

Sildenafil citrate (Viagra) as a corrosion inhibitor for carbon steel in hydrochloric acid solutions

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Abstract The inhibition effect of sildenafil citrate (Viagra) on the corrosion of carbon steel in 1 M HCl was studied by weight loss, polarization, electrochemical impedance spectroscopy, and UV–Vis spectrophotometry. The results showed that sildenafil citrate is a good corrosion inhibitor for carbon steel in acidic media and acts as mixed type (cathodic/anodic) inhibitor. The adsorption of the inhibitor was well described by the Langmuir adsorption isotherm. Some thermodynamic parameters such as adsorption heat, adsorption entropy, and adsorption free energy were calculated. Kinetic parameters such as the apparent activation energy and pre-exponential factor were calculated and discussed.

Keywords Sildenafil citrate · Carbon steel · Inhibition · Corrosion inhibitor

Introduction

Inhibition of carbon steel is a matter of theoretical and practical importance [1]. Hydrochloric acid is generally used as a pickling acid for steel. Its function is to remove undesirable oxide coatings and corrosion products. Corrosion inhibitors used in acid treatment solutions significantly reduce the overall and local pickling attack and the hydrogen absorption of steel strips. The inhibitors are

extremely effective even in very small concentrations. At the same time, the lower iron dissolution leads to a considerable prolongation of the lifetime of the steel structures, and the acid consumption is reduced.

The investigation of more environmentally acceptable corrosion inhibitors is of great practical interest. Recently many attempts have been made to replace the environmentally unfavorable inorganic compounds by ecologically more attractive alternatives. Among the alternative corrosion inhibitors, organic compounds containing polar functions with nitrogen, oxygen, or sulfur atoms as well as heterocycles containing conjugated double bonds have been reported as effective inhibitors of carbon steel corrosion in acidic media [2–8]. The inhibition property of these compounds is attributed to their molecular structure. The planarity and the lone electron pairs in the heteroatoms are important features that determine the adsorption of these molecules on metallic surfaces in acid solutions, where they slow down the cathodic reaction as well as the anodic process of dissolution of the metal. This effect is obtained by forming a diffusion barrier or by blocking the reaction sites and thereby reducing the corrosion rate [9].

The aim of this work was to study the inhibiting action of sildenafil citrate (Fig. 1) on the corrosion behavior of carbon steel (type L-52) used in petroleum pipelines (Egypt) in 1 M HCl solutions at five levels of inhibitor concentrations and three different temperatures. Corrosion inhibition was investigated using weight loss and galvanostatic polarization methods (Tafel) and their results were compared. The thermodynamic parameters of dissolution and adsorption processes were calculated using weight loss behavior. Carbon steel samples and their solutions before and after immersion were analyzed by scanning electron microscopy and UV–Vis spectrophotometry for further confirmation.

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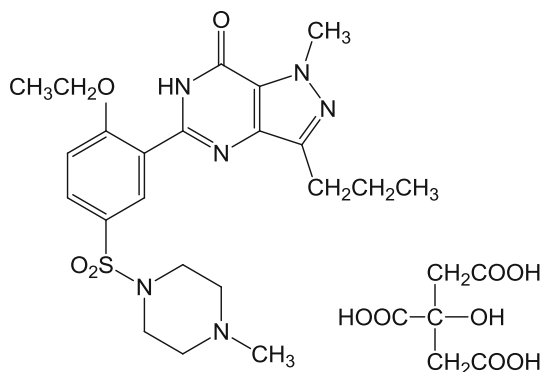


Fig. 1 Chemical formula of sildenafil citrate

Results and discussion

Weight loss studies

The corrosion of carbon steel in 1 M HCl in the absence and presence of various concentrations (5×10^{-6} to 5×10^{-3} M) of sildenafil citrate was studied by weight loss experiments. The corrosion rate (R_{corr}) and the percentage protection efficiency IE (%) were calculated according to the following equations [10, 11]:

$$R_{\text{corr}} = \frac{\Delta m}{St} \quad (1)$$

$$\text{IE}(\%) = \frac{w_0 - w}{w_0} \quad (2)$$

where Δm (mg) is the mass loss, S (cm^2) is the area, t (h) is the immersion period, and w_0 ($\text{mg cm}^{-2} \text{ h}$) and w ($\text{mg cm}^{-2} \text{ h}$) are the corrosion rates of mild steel without and with the inhibitor, respectively. The values of inhibition efficiencies and corrosion rates obtained from gravimetric measurements with the addition of different concentrations of sildenafil citrate after 24 h immersion in 1 M HCl solutions at various temperatures are summarized in Table 1. The addition of this compound inhibits the acid corrosion of steel at all concentrations used in this study. The inhibition efficiency increases with the increase in concentration. The optimum concentration for maximum efficiency was found to be 5×10^{-3} M. At the optimum

concentration, the efficiency attains 98.1% at 20 °C. A further increase of inhibitor concentration does not significantly change the protective effect.

The corrosion inhibition can be attributed to the adsorption of the inhibitor at the steel/acid solution interface. The ability of the molecule to chemisorb on the steel surface was dependent on the heteroatoms and the electron density on these atoms [12]. The high inhibitive efficiency is due to the bonding of (adsorbed) sildenafil citrate onto the metal surface; the strong bonding is mainly attributed to higher electron densities at active functional groups present in the adsorbate molecule.

Adsorption isotherm

Since the corrosion inhibition process is based on the adsorption of the inhibitor molecules on the metal surface, the degree of surface coverage (θ) for different concentrations of sildenafil citrate at different temperatures was evaluated by the weight loss method by using the following equation [13]:

$$\theta = \frac{w_0 - w}{w_0} \quad (3)$$

where w and w_0 are the corrosion rates in the presence and absence of inhibitor, respectively. It can be seen that the values of surface coverage increased with increasing inhibitor concentration as a result of more inhibitor molecules being adsorbed on the steel surface.

It is essential to know the mode of adsorption and the adsorption isotherm that fits the experimental results. The most frequently used adsorption isotherms are Langmuir, Temkin, and Frumkin with the following general formula:

$$f(\theta, x) \exp(-2a\theta) = KC \quad (4)$$

Plots of the data for each isotherm showed that the adsorption of the investigated compound agreed with the Langmuir isotherm given below [14]:

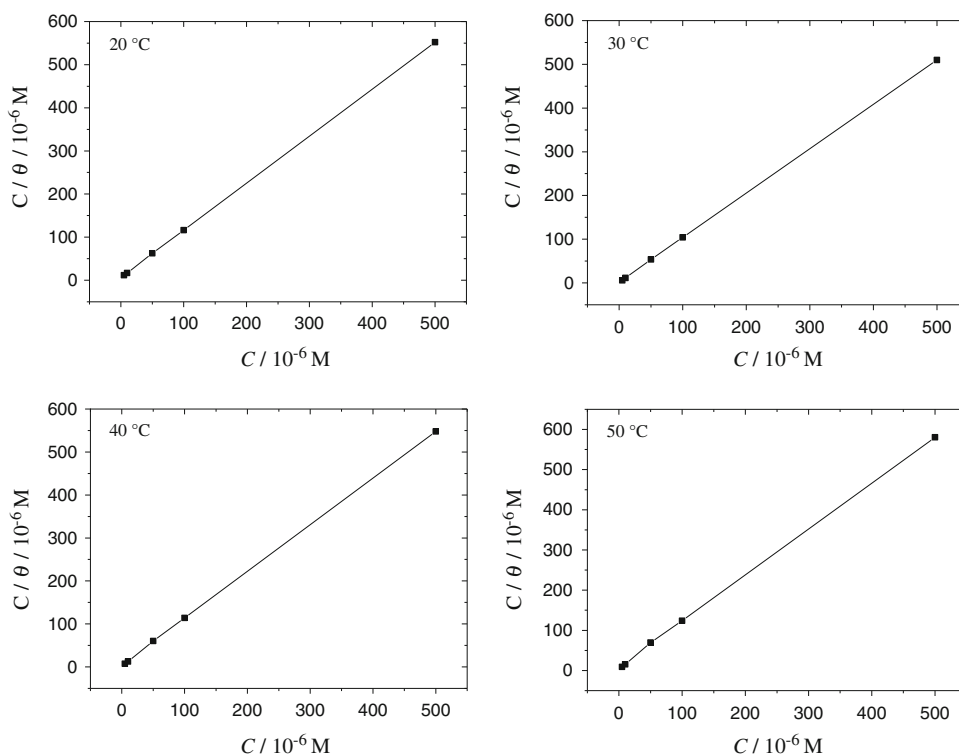
$$\frac{C}{\theta} = \frac{1}{K} + C \quad (5)$$

where K is the adsorption equilibrium constant and θ is the surface coverage. The linear regressions between C/θ and

Table 1 Corrosion rate of carbon steel and inhibition efficiency obtained from weight loss in the absence and presence of different concentrations of sildenafil citrate in 1 M HCl at different temperatures

Inhibitor concentration/M	Corrosion rate/ $10^{-3} \text{ mg cm}^{-2} \text{ h}^{-1}$				Inhibition efficiency/IE %			
	20 °C	30 °C	40 °C	50 °C	20 °C	30 °C	40 °C	50 °C
HCl (1 M)	136	210	780	940				
5×10^{-6}	21.4	42	246	425	84.3	80	68.5	54.8
1×10^{-5}	15	32	152	322	88.9	84.7	80.5	65.8
5×10^{-5}	9.8	22	132	263	92.8	89.5	83.1	72.1
1×10^{-4}	5.2	14	96	180	96.2	93.4	87.7	80.9
5×10^{-4}	2.6	8	68	130	98.1	96.2	91.3	86.2

Fig. 2 Relation between C/θ (10^{-6} M) and C (10^{-6} M) at different temperatures



C for each temperature over the concentration range 5×10^{-6} to 5×10^{-3} M are drawn in Fig. 2 and the parameters are listed in Table 2. The results show that all the linear correlation coefficients and all the slopes are close to one and confirm that the adsorption of sildenafil citrate in 1 M HCl follows the Langmuir adsorption isotherm [10, 15]. A considerable deviation of the slopes from unity shows that the isotherm cannot be strictly applied. This deviation is attributable to interaction between adsorbate species on the metal surface [16].

A modified Langmuir adsorption isotherm [17, 18] could be applied to this phenomenon, which is given by the corrected following equation:

$$\frac{C}{\theta} = \frac{1}{K} + nC \quad (6)$$

The adsorption coefficient K decreases with an increase in experimental temperature (Table 2), indicating that the interactions between the adsorbed molecules and the metal surface are weakened and, consequently, the adsorbed

molecules become easily removable. Such data explain the decrease in the protection efficiency with increasing temperature.

Thermodynamic parameters

The fundamental thermodynamic functions are very important to explain the adsorption phenomenon of inhibitor molecules. Using the obtained adsorption coefficients, the heat of adsorption, free energy of adsorption, and adsorption entropy can be calculated.

The heat of adsorption was calculated according to the Langmuir adsorption isotherm [19] expressed by

$$\frac{\theta}{(1-\theta)} = AC \exp\left(\frac{-\Delta H_{\text{ads}}}{RT}\right) \quad (7)$$

where T is temperature, A is an independent constant, C is the inhibitor concentration, R is the gas constant, ΔH_{ads} is the heat of adsorption, and θ is the surface coverage by the inhibitor molecule. Equation 7 can be converted to logarithmic scale:

$$\log \frac{\theta}{1-\theta} = \log A + \log C - \left(\frac{\Delta H_{\text{ads}}}{2.303RT}\right) \quad (8)$$

The heat of adsorption can therefore be obtained from the slope of the regression between $\log \theta/(1-\theta)$ and $(1/T)$. Figure 3 indicates that there is a good linear relationship between $\log \theta/(1-\theta)$ and $(1/T)$, meaning that it is reliable to utilize the Langmuir adsorption isotherm equation to

Table 2 Parameters of linear regression between C/θ and C

Temperature/°C	K	Slope	Linear correlation coefficient (R^2)
20	1.05	1.0165	0.99998
30	0.892	1.042	0.99994
40	0.434	1.098	0.99991
50	0.232	1.148	0.99969

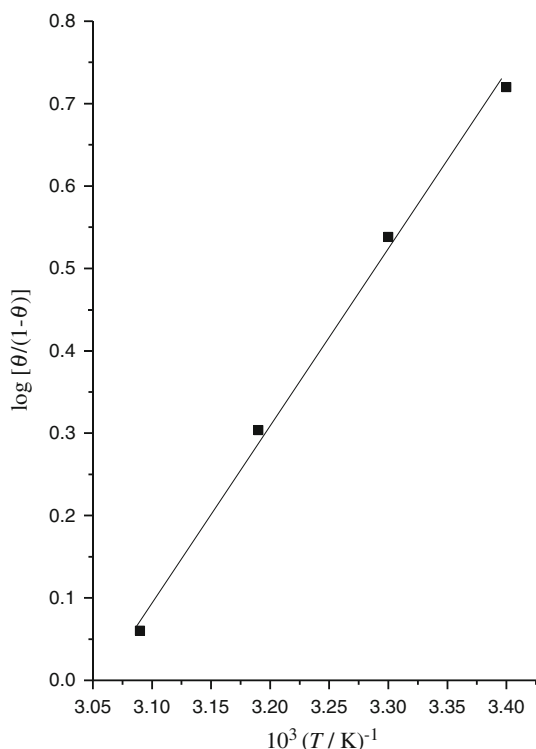


Fig. 3 Relationship between $\log \theta/(1-\theta)$ and $(1/T)$

calculate the heat of adsorption. The heat of adsorption (ΔH_{ads}) can be approximately regarded as the standard heat of adsorption ($\Delta H_{\text{ads}}^\circ$) under experimental conditions [20]. The standard free energy of adsorption ($\Delta G_{\text{ads}}^\circ$) was calculated from the equilibrium constant of adsorption using the following equation [21]:

$$K = \frac{1}{55.5} \exp\left(\frac{\Delta G_{\text{ads}}^\circ}{RT}\right) \quad (9)$$

Then the standard adsorption entropy ($\Delta S_{\text{ads}}^\circ$) can be obtained using the following thermodynamic fundamental equation [22]:

$$\Delta G_{\text{ads}}^\circ = \Delta H_{\text{ads}}^\circ - T\Delta S_{\text{ads}}^\circ \quad (10)$$

All the obtained thermodynamic parameters are shown in Table 3.

Table 3 Thermodynamic parameters of adsorption of sildenafil citrate on the steel surface at different temperatures

Temperature/ $^\circ\text{C}$	$\Delta G_{\text{ads}}^\circ/\text{kJ mol}^{-1}$	$\Delta H_{\text{ads}}^\circ/\text{kJ mol}^{-1}$	$\Delta S_{\text{ads}}^\circ/\text{J mol}^{-1} \text{K}^{-1}$
20	-9.89	-40.74	-105.26
30	-9.55	-40.74	-104.93
40	-8.06	-40.74	-104.39
50	-6.83	-40.74	-103.96

The negative values of $\Delta G_{\text{ads}}^\circ$ suggested that the adsorption of sildenafil citrate onto the steel surface was a spontaneous process and its values also indicate that the inhibition process becomes less effective as the temperature is increased from 20 to 50 $^\circ\text{C}$. The values of adsorptive equilibrium constant K reveal better adsorption, which leads to an increase in the inhibition efficiency [22, 23].

The negative values of $\Delta G_{\text{ads}}^\circ$ also suggest a strong interaction between the adsorbed inhibitor molecule and the carbon steel surface [24]. The negative values of $\Delta H_{\text{ads}}^\circ$ indicate that adsorption of sildenafil citrate on the steel surface is favored at low temperatures (exothermic process) [25], which indicates that IE (%) decreases with increasing temperature. Generally, an exothermic process signifies either physi- or chemisorption. The heat of physical adsorption is relatively low, in the order of 4–41 kJ mol^{-1} , whereas that of chemisorption is much higher, of a magnitude of 100–500 kJ mol^{-1} [26]. These concepts can be made valid for the adsorption of sildenafil citrate onto the steel surface, whereby it can be affirmed that this is due to a physical phenomenon.

Using Eq. 10, we obtained negative $\Delta S_{\text{ads}}^\circ$ values in the order of 102.93–105.26 $\text{J mol}^{-1} \text{K}^{-1}$ (see Table 3). In general, adsorption produces a certain order in the system, giving negative entropy. This is the case with the adsorption of many organic compounds [27–29] and is what we found for sildenafil citrate adsorption on carbon steel surface.

Kinetic parameters

A kinetic model is another useful tool to explain the mechanism of corrosion inhibition for the inhibitor. It has been reported by a number of authors [30–32] that for the acid corrosion of steel, the natural logarithm of corrosion rate ($\text{mg cm}^{-2} \text{h}^{-1}$) is a linear function of $1/T$ (following the Arrhenius equation) [33]:

$$\ln R_{\text{corr}} = \frac{-E_a}{RT} + \ln A \quad (11)$$

where E_a represents the apparent activation energy, R the gas constant, T the temperature, A the pre-exponential factor, and W is the corrosion rate.

Figure 4 shows the Arrhenius plot for the blank and various dye concentrations, and it is found that almost all the regression coefficients are very close to one, which means that the relationship between $\ln R_{\text{corr}}$ and $1/T$ is good. The apparent activation energy and pre-exponential factor can be calculated according to the slope and intercept of the regression, respectively. All the kinetic parameters were calculated and are listed in Table 4. According to Putilova et al. [34], the activation energies in

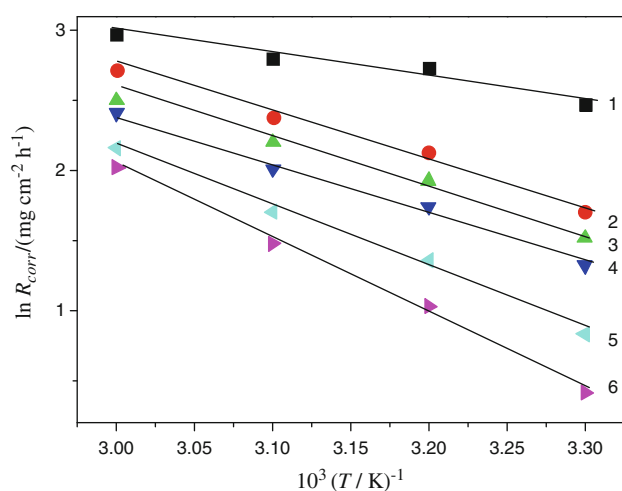


Fig. 4 Arrhenius plots related to the corrosion rate of carbon steel in the absence and presence of various concentrations of sildenafil citrate in 1 M HCl. (1) 1 M HCl, (2) 5×10^{-6} M, (3) 10^{-5} M, (4) 5×10^{-5} M, (5) 10^{-4} M, (6) 5×10^{-4} M

Table 4 Activation energy for carbon steel in 1 M HCl in the absence and presence of different concentrations of sildenafil citrate

Inhibitor concentration/M	$E_a/\text{kJ mol}^{-1}$
HCl (1 M)	38.50
5×10^{-6}	84.47
1×10^{-5}	88.70
5×10^{-5}	90.98
1×10^{-4}	100.37
5×10^{-4}	126.70

the presence of inhibitors may be higher, equal to, or lower than those in the absence of the inhibitor. In the present study, the apparent activation energy increased with increasing concentration of sildenafil citrate as a result of the appreciable decrease in the adsorption of the inhibitor on the metal surface with increase of temperature and corresponding increase in the reaction rate because of the greater area of the metal that is exposed to acid [35].

A decrease in inhibition efficiency with rise in temperature, with accordant increase in corrosion activation energy in the presence of inhibitor compared with that in its absence, is good evidence for a physisorption mechanism of sildenafil citrate on the steel surface [26].

Galvanostatic polarization measurements

The anodic and cathodic polarization behavior of carbon steel in 1 M HCl in the absence and presence of different concentrations of sildenafil citrate is given in Fig. 5. The extrapolation method for the polarization curves was applied and the data for corrosion potential (E_{corr}),

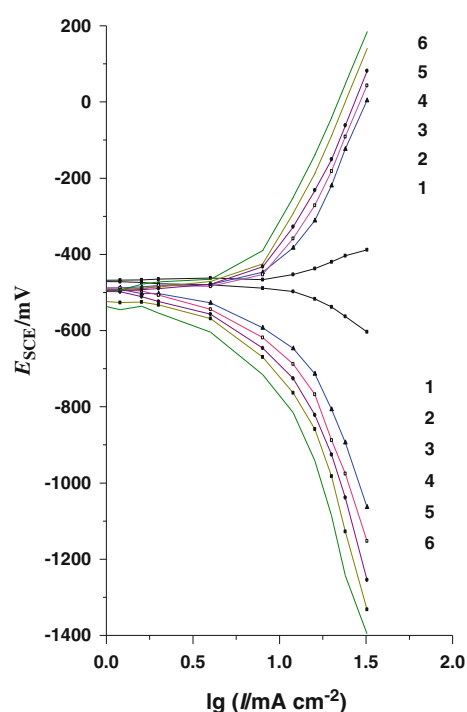


Fig. 5 Cathodic and anodic polarization curves of carbon steel in 1 M HCl solution in the absence and presence of different concentrations of sildenafil citrate: (1) blank, (2) 5.0×10^{-6} M, (3) 1.0×10^{-5} M, (4) 5.0×10^{-5} M, (5) 1.0×10^{-4} M, (6) 5.0×10^{-4} M

Table 5 Electrochemical parameters for carbon steel in the absence and presence of different concentrations of sildenafil citrate in 1 M HCl solution at 30 °C obtained from Tafel polarization curves

Inhibitor concentration/M	$E_{\text{corr}}/\text{mV (SCE)}$	$b_a/\text{mV dec}^{-1}$	$b_c/\text{mV dec}^{-1}$	$I_{\text{corr}}/\text{mA cm}^{-2}$	IE/%
HCl (1 M)	-435	54	71	0.820	–
5×10^{-6}	-481	191	271	0.12	85.4
1×10^{-5}	-490	198	280	0.09	89.0
5×10^{-5}	-488	208	296	0.06	92.7
1×10^{-4}	-487	216	311	0.03	96.3
5×10^{-4}	-483	220	330	0.011	98.7

corrosion current density (I_{corr}), and Tafel slopes (b_c and b_a) are shown in Table 5. The results in Fig. 5 and Table 5 illustrate that as the additive concentration increases there is a shift in the corrosion current density (I_{corr}) to lower values relative to the blank. Meanwhile, the corrosion potential (E_{corr}) is shifted to the more negative direction. The results indicate that the additives provide an inhibition effect on the corrosion of carbon steel electrodes in 1 M HCl solutions and behave mainly as a cathodic-type inhibitor.

The value of I_{corr} decreases with increasing inhibitor concentration and the Tafel slopes remain almost unchanged,

indicating that the presence of these compounds in the solution has no effect on the mechanism of the dissolution process of the metal and the adsorbed molecules mechanically screen the coated part of the electrode and therefore protect it from the action of the corrosion medium [36, 37].

The reaction mechanism of the corrosion process in 1 M HCl solution free from inhibitor is different from that in the presence of the inhibitor. From the inspection of data given in Table 5, it is clear that in the presence of inhibitor the value of b_c is greater than that in free acid solution. This behavior could be due to the decrease of the cathodic transfer coefficient, which can be ascribed to the thickening of the electric double layer or the formation of multi-molecular layers on the metal surface [38]. Also, the anodic Tafel slope (b_a) in the inhibited solution is higher than that obtained in the acid inhibitor-free solutions. This increase in anodic Tafel slope suggests a mode of inhibition involving an interposition of the additives into the charge transfer process for the anodic reaction [39], which may lead to a morphological change of the electrode surface brought about by the anodic dissolution [40].

The percentage inhibition efficiency, IE (%), was calculated using the following equation and is listed in Table 5:

$$IE(\%) = \left[1 - \frac{I_{\text{corr}}}{I_{\text{corr}}^0} \right] \times 100 \quad (12)$$

where I_{corr}^0 and I_{corr} are the uninhibited and inhibited corrosion current densities, respectively. The corrosion current densities are calculated from the intersections of the cathodic curves with stationary corrosion potentials (E_{corr}). The obtained IE (%) values (Table 5) reveal that the order of inhibition efficiency increases with increasing inhibitor concentration.

Electrochemical impedance studies (EIS)

Electrochemical impedance measurements were carried over the frequency range from 10 kHz to 100 MHz at open circuit potential. The sample equivalent Randle circuit for the studies is shown in Fig. 6, where R_s ($\Omega \text{ cm}^2$) represents the solution and corrosion products film in series with the parallel combination of resistor R_{ct} (charge transfer resistance) and capacitor C_{dl} (double layer capacitance) which represents the corroding interface.

The Nyquist representation of the impedance behavior of carbon steel in 1 M HCl with and without addition of various concentrations of inhibitor is given in Fig. 7. It is seen that addition of inhibitor increases the value of R_{ct} from 62 to 918 $\Omega \text{ cm}^2$ and reduces C_{dl} from 91.96 to 15.40 $\mu\text{F cm}^{-2}$.

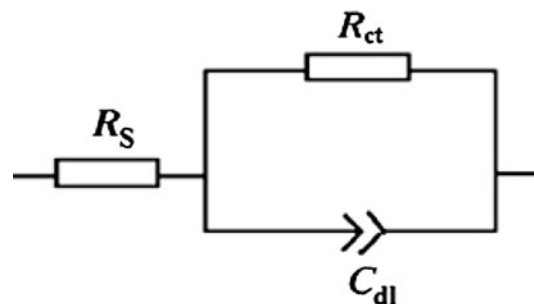


Fig. 6 Electrical equivalent circuit (R_s = uncompensated solution resistance, R_{ct} = charge transfer resistance, and C_{dl} = double layer capacitance)

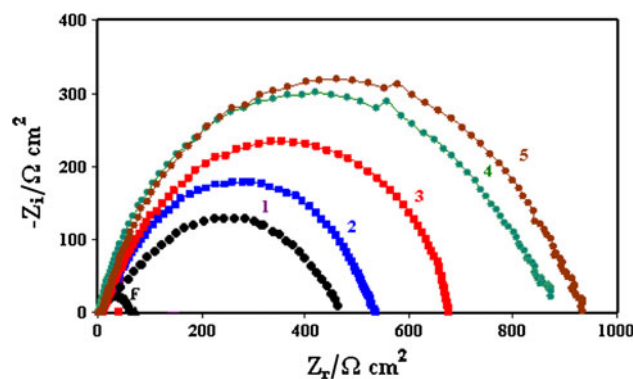


Fig. 7 Nyquist plots for carbon steel in 1 M HCl in the absence and presence of different concentrations of sildenafil citrate: (F) free, (1) 5.0×10^{-6} M, (2) 1.0×10^{-5} M, (3) 5.0×10^{-5} M, (4) 1.0×10^{-4} M, (5) 5.0×10^{-4} M

The R_{ct} values of the investigated compound increase with increasing inhibitor concentration. At the same time the C_{dl} has the opposite trend over the whole concentration range. These observations clearly highlight that the corrosion of carbon steel in 1 M HCl is controlled by a charge transfer process. The decrease in C_{dl} is due to the gradual replacement of water molecules by the adsorption of the organic molecules at the metal/solution interface, leading to a protective film on the steel surface, and then decreasing the extent of dissolution reaction [41]. The characteristic parameters associated with the impedance diagrams (R_{ct} , C_{dl}), θ , and IE (%) are given in Table 6. IE (%) and θ were calculated from the following equations:

$$\theta = \left[\frac{(I/R_{ct})_0 - (I/R_{ct})}{(I/R_{ct})_0} \right] \quad (13)$$

$$IE(\%) = \left[\frac{(I/R_{ct})_0 - (I/R_{ct})}{(I/R_{ct})_0} \right] \times 100 \quad (14)$$

where R_{ct0} and R_{ct} are the uninhibited and inhibited charge transfer resistance, respectively [42].

Table 6 Impedance data and surface coverage for carbon steel in 1 M HCl in the absence and presence of different concentrations of sildenafil citrate at 25 °C

Inhibitor conc./M	$R_{ct}/\Omega \text{ cm}^2$	$C_{dl}/\mu\text{F cm}^{-2}$	θ	$IE_R/\%$
HCl (1 M)	62	91.96	–	–
1	270	34.25	0.77	77.0
2	524	30.25	0.88	88.2
3	681	26.68	0.91	90.9
4	840	20.51	0.93	92.6
5	918	15.40	0.93	93.3

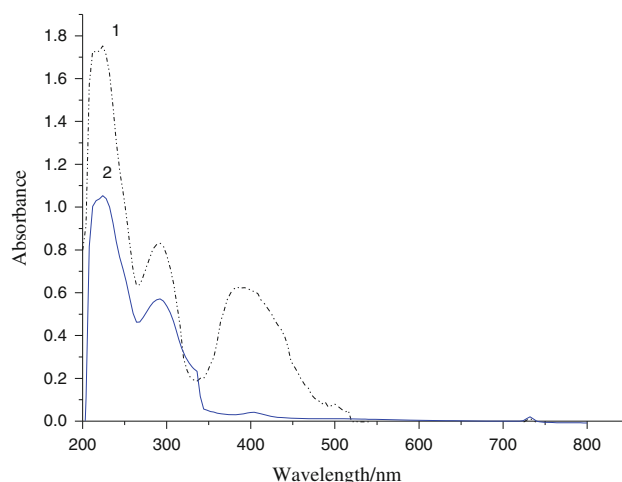
Inhibition mechanism

The mechanism of action of the inhibitors in acid solutions has been studied extensively. It is generally believed that these compounds are adsorbed on the metal surface and prevent further dissolution of metal through blocking of either the cathodic or anodic reaction or both. Another group of organic inhibitors, which have been the focus of attention in recent years, are those organic compounds capable of forming insoluble complexes, or chelates, with metallic ions present on the surface of metal.

The inhibition efficiency of sildenafil citrate against the corrosion of carbon steel in 1 M HCl can be explained on the basis of the number of adsorption sites, their charge density, molecular size, mode of interaction with the metal surface, and ability to form metallic complex. We note that a plausible mechanism of corrosion inhibition of carbon steel in 1 M HCl by the compound under study may be deduced on the basis of adsorption.

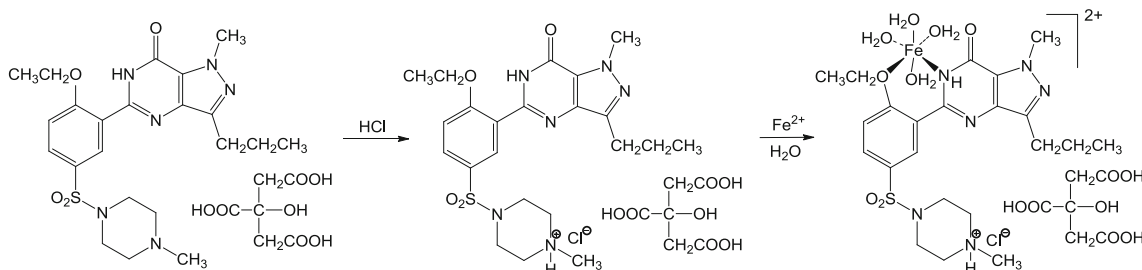
The adsorption of sildenafil citrate could occur as a result of the formation of links between the d orbital of iron atoms, involving the displacement of water molecules from metal surface, and the lone electron pairs present on the N and O atoms of the heterocyclic rings. Moreover, this compound may also adsorb through the electrostatic interactions between the protonated (acid) form and the negatively charged metal surface.

On the other hand, the chemical structure of sildenafil citrate (Fig. 8) is characterized by the presence of chelation

**Fig. 9** UV–Vis spectra of the solutions containing 5×10^{-4} M sildenafil citrate in 1 M HCl before carbon steel immersion (1) and after 24 h immersion (2)

centers involving oxygen and nitrogen atoms with lone pairs of electrons. Therefore, the formation of complexes of sildenafil citrate with iron ions released during the corrosion reaction is also considered possible.

In order to confirm the possibility of the formation of a sildenafil citrate–Fe complex, UV–Vis absorption spectra obtained from the corrosive solution in the presence of 10^{-3} M of sildenafil citrate before and after 24 h of steel immersion are shown in Fig. 9. The electronic absorption spectra of sildenafil citrate before the steel immersion (curve 1) display two bands in the UV region and one band in the visible region. The shorter wavelength band with λ_{max} at 220 nm is ascribed to π – π^* transitions of the benzenoid system of the compound. The second UV band (λ_{max} at 285 nm) can be attributed to π – π^* transitions within the heterocyclic moiety of the compound. The localization of this band at a longer wavelength, relative to the former one, can be ascribed to the higher delocalization of π electrons of the heterocyclic moiety. On the other hand, the compound displays a main broad visible band (within the range 370–500 nm). This band can be assigned to a π – π^* transition involving the whole electronic system of the

**Fig. 8** Chemical formula of sildenafil citrate in both protonated and complex forms

compound with a considerable charge transfer character through N–N linkage [43, 44]. After 1 day of steel immersion (curve 2), it is clearly seen that the CT band has been completely disappeared, suggesting the interaction between sildenafil citrate and Fe^{2+} ions in the solution. These experimental findings give evidence for the possible formation of a complex between Fe^{2+} cation and sildenafil citrate in 1 M HCl.

Conclusions

On the basis of the collected data, the following conclusions may be drawn:

1. Sildenafil citrate inhibits carbon steel corrosion in 1 M HCl solution and the inhibition efficiency increases with sildenafil citrate concentration at all temperatures studied.
2. The inhibition efficiency of sildenafil citrate decreases with temperature and its decrease leads to increased activation energy of the corrosion process, which suggests a physical adsorption mechanism.
3. The adsorption of sildenafil citrate on the surface of steel obeys the Langmuir adsorption isotherm.
4. The galvanostatic polarization data indicate that the inhibitor under study is of mixed type, but with a predominant cathodic effect.
5. The results of EIS indicate that the double layer capacitances decrease with respect to the blank solution when the inhibitor is added.
6. The UV–Vis studies reveal the formation of an Fe–sildenafil citrate complex, which may be also responsible for the observed inhibition

Experimental

Materials

The carbon steel specimen (L-52) used for this study has the following composition: C, 0.26 wt%; Mn, 1.35 wt%; P, 0.04 wt%; S, 0.05 wt%; Nb, 0.005 wt%; V, 0.02 wt%; Ti, 0.03 wt%; and Fe to balance. The galvanostatic polarization measurements were performed using specimens in the form of rods of 1 cm^2 exposed surface area as a working electrode. For weight loss tests, small rectangular coupons with dimensions of $2.0 \times 2.0 \times 0.8\text{ cm}^3$ were used. The testing media were aqueous aerated 1 M HCl solutions without and with different concentrations of sildenafil citrate. All chemicals used in this study were analytical grade (Aldrich).

Apparatus

The weight loss measurements were carried out in large test tubes ($20 \times 5\text{ cm}^2$ size) suspended in a thermostated water bath. Each tube was open to air. The galvanostatic cathodic and anodic polarization measurements were carried out using a three-compartment glass cell and an EG&G model 363 potentiostat/galvanostat corrosion measurement system. A platinum electrode was used as a counter electrode (separated from the cell solution by a sintered glass frit) and a saturated calomel electrode (inside a Luggin's probe) as a reference electrode. The impedance measurements were carried out at open circuit potential (E_{ocp}) in the frequency range from 10 kHz to 100 MHz with signal amplitude perturbation of 5 mV by using a computer-controlled potentiostat (Auto Lab 30, Metrohm). All experiments were performed using a three-electrode system at 25 °C. The UV–Vis spectrophotometric experiments were carried out using a JASCO UV–VIS 530 spectrophotometer and 10-mm matched silica cell.

Weight loss measurements

The carbon steel coupons were successively abraded with SiC paper to a final finish using 1,200 grade paper. Before immersion in the test solution (50 cm^3), the dimensions of each coupon were ascertained. They were then degreased in AR grade acetone, etched in HCl for 30 s, washed with doubly distilled water, followed by acetone, dried, and weighed. The cleaned coupons were weighed before and after immersion in 50 cm^3 of the test solution for a period of time up to 24 h. The average weight loss for two identical experiments was taken and expressed in mg cm^{-2} .

Galvanostatic polarization

The working electrode was polished and pre-polarized prior to recording the cathodic and anodic polarization curves at each concentration of the tested solution at 25 °C. All the polarized curves were obtained at regular intervals. The duration of potential stabilization at each current density value was between 3 and 5 min.

UV–Vis spectra

A UV–Vis spectrophotometric method was used to perform some experiments on the electrolyte solution of the inhibited system before and after immersion of carbon steel.

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