
The variation of the inhibition efficiency of this inhibitor is almost constant from the first 60 minutes of immersion, which allowed us to say that the immersion time has no significant effect on the corrosion inhibition of carbon steel in M $HClO_4$, is shown in Figure 1. The weight loss of carbon steel is nearly varied linearly with immersion period in the absence and presence of inhibitor as seen in Figure 2.

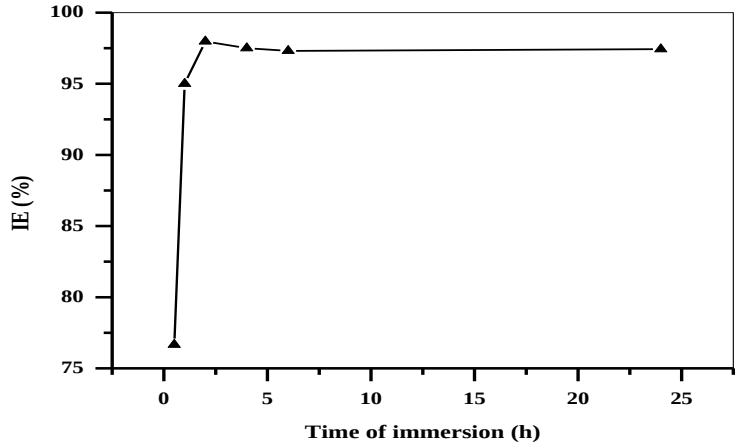


Fig. 1: Variation of the Inhibition Efficiency with Immersion Time for Carbon Steel 1M $HClO_4$ Containing 10^{-3}M of KI at 303 K.

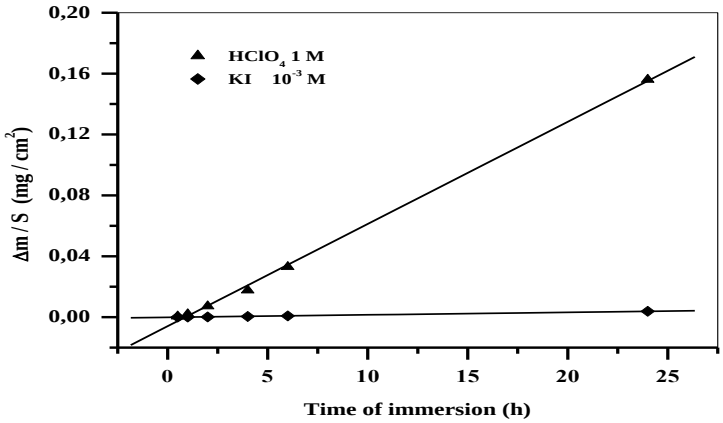


Fig. 2: Weight Loss Versus Immersion Time of XC38 in 1 M $HClO_4$ Without and with 10^{-3} M of KI at 303 K.

3.2. Effect of temperature

The effect of temperature on the inhibition effectiveness at various concentration of potassium iodide was studied in the temperature domain (293–333 K) at 2 h of immersion. The values of inhibition efficiency and corrosion rate obtained from weight loss method are showed in figure 3 and 4.

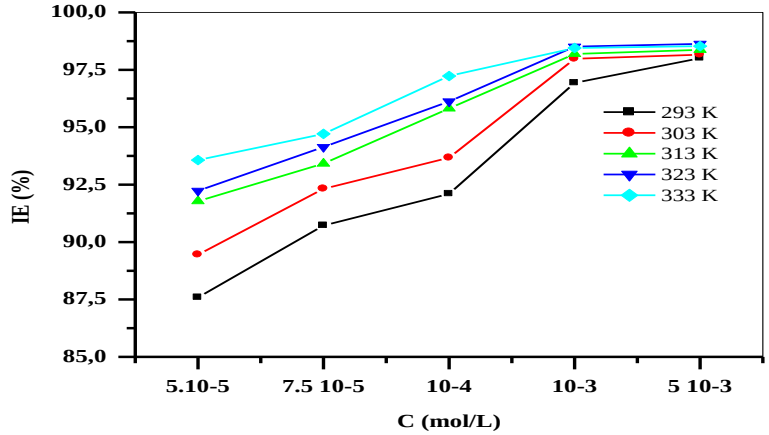


Fig. 3: Variation of Inhibition Efficiency (IE%) with Concentration of KI for Carbon Steel in 1 M $HClO_4$ at Different Temperatures.

The inhibition was estimated to be superior to 87.59 %, even at concentrations as low as 5 10^{-5} M, and the maximum efficiency of 97.98 % was recorded at 10^{-3} M. The same study was carried out in the Hydrochloric acid where the maximum efficiency at 10^{-3} M, was 59.37% and 6.25 % at low concentration (5 10^{-5} M) (Benchadli et al. 2018). From the graph it is evident that the concentration change had only marginal influence on inhibition efficiency. It was also observed that corrosion rate decreased with increase in inhibitor concentration.

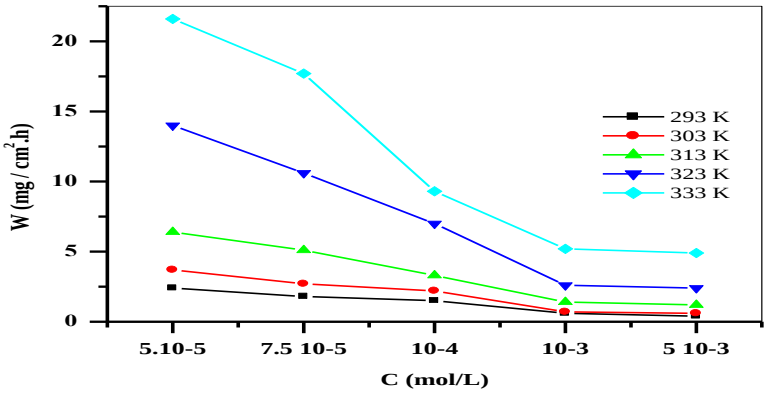


Fig. 4: Variation of Corrosion Rate with the Concentrations of KI for Carbon Steel in 1 M $HClO_4$ at Different Temperatures.

The study of the effect of temperature on the inhibition efficiency and corrosion rate facilitates the calculation of kinetic and thermodynamic parameters for the inhibition and the adsorption processes.

3.3. Thermodynamic parameters and adsorption isotherm

The adsorption is also influenced by the structure and the charge of the metal surface, and the type of testing electrolyte (Obot et al. 2009). In acid environment, the inhibitor acts generally by chemisorption and/or physical adsorption at the metal surface (Elmsellem et al. 2014). The inhibition of the corrosion of carbon steel in 1 M $HClO_4$ medium acid with addition of different concentrations of potassium iodide can be explained by the adsorption of the iodide ions on the metal surface. Inhibition efficiency was directly proportional to the fraction of the surface covered by the adsorbed molecules (θ). The values of the degree of surface coverage were evaluated at different concentrations of the inhibitors.
The degree of surface coverage (θ) was calculated using following equation (3):

$$\theta = 1-(w_{inh}/w_{corr}) \quad (3)$$

The Langmuir adsorption isotherm plot for the adsorption of various concentrations of the inhibitor was shown in Figure 5. According to the Langmuir isotherm model (Benabdellah et al. 2006).

$$C_{inh}/\theta = C_{inh} + 1/K_{ads} \quad (4)$$

Where K_{ads} is the equilibrium constant of the equilibrium adsorption process. This isotherm assumes that adsorbed molecule occupies only one site and it does not interact with other adsorbed species (Abdel Hameed et al. 2011). The linear regression parameters between C_{inh}/θ and C_{inh} are listed in Table 1. The strong correlation (R^2=1) showed that the adsorption of the inhibitor molecules in 1M $HClO_4$ acid on the surface of electrode obeyed to the Langmuir's adsorption isotherm (Tang et al. 2003).

Table 1: Thermodynamic Parameters for the Adsorption of KI in $HClO_4$ Solution on Carbon Steel Electrodes at Different Temperatures.

T (K)	R^2	$10^4 x K_{ads}$ (L/mol)	ΔH_{ads} (KJ/mol)	ΔG_{ads} (KJ/mol)	ΔS_{ads} (J/mol K)
293	1	12.966		-38,462	213.160
303	1	22.167	23.994 (eq.6)	-41,125	214.914
313	1	30.181		-43,286	214.952
323	1	33.240		-44,928	213.380
333	1	46.042	23,730 (eq.7)	-47,221	213.858

It can be observed that K_{ads} values increase with the increasing temperature. The high values of K_{ads} suggest that interaction between adsorbed molecules and the metal surface is strong, indicating that the inhibitor molecules are not easily removable from the surface by the solvent molecules (Desimone et al. 2011).
Adsorption equilibrium constant (K_{ads}) and free energy of adsorption (ΔG_{ads}) were calculated using the following relationship (Fekry et al. 2010):

$$\Delta G_{ads} = -RT\ln (55.5\ K_{ads}) \quad (5)$$

Where, 55.5 is the concentration of water in solution in mol/L and R is the universal gas constant and T is the absolute temperature.

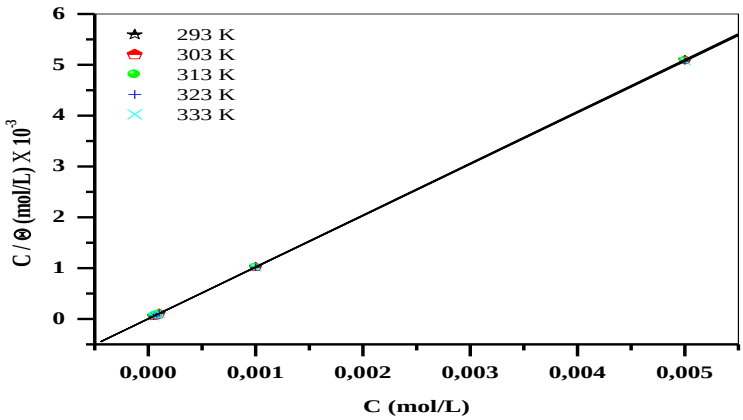


Fig. 5: Relationship between C_{inh}/Θ and Inhibitor Concentration C_{inh}.

To obtain the adsorption heat (ΔH_{ads}), the regression between Ln (K_{ads}) and 1/T (Figure 6) was dealt with and straight line obtained with slope equal to ($-\Delta H_{ads}/R$). The adsorption heat could be calculated according to theVan't Hoff equation (Tang et al. 2003).

$$\ln K_{ads} = (-\Delta H_{ads}/RT) + Const \quad (6)$$

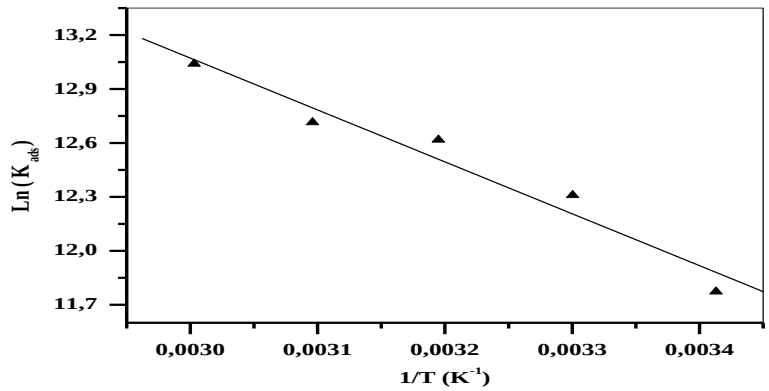


Fig. 6: Relationship between Ln (K_{ads}) and 1/T for Carbon Steel Corrosion in 1M $HClO_4$ Solution with Potassium Iodide.

Generally, the values of adsorptive free enthalpy up to - 20 kJ/mol are consistent with the electrostatic interaction between the charged molecules and the charged metal (physisorption), while those negative values higher than - 40 kJ/mol involve sharing or transfer of electrons from the inhibitors to the metal surface to form a coordinate type of bond (chemisorption) (Bensajjay et al. 2003).

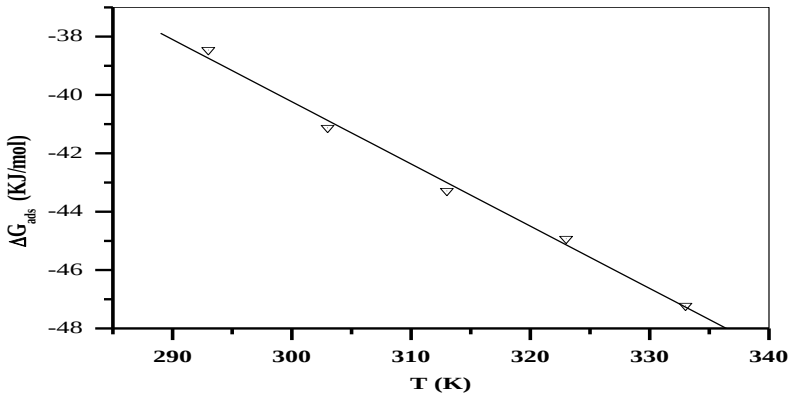


Fig. 7: Relationship between ΔG_{ads} and Absolute Temperature.

ΔG_{ads} is related to the enthalpy change and entropy change of adsorption process, ΔH_{ads} and ΔS_{ads}, respectively by Gibbs equation

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads} \quad (7)$$

Using the obtained values of ΔG_{ads} from the modified Langmuir isotherm, we can plot ΔG_{ads} versus T (Fig. 7). These plots give straight lines with slopes ($-\Delta S_{ads}$) and intercepts (ΔH_{ads}) (Hassan et al. 2007). The endothermic adsorption process ($\Delta H_{ads} > 0$) is attributed unequivocally to chemisorption (Durnie et al. 1997). In the present case, the positive values of the enthalpy of adsorption indicate that the adsorption of the tested compounds is an endothermic process. The magnitude of ΔG_{ads} values obtained from weight loss measurements was in the range of -38 to -47 kJ/mol which also shows chemisorptions of the inhibitor. Moreover the ΔG_{ads} values increase with increasing temperature, which is due to the fact of strong chemisorption at higher temperatures. ΔS_{ads}=213.21 J/mol.K found by Gibbs equation. The value of ΔS_{ads} is positive in the adsorption process indicating that the presence of inhibitor increases the solvent entropy (Hameed et al. 2011). The value of the enthalpy and entropy of adsorption found by the two methods such as Van't Hoff and Gibbs relations are in good agreement.

3.4. Kinetic parameters of activation

The Arrhenius equation is employed to study the effect of temperature on the rate of corrosion of carbon steel in acid media containing various concentrations of inhibitor as expressed by equation (8) (Singh et al. 2012; Attar et al. 2014).

$$w = A + \exp(-E_a / RT) \quad (8)$$

Where w is the corrosion rate of carbon steel, A is Arrhenius pre-exponential factor, E_a is the activation energy, R is the gas constant and T is the temperature

The activation energy (E_a) at different concentrations of the inhibitor at various temperatures was determined by plotting ln(w) Versus 1/T (Figure 8).

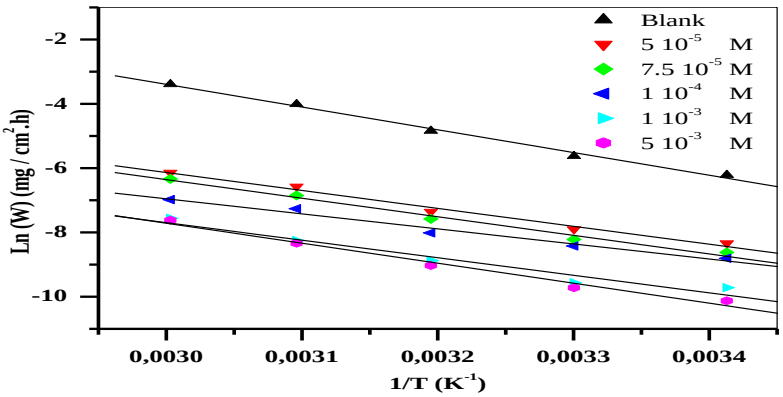


Fig. 8: Arrhenius Plot for the Dissolution of Carbon Steel in 1 M $HClO_4$ with and Without Inhibitor at Various Temperatures.

The enthalpy and entropy of activation for the metal dissolution process are determined using the transition state Eq. (9)

$$\ln(w/T) = - \Delta H_a/RT + \ln(RT/Nh)+(\Delta S_a/R) \quad (9)$$

Where h is Plank's constant and N is Avogadro's number R is the universal gas constant, ΔH is the enthalpy of activation and ΔS is the entropy of activation. A plot of ln(w/T) versus 1/T gave a straight line (Figure. 9) with slope ($-\Delta H_a/R$) and intercept [$\ln(R/Nh) + (\Delta S_a/R$] From the plot, the values of ΔH_a and ΔS_a were calculated and tabulated in Table 3, (Correlation (R^2>0.98).

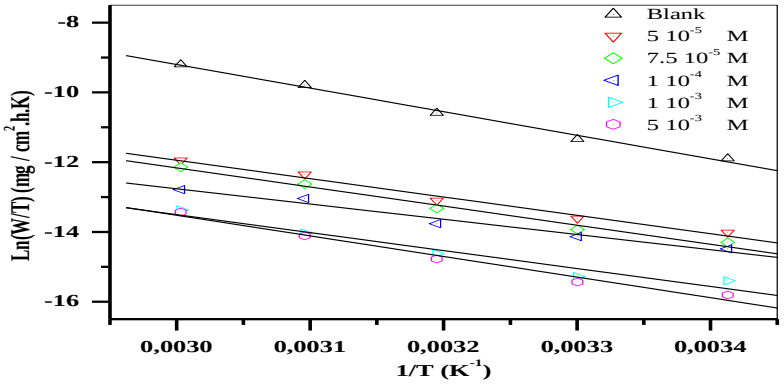


Fig. 9: Transition Arrhenius Plots of Carbon Steel in 1 M $HClO_4$ with and without Inhibitor at Various Temperatures.

Table 2: Activation Parameters for the Carbon Steel Dissolution in 1 M $HClO_4$ in Absence and Presence of Different Concentrations of KI

C_{Inh} (M)	E_a (KJ/mol)	ΔH_a (KJ/mol)	ΔS_a (J/mol.K)	ΔH_{a313K}($=E_a$-RT KJ/mol)	$\Delta G_{a\ 313\ K}$ (KJ/mol)
0.0	58.794	56.200	-105,437	56.191	89.201
5 10^{-5}	46.338	43.743	-165,622	43.785	95.582
7.5 10^{-5}	48.053	45.459	-162,304	45.450	96.260
10^{-4}	38.914	36.320	-194,688	36.311	97.257
10^{-3}	45.376	42.782	-181,468	42.773	99.581
5 10^{-3}	51.689	49.095	-162,677	49.086	100.012

Further, the values ΔH_a obtained from the Eq. (9) and those values obtained from equation, $\Delta H=E_a$-RT are in good agreement with each other.
The change in activation free energy (ΔG_a) of the corrosion process can be calculated at each temperature by applying the equation:

$$\Delta G_a = \Delta H_a - T\Delta S_a \quad (10)$$

The values of the apparent activation energy E_a for the inhibited solutions are lower than that for the uninhibited one, indicating a chemisorption process of adsorption (Dehri et al. 2006). The positive sign of the enthalpies ΔH_a reflects the endothermic nature of the steel dissolution process and that mean the dissolution of steel is difficult (Mohamed et al. 2015). The negative values of ΔS_a in the inhibited and uninhibited systems imply that activation complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease disorder takes place on going from reactants to the activated complex (Abd El-Rehim et al. 2001). In corrosion context, the activation Gibbs free energy is the excess energy needed to transform metal atoms at the metal surface into solvated metal ions (David et al. 2010).

4. Conclusion

On the basis of the experimental results obtained in the present study, the following conclusions can be drawn.

- The protection efficiency of the inhibitor depends on its concentration, immersion time and temperature.
- The efficiency (IE%) increase with increasing concentration and temperature.
- The corrosion process was inhibited by adsorption of the inhibitor molecule on the carbon steel surface.
- Adsorption of inhibitor on carbon steel surface from 1 M $HClO_4$ obeys Langmuir adsorption isotherm.
- The negative values of ΔG_{ads} showed the spontaneity of the adsorption.
- The inhibitor molecules adsorbed on the surface of carbon steel through chemisorption adsorption.

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