

The Effect of Silene Marmarica Extract on The Corrosion and Kinetics of The Dissolution Process of Steel in Acidic Solution

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Abstract: Silene Marmarica is a new green inhibitor to replace toxic chemicals. Corrosion of mild steel in 1 mol L⁻¹ hydrochloric acid solution was studied in absence and presence of Silene Marmarica by using potentiodynamic polarization and electrochemical impedance spectroscopy techniques at different temperatures ranged from 30 to 45 °C. The results showed that the presence of Silene Marmarica inhibits the corrosion of steel in 1 mol L⁻¹ hydrochloric acid. The Langmuir adsorption isotherm was used to calculate the thermodynamic parameter ΔG_{ads}° . The activation parameters E_a , ΔH^* and ΔS^* were calculated using Arrhenius equation.

Keywords: electrochemical techniques, adsorption, corrosion, thermodynamic properties.

1 Introduction

Numerous chemical compounds are used for the prevention and control of corrosion by inhibiting the aggressive attack of the medium in contact with metallic constructions. Iron and its alloys are the metallic surfaces most frequently exposed to corrosion in both industrial and general environmental settings. These metallic materials are more susceptible to corrosion in an acidic medium than in an alkaline medium. A large number of organic compounds containing nitrogen, oxygen and sulfur, as hetero atoms are found to cause a decrease in the corrosion rates of steel in hydrochloric acid (HCl) solutions.[1-3] Organic compounds containing π -bonds in their structures are among the best corrosion inhibitors. The electronic structure of inhibiting molecules has a notable effect on the adsorption of these compounds. The literature also indicates that the electron density on the hetero atom, the presence of aromaticity, and the presence of functional groups such as -CHO, -N \equiv N, R-OH, has a pronounced effect on the degree of adsorption.[4-9] 1-phenyl-3-methylpyrazole-5-one, (4-amino-2-methyl-5-pyrimidinylmethylthio) acetic acid and 3-(4-amino-2-methyl-5-pyrimidinylmethyl)-5-(2-hydroxyethyl)-4-methylthiazolium chloride hydrochloride have been used as corrosion inhibitors for carbon steel in 0.5 mol L⁻¹ hydrochloric acid solution and the protection efficiency was found to be 90% at 25 °C.[10-11]

Nontoxic and environmentally benign compounds have been evaluated as corrosion inhibitors. Among them, tryptamine,[12] succinic acid,[13] L-ascorbic acid,[14] sulfamethoxazole[15] and cefatoxime[16] are effective

corrosion inhibitors in acidic environments. Recently, herb plants have been investigated as green corrosion inhibitors in different media. [17-25] Noteworthy is that these natural products are biodegradable and nontoxic. Different parts of the plants such as seeds, [26,27] fruits,[28] leaves,[29] and flowers [30-33] were extracted and used as corrosion inhibitors for steel in acidic solution. The effect of lupine as a corrosion inhibitor for steel in an aqueous solution of 1 mol L⁻¹ sulphuric acid and 2 mol L⁻¹ hydrochloric acid was evaluated by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. The potentiodynamic polarization curves showed that the lupine extract acts as a mixed-type inhibitor. Two conclusions could be extrapolated from this information, firstly it could be used as an effective corrosion inhibitor for steel in acidic media and secondly the extract had greater effect on inhibiting corrosion in hydrochloric acid solution than in sulphuric acid. [34] The present study aims to evaluate the potential of Silene Marmarica as a corrosion inhibitor for steel in a 1 mol L⁻¹ HCl solution by using electrochemical methods. It also aims to determine the kinetic and thermodynamic parameters required for the dissolution of steel in 1 mol L⁻¹ HCl.

2 Methods and Materials

2.1 Electrochemical Tests

Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) were measured using 604 ACM Instrument. The frequency range for EIS measurements was $0.01 \leq f \leq 3 \times 10^4$ Hz, with applied potential signal amplitude of 10 mV around the rest of the

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potential. Polarization curves were measured at a rate of 20 mV/min. The data was obtained in a three electrode mode cell. A graphite rod and a saturated calomel electrode were used as counter and reference electrodes. The working electrode was steel rods with the following chemical composition (wt. %): C 0.21; S 0.04; Mn 2.5; P 0.04; Si 0.35; and the remainder was Fe. The steel samples were fixed in polytetrafluoro ethylene (PTFE) rods by an epoxy resin in such a way that only one surface was left uncovered. The exposed area (0.28 cm²) was mechanically polished with a series of emery papers of variable grades ranging from 100 to 1000. The samples were then washed thoroughly with distilled water followed by Analytical grade ethanol and finally with distilled water, just before insertion into the cell.

2.2 Solution Preparation

2.2.1 Preparation of the test solutions

Analytical grade (Aldrich chemicals) concentrated hydrochloric acid, 37% HCl was used without further purification and added to doubly distilled water to prepare a stock solution of 1 mol L⁻¹ hydrochloric acid.

2.2.2 Preparation of the extract solutions

Silene Marmarica is a combination of four naturally occurring bicyclic mono-terpenoids and is an edible substance. It is composed of Thujon, Borneol, Cineol and Pinene; the chemical structure of these natural products is given in Figure 1. All solutions were prepared using double distilled water. Stock solutions of Silene Marmarica were obtained by refluxing 10 g of the dry plant in 100 mL of distilled water for 60 min. The refluxed solution was filtered to remove any insoluble impurities. The concentration of the stock solution was measured by evaporating 10 mL of the filtrate and weighing the residue. The concentration of the stock solution was expressed in terms of parts per million (ppm).

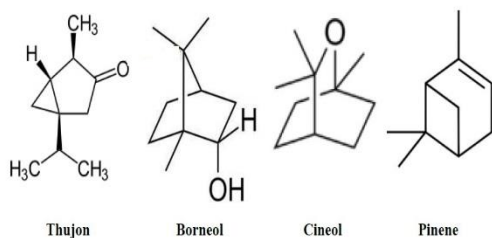


Figure 1. Chemical composition of Silene Marmarica.

3 Results and Discussion

3.1 Potentiodynamic polarization measurements.

Tafel polarization curves for steel in 1 mol L⁻¹ HCl

in the absence and presence of different concentrations of Silene Marmarica are shown in Figure 2.

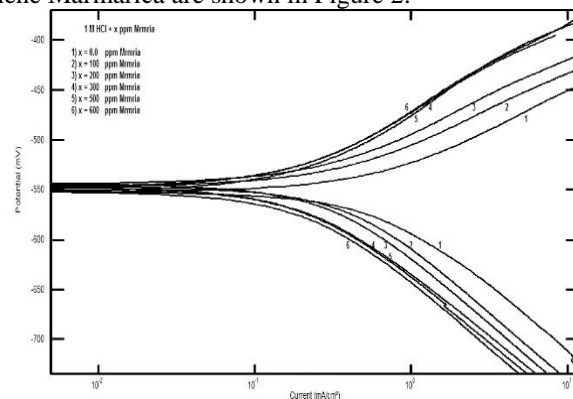


Figure 2. Potentiodynamic polarization curves for steel in 1 mol L⁻¹ HCl containing different concentrations of Silene Marmarica at 30 °C.

Both the cathodic and the anodic parts of the tafel lines were affected upon addition of different concentrations of the extract to the acid. This indicates that Silene Marmarica acts as a mixed type inhibitor and affects both the anodic dissolution and hydrogen evolution at the cathode. The potentiodynamic polarization parameters and the inhibition efficiency are calculated and given in Table 1. The values of the inhibition efficiency were calculated according to the following equation:

$$\% \text{ inhibition} = [(i_{\text{corr}} - i_{\text{corr}}') / i_{\text{corr}}] \times 100 \quad (1)$$

Where i_{corr} and i_{corr}' are the uninhibited and the inhibited corrosion current densities respectively. It has been found that i_{corr} decreases in the presence of the extract, this indicates that Silene Marmarica act as a good corrosion inhibitor for steel in 1 mol L⁻¹ HCl. This is further reinforced by the fact that, as the concentration of the extract used is increased the corrosion current densities are further decreased. Therefore the value of the inhibition efficiency increases by increasing the extract concentration. Both the cathodic and anodic tafel slopes (β_a and β_c) were almost unchanged in the presence of the extract indicating that the inhibitor acts by adsorption onto the metal surface.

Table 1. Potentiodynamic polarization parameters for steel in 1 mol L⁻¹ HCl in presence of different concentrations of Silene Marmarica.

Marmarica concentration (ppm)	β_a (V dec ⁻¹)	β_c (V dec ⁻¹)	$-E_{\text{corr}}$ (mV)	i_{corr} (mA cm ⁻²)	% Inhibition
0.0	89.9	104.3	560.1	0.5157	----
50	77.3	103.7	543.9	0.3954	23.3
75	72.2	106.7	543.9	0.2936	43.1
100	76.8	111.6	539.2	0.2871	44.3
200	78.4	107.7	546.5	0.2141	58.5
250	77.1	109.8	534.4	0.1916	62.8
350	80.9	106.5	548.4	0.1875	63.6
400	84.5	104.8	537.6	0.1770	65.7
500	85.4	112.9	548.9	0.1490	71.1
600	83.5	107.1	549.2	0.1550	69.9

3.2 Electrochemical impedance spectroscopy (EIS) measurements

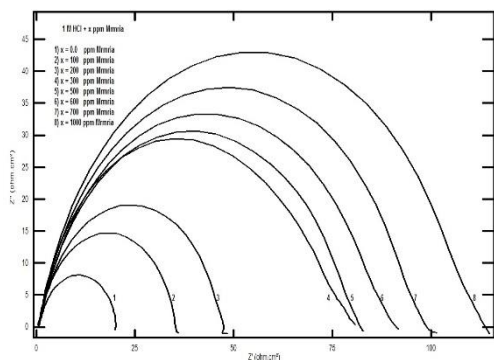


Figure 3. Nyquist plots for steel in 1 mol L⁻¹ HCl containing various concentrations of Silene Marmarica at 30 °C.

Nyquist plots for steel in 1 mol L⁻¹ HCl for different concentrations of Silene Marmarica are shown in Figure 3. Nyquist plots show only one capacitive depressed semicircle. It is evident from the plots that the diameter of semicircle increases by increasing the concentration of the inhibitor. This indicates that Silene Marmarica behaves as good corrosion inhibitor for steel in 1 mol L⁻¹ HCl and also shows that the inhibition efficiency increases by increasing the concentration of Silene Marmarica extract added to the HCl solution. The impedance spectra for different Nyquist plots was analyzed by fitting the experimental data using the ZSimp Win program, which is an electrochemical

impedance Modeling software, to a simple equivalent circuit model represented in Figure 4. The equivalent circuit model includes the solution resistance, R_s , and the circuit includes a capacitor, C_{dl} , which represents the capacitance of the double layer formed at the interface between the metal and the solution. The capacitor, C_{dl} , is placed in parallel to the charge transfer resistance element, R_{ct} , which represent the resistance of the charge transfer.

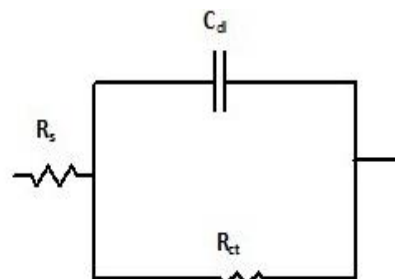


Figure 4. The equivalent circuit model.

The values of the electrochemical parameters obtained from EIS for steel in the 1 mol L⁻¹ HCl solution containing different extract concentrations and the inhibition efficiency (% inhibition) are given in Table 2. The inhibition efficiency was calculated from the impedance measurements using the following equation:

$$\% \text{ inhibition} = [(R_{ct} - R_{ct0}) / R_{ct}] \times 100 \quad (2)$$

Where; R_{ct0} and R_{ct} are the charge transfer resistances in the absence and presence of different concentrations of Silene Marmarica extract.

Table 2: EIS parameters for steel in 1 mol L⁻¹ HCl in the presence of different concentrations of Silene Marmarica at 30 °C.

Concn (ppm)	R_s (ohm.cm ²)	C_{dl} (F.cm ⁻²)	R_{ct} (ohm.cm ²)	%Inh
0.0	0.58	3.10 E ⁻⁴	20.4	---
50	0.49	2.70 E ⁻⁴	23.6	13.5
75	0.47	2.03 E ⁻⁴	31.2	34.6
100	0.51	1.60 E ⁻⁴	35.0	41.7
150	0.53	1.90 E ⁻⁴	39.8	48.7
200	0.44	1.60 E ⁻⁴	46.8	56.4
250	0.44	2.10 E ⁻⁴	59.1	65.5
350	0.38	1.90 E ⁻⁴	71.2	71.3
400	0.38	1.90 E ⁻⁴	76.5	73.3
500	0.38	1.89 E ⁻⁴	86.6	76.4
700	0.36	1.48 E ⁻⁴	96.2	78.7
800	0.47	1.33 E ⁻⁴	112.6	81.8
1000	0.35	1.42 E ⁻⁴	110.6	81.2

It can be concluded from the impedance data in Table 2 that the presence of Silene Marmarica enhances the charge transfer resistance (R_{ct}) and reduces the values of C_{dl} . The decrease in C_{dl} is thought to be due to the adsorption of the active ingredient of the extract on the metal surface. The formation of this adherent film covering the metal surface

results in a decrease in the double layer thickness. In order to understand the nature of the adsorption process between the inhibitor and the metal surface, the variations of percentage inhibition with the different concentrations of plant extracts are shown in Figure 5. The percentage inhibition was calculated from impedance measurements as

outlined above and is plotted on the vertical axis against the concentration of Silene Marmarica extract plotted on the horizontal axis. These curves are characterized by a steep initial incline indicating the formation of a mono-layer adsorbate film on the steel surface. At higher concentrations, concentrations of greater than 500 ppm, the inhibitory effect became constant; this suggests complete saturation of the surface by the inhibitor molecules.

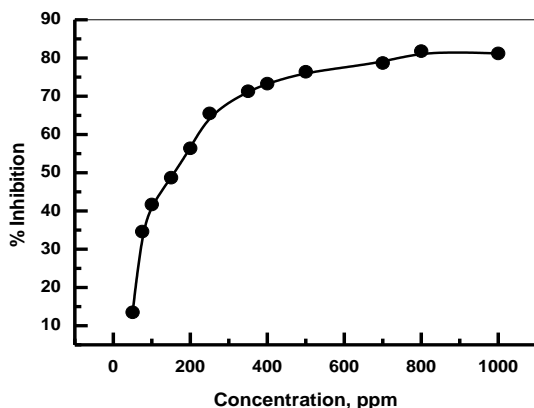


Figure 5. Variations of percentage inhibition of the corrosion of steel in 1 mol L⁻¹ HCl with different concentrations of Silene Marmarica extract.

3.3 Determination of the thermodynamic parameters

The adsorption of extract molecules onto the steel surface has been considered as the main reason for corrosion inhibition. Assuming that the percentage area covered by the inhibitor molecules is directly proportional to retardation of the rate of corrosion, the compounds obey the Langmuir adsorption isotherm. [35] Langmuir isotherm is given by the following equation, [36]

$$\left[\frac{\theta}{1-\theta}\right] = KC \text{ or } \log(\theta/1-\theta) = \log C + \log K \quad (3)$$

Where K is the equilibrium (binding) constant of the adsorption process, the magnitude of K is directly proportional to the inhibition efficiency. The greater the value of K the greater the inhibition efficiency and *vice versa*. The validity of the Langmuir isotherm is confirmed from the linearity of a graph resulting from a plot of $\log(\theta/1-\theta)$ vs. $\log C$, requiring the slope of the graph to be unity. The plots of Langmuir are shown in Figure 6. It was observed that although these plots are linear ($R = 0.996$), the gradient is never unity, contrary to what is expected for the ideal Langmuir adsorption isotherm. The departure in the values of the slopes of the Langmuir plots from unity may be attributed to the mutual interaction between adsorbed molecules in close vicinity. [37]

The standard free energy of adsorption $\Delta G^{\circ}_{\text{ads}}$ at different temperatures was calculated from the following equation [38, 39].

$$\Delta G^{\circ}_{\text{ads}} = -RT \ln(55.5K_{\text{ads}}) \quad (4)$$

Where R is the universal gas constant, T is the absolute temperature in kelvin, K is the binding constant and the value of 55.5 is the concentration of water in the solution expressed in M.

The values for the binding constant K are obtained from the application of Langmuir adsorption isotherm to the data at different temperatures 303, 308, 313 and 318 K as represented in Figure 6. The values of K obtained from the Langmuir plot and $\Delta G^{\circ}_{\text{ads}}$ obtained from the equation:

$$(\Delta G^{\circ}_{\text{ads}} = -RT \ln(55.5K_{\text{ads}}))$$

At different temperatures are documented in Table 3. Generally, it is reported that $\Delta G^{\circ}_{\text{ads}}$ values of approximately -20 kJ mol⁻¹ or lower are consistent with an electrostatic interaction between the charged molecules and the charged metal (physisorption). Values lower than -40 kJ mol⁻¹, are involved in charge sharing or charge transfer from the inhibitor molecules to the metal surface to form a coordinate type bond (chemisorption). [40] The low values of $\Delta G^{\circ}_{\text{ads}}$ obtained in this research are characteristic of weak interaction indicating physical adsorption. The negative value associated with the $\Delta G^{\circ}_{\text{ads}}$ parameter indicates spontaneous adsorption of the extract on the steel surface. The values of $\Delta G^{\circ}_{\text{ads}}$ decreased as the temperature increased, this indicates that adsorption of the extract onto the metal surface decreased at high temperatures.

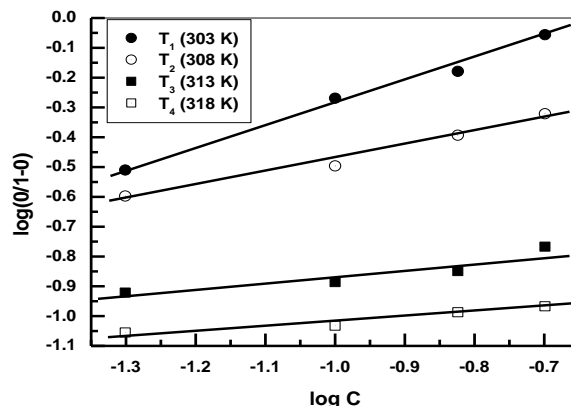


Figure 6. Application of the Langmuir model to the results of adsorption of different extracts on steel surface in 1 mol L⁻¹ HCl at different temperatures.

Table 3. Values of K obtained from the Langmuir adsorption isotherm and $\Delta G^{\circ}_{\text{ads}}$ at different temperatures.

Temperature (K)	303	308	313	318
K	2.79	1.03	0.232	0.135
$\Delta G^{\circ}_{\text{ads}}$ (kJ mol ⁻¹)	-12.7	-10.4	-6.6	-5.3

3.4 Determination of the activation parameters

It has been reported that, [41-43] the logarithm of the rate of corrosion (V) is a linear function with $1/T$. We use the Arrhenius equation to investigate these phenomena and see how it correlates with the results we obtained using different concentrations of Silene Marmarcia extract to reduce corrosion:

$$\ln V = \ln A - (E_a/RT) \quad (5)$$

Where E_a is the apparent effective activation energy, T is the absolute temperature, R is the universal gas constant and A is Arrhenius pre-exponential factor. The corrosion rates were taken from the analysis of the potentiodynamic polarization measurements. An alternative formulation of the Arrhenius equation is the transition state equation shown below:

$$V = (RT/Nh) \exp(\Delta S^*/R) \exp(-\Delta H^*/RT) \quad (6)$$

Where; N is Avogadro's number, h the plank's constant, ΔH^* is the enthalpy of activation and ΔS^* is the entropy of activation.

Figures 7 and 8 show that linear plots are produced when we plot $(\ln V)$ versus $(1/T)$ and $(\ln V/T)$ versus $(1/T)$ using data collected in an experiment where steel was dissolved in the presence of 100 ppm Silene Marmarcia at a number of different temperatures. This data was used to calculate the values of the activation parameters E_a , ΔH^* and ΔS^* are calculated. The resulting values of the activation parameters are given in Table 4.

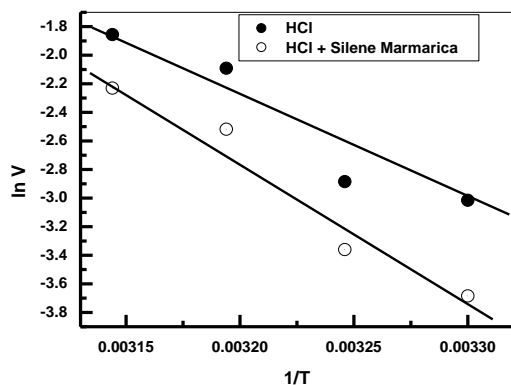


Figure 7. Linear fit for $(\ln V)$ data vs. $(1/T)$ for steel dissolution in 1 mol L^{-1} HCl solutions in the absence and presence of 100 ppm Silene Marmarcia.

As observed from the data given in table 4, the activation energy E_a and the enthalpy change ΔH^* for the solutions containing the Silene Marmarcia extract were higher than that for the solutions where no extract was added. Our earlier conclusions show that corrosion is inhibited in the presence of the Silene Marmarcia extract, thus here we can conclude that both the activation energy and the enthalpy change are higher for the solution where inhibition occurs using the extract. We propose from these observations that

the extract decreases the rate of corrosion by increasing the energy barrier for the corrosion reaction to occur. As mentioned earlier this may be explained by suggesting the formation of an adsorptive film. Overall the addition of the Silene Marmarcia extract results in the formation of an adsorptive film which increases the activation energy for corrosion and therefore decreases the rate at which corrosion occurs. The table also illustrates that ΔS^* has negative values for the test solutions, indicating a larger negative value when the extract is present in the solution. This implies that the activated complex represents an association rather than a dissociation step, meaning that a decrease in disorder takes place on going from reactants to the activated complex. [44]

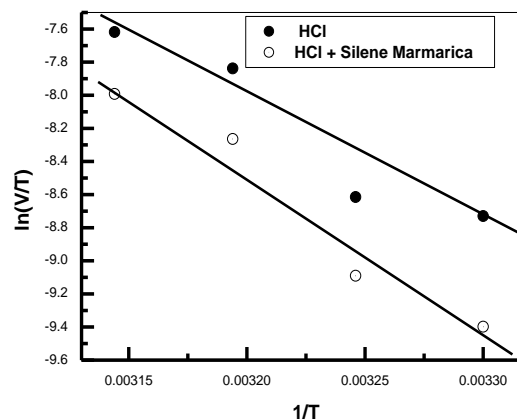


Figure 8. Linear fit for $(\ln V/T)$ data vs. $(1/T)$ for steel dissolution in 1 mol L^{-1} HCl solutions in the absence and presence of 100 ppm Silene Marmarcia.

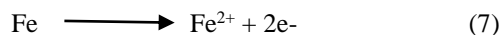
Table 4. Activation parameters of steel dissolution in 1 mol L^{-1} HCl in absence and presence of 100 ppm Silene Marmarcia.

Solution composition	Activation parameters		
	E_a (kJ mol^{-1})	ΔH^* (kJ mol^{-1})	ΔS^* ($\text{J mol}^{-1} \text{ K}$)
1 mol L^{-1} HCl	71.3	58.6	-45.7
1 mol L^{-1} HCl + 100 ppm Silene Marmarcia	83.8	81.3	-190.4

3.5 Explanation for inhibition

Components of the extract adsorbed over the mild steel surface blocking the active sites in which direct acid attack causes corrosion thereby protecting the metal from corrosion. Three of the components of the Silene Marmarcia extract have an oxygen heteroatom in their structure, Thujon contains a ketone functional group, Borneol contains an alcohol functional group, Cineol contains an ether functional group and the final compound in the extract Pinene contains an unconjugated double bond. Thus inhibition of the corrosion of steel may be

attributed to the adsorption of the extract components through these centers, which are regarded as centers of adsorption onto the metal surface. While adsorbed they create a barrier to mass and charge transfer and thus isolate the metal from further attack of the corrosive anions.[45-46] The inhibitor may then combine with freshly generated Fe^{2+} ions on the steel surface, forming metal-inhibitor complexes:



The resulting complex could, depending on its relative solubility, either inhibit or catalyze further metal dissolution; hence the integrity depends on the environments capacity to dilute it. The results obtained so far suggest that the components of the extract exhibited good inhibitor efficiency during steel corrosion in 1 mol L^{-1} HCl solution. Owing to the complex chemical composition, it is difficult to assign the inhibitive effect to a particular constituent. Initial phytochemical analysis of the extract identified the presence of Thujon, Borneol, Cineol and Pinene. Mutual adsorptive effects of these compounds and other components present in the extract cannot be ruled out in the adsorption process. The adsorption of these components on the mild steel surface reduces the surface area available for corrosion. [47-48].

Conclusions

The extract of Silene Marmarica acts as a good inhibitor of the corrosion of steel in 1 mol L^{-1} HCl solution and is considered to be a mixed type inhibitor. The inhibition efficiency was found to increase by increasing extract concentration up to a maximum value. Langmuir adsorption isotherm is applicable to fit the data indicating ideal behavior in the adsorption processes of these extracts on the steel surface. The Kinetic and Thermodynamic parameters were calculated. E_a and ΔH^\ddagger values in the presence of the Silene Marmarica are higher than that for the uninhibited acid solution. The ΔS^\ddagger values are larger and negative indicating that the transition state is an association rather than a dissociation step. ΔG_{ads} is negative indicating a spontaneous process of adsorption.

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