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RESEARCH ARTICLE

Adsorption Isotherm and Activation Energy of Inhibition of Alkaloids on Mild Steel Surface in Acidic Medium

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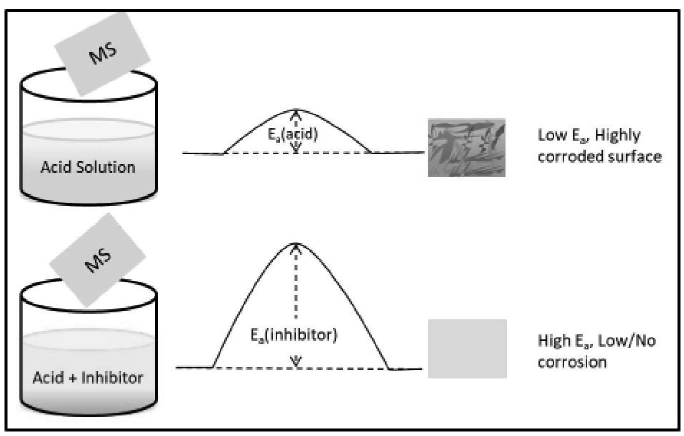
Highlights

- Alkaloids have been extracted from three different plants
- The alkaloids have been used as corrosion inhibitors for mild steel
- The weight loss measurement method was used to study the corrosion inhibition
- Adsorption of inhibitor obeys Langmuir isotherm
- Various thermodynamic parameters have been calculated.

Abstract

Alkaloids as green inhibitors were extracted from three different plants Rhynchostylis retusa, Artimesia vulgaris, and Solanum tuberosum. Weight loss measurement in mild steel has been carried out in the presence and absence of green inhibitors individually in an acidic medium. Weight loss measurements at different temperatures are used to calculate thermodynamic parameters. The weight loss measurements at different concentrations are used to find adsorption isotherm and found that it obeys Langmuir adsorption isotherm with R^2 values 1, 1, 0.996 for three inhibitors. Activation energy, enthalpy, and entropy of the three inhibitors have been calculated. It is found that the value of all these parameters increased in the addition of inhibitors. The free energy of the system is calculated and found (-17.46 kJ mol^{-1}) indicating that the adsorption process is spontaneous and there is physical adsorption at the MS-Inhibitor interface.



Keywords: *Alkaloid, extraction, weight loss, adsorption isotherm, thermodynamics*

Introduction

Mild steel (MS) is a ferrous alloy and the best-preferred construction material due to its availability, excellent mechanical properties, ease of fabrication, and low purchasing cost [1-3]. However, corrosion of MS is a serious concern, especially in acidic environments such as petrochemical, chemical plants, gasoline pipelines, and processes such as acid pickling, de-scaling,

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and cleaning of boilers where corrosion is causing substantial damage to the mechanical as well as surface properties of MS [4, 5]. Corrosion occurs when the protective mechanism has been broken down, leaving the metal vulnerable to attack leading to substantial economic losses [6].

Various means like surface modification, alloy formation, cathodic protection, and coatings are adopted for the prevention of MS corrosion [7]. But, such methods apply only to those MS where there is a non-acidic environment like manufacturing of infrastructures, buildings, and industries. The use of inhibitors is a more accepted practice for the corrosion control for MS used in acidic environments. Not all the substances used as inhibitors are friendly to the ecosystem and harms man, animal, and aquatic environment [6, 8]. Extracts are, therefore, recently are studying as corrosion inhibitors due to their low or no toxicity, eco-friendliness, availability, affordability, and effectiveness [6, 9, 10]. Extracts contain many biodegradable phytochemical compounds, including tannins, alkaloids, flavonoids, carbohydrates, phenolics, terpenoids, saponins, proteins, etc. [6, 11]. These phytochemicals usually bear polar functional groups containing heteroelements like nitrogen, sulfur, or oxygen, as well as triple or double conjugate bonds. Such functional groups act as major adsorption centers [11].

The heteroelements on the phytochemical molecules are active adsorption sites that interact with the MS surface. A layer of phytochemical gets adsorbed on it that acts as a barrier for metal to the corrosive environment. The preferable trend of the heteroatoms to be adsorbed on the MS surface is $O < N < S < P$ [14]. However, it is hard to find sulfur and phosphorus on extracts, and therefore, research on plant-based corrosion inhibitors focuses on nitrogen and oxygen, containing phytochemicals. Many pieces of literature have reported the methanol extract of the plant as a green inhibitor, such as extract of *Lantana camara* [2], *Aloe vera* [12], *Jasminum nudiflorum* [13], *Euphorbia royleana* [14], Bamboo [15], *Ficus hispida* [16], *Aniba rosaeodora* [17], *Mansoa alliacea* [18], Ginkgo [19], *Annona squamosal* [20], and *Artemisia vulgaris* [26]. The methanol extract contains a mixture of phytochemicals that have synergetic effects on inhibition. This study only focused on the use of alkaloids. Alkaloids are heterocyclic compounds containing at least single nitrogen in a ring. Not only nitrogen but there are also various functional groups containing nitrogen and oxygen that get adsorbed on the MS surface. Alkaloids were extracted from three different plants. *Rhynchostylis retusa* (RR) is reported as the alkaloid-containing plant in its rhizome, leaves, and flowers [21, 22]. *Artemisia vulgaris* (AV) is registered as a plant with high alkaloids like 1-nepthylamine, 2-nepthylamine, 3-aminobiphenyl, 4-aminobiphenyl, etc. [23, 26]. *Solanum tuberosum* (ST) is also registered as a high alkaloid-containing plant in its stem. α-solanine and α-chaconine are more common alkaloids found in ST [24]. Hetero-elements, especially nitrogen in the extracted alkaloids, get adsorbed on the MS surface and acts as a barrier to control the corrosion of MS in corrosive media. Adsorption of inhibitor on the MS surface increases the activation energy resulting the decreasing the corrosion rate. Thermodynamic and kinetic parameters for synthetic inhibitors are reported. There are large numbers of green inhibitors reported in corrosion science but barely found the calculation of thermodynamic parameters and adsorption isotherms. So, this study aims the use alkaloids as a green inhibitor to calculate thermodynamic parameters and to identify the adsorption isotherm. Alkaloids were extracted from these plants by the solvent extraction method. Preliminary tests were carried out to confirm the alkaloids and used as an inhibitor for MS in an acidic environment. Thermodynamic parameters and adsorption isotherm have been undertaken.

Experimental Methods

Preparation of specimens

A flat sheet of mild steel was collected from Katuwal Greel Udhyog and Aakash Metal Workshop in Kathmandu, Nepal, and cut into coupons of dimension (4×4×0.55) cm^3. Each coupon was polished by silicon carbide (SiC) paper of 100-1200 grits size, to obtain a clean and corrosion-free surface. Before each experiment, the dimension of each coupon was measured with a digital vernier caliper. Each coupon was washed with hexane, ultrasonicated in ethanol, air-dried, and stored in a desiccator. The process was repeatedly carried out for every experiment.

Extraction of alkaloids

The rhizomes of RR were collected from Godavari, Dhulikhel, and Dakhinkali, Nepal, the stems of ST were collected from Dhulikhel, Nepal. The stems of AV were collected from Budhanilkhantha, Nepal. Collected samples were washed and shade dried. The dried sample was ground into powder form by a grinding mill. 100 g of powder of each sample was soaked in methanol separately and kept for 15 days, followed by filtration. The filtrate was taken as methanol extract. The pH of methanol extract was made alkaline (pH more than 10) by using 5% tartaric acid and ammonia solution. Alkaloid fraction was separated using dichloromethane (DCM) in the separating funnel. A dark green slurry of alkaloids in the organic layer was collected. A small amount of Na_2SO_3 was added to the alkaloid fraction to remove trace water. The solution was then filtered. The organic layer thus obtained was separated, concentrated by using a rotatory evaporator under reduced pressure, and evaporated (below 40 °C) up to dry to obtained alkaloids of methanol extract of RR, ST, and AV. The presence of alkaloids was confirmed by making a qualitative test called Mayer's test.

Preparation of medium

Corrosive and inhibition mediums were prepared by taking sulphuric acid and alkaloids in the same acid respectively. In a 1000 mL volumetric flask, 55.6 mL of concentrated H_2SO_4 (Fisher Scientific, 98 %, sp. gr. 1.84) was taken and diluted up to the mark with distilled water to prepare 1 M H_2SO_4 solution. One gram of alkaloid of each RR, AV, and ST was dissolved in 40 mL of methanol separately, followed by adding 1 M H_2SO_4 to make 1000 mL solution in the separate volumetric flask. Each solution in a volumetric flask was filtered to remove the un-dissolved extract. The filtrates were labeled as 1000 ppm of stock solutions. Alkaloid solutions of required concentrations were prepared from those stock solutions by serial dilutions.

Weight Loss Measurements

An electronic analytical balance (Ohaus Corporation USA, Model: E1RR80) was used to measure the weight of MS coupons before and after the immersion in acid and inhibitor solution. Weight loss measurement was applied in the inhibitor solution of different concentrations (200, 400, 600, 800, and 1000 ppm) to determine the rate of corrosion. Similarly, the temperature effect was studied at 298, 308, 318, and 328 K at three hours immersion in 600 ppm acidic inhibitor solution. The inhibition efficiency (IE %) was determined using the formula:

$$\text{Inhibition efficiency (IE \%)} = \frac{w_o - w_i}{w_o} \times 100 \quad \ldots \quad (1)$$

Where W_0= weight loss in the absence of inhibitors, W_i = weight loss in the presence of inhibitors

The data obtained from this weight loss experiment at different temperature intervals and different concentration intervals were used to calculate the free energy change, activation energy, enthalpy, and entropy change of the corrosion cell. Similarly, the Langmuir adsorption isotherm was also checked based on measured data.

Results and Discussion

Test for alkaloids

Alkaloids in the separated fraction were tested by Mayer's test method and confirmed. For this, a small amount of extract was treated with Mayer's reagent ($HgCl_2$ + KI), a yellow precipitate appeared, indicating the presence of alkaloids.

Adsorption Isotherm

It is a well-known fact that when solid substances are immersed in solutions, molecules from the solution get adsorbed on the solid surface. Likewise, here MS coupons are immersed in acid as well as inhibitors solution. On immersing MS coupons only in acid solution, acid molecules get adsorbed, and a vigorous reaction occurs causing deterioration of MS coupon. Similarly, in the presence of a mixture of acid and inhibitor solution, at first, inhibitor molecules get adsorbed on the MS surface results in a decrease in the deterioration of MS. For a clear explanation of this adsorption process, it is better to know the adsorption isotherm. To know the adsorption isotherm and the type of adsorption between MS and inhibitor molecule, it is better to check adsorption isotherms. Adsorption isotherm gives the basic information on the interaction between the inhibitor and MS surface. At first, water molecules get adsorbed on the MS surface in an aqueous solution. And these adsorbed water molecules are then replaced by inhibitor molecules. So, the adsorption of inhibitor molecules from an aqueous solution is a quasi-substitution process [6, 25, 26]. Langmuir adsorption isotherm equation, (equation 2) is applied to find whether the adsorption process is monolayer or multilayer.

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \quad \ldots (2)$$

The linear relationship between the fraction of covered surface (θ) value and C_{inh} should be established to know the adsorption isotherm. When a graph of $\frac{C_{inh}}{\theta}$ VS C_{inh}, is plotted, a straight line obtained whose intercept value gives the quantitative assessment of adsorption constant.

The inhibitor used here is no single molecule of alkaloid, so each component/compound may have equal/synergetic/or tug of war relation among the molecules for inhibition. For three different inhibitors, Langmuir adsorption isotherm was checked. The R^2 values for three inhibitors are found 1, 1, and 0.996, respectively for RR, AV, and ST in given Fig. 1. It indicates mono-layer adsorption of inhibitors on the MS surface and no interaction between the adsorbed molecules.

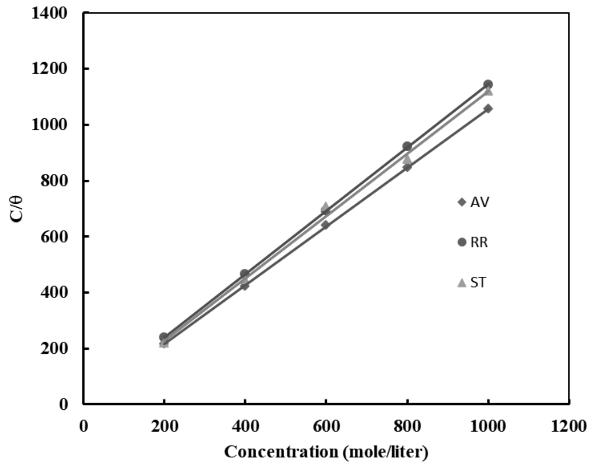

Fig. 1: *Langmuir adsorption isotherm plot for mild steel in 1 M H_2SO_4 with different concentrations of RR, AV, and ST alkaloids.*

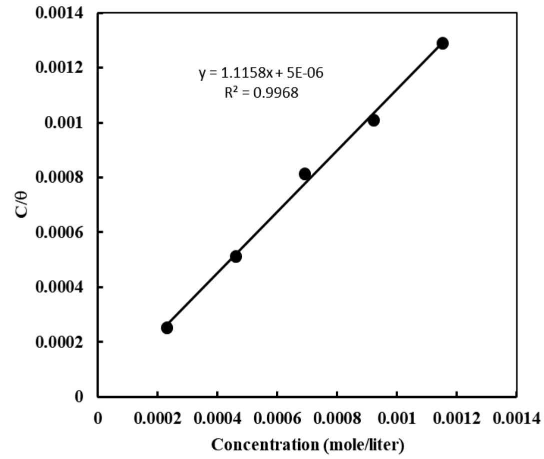

Fig. 2: *Langmuir adsorption isotherm plot for mild steel in 1 M H_2SO_4 as a reference of the molar concentration of α - solanine*

The first figure shows that there is entirely monolayer adsorption. For calculation of the free energy of the system, the molar concentration of the solution is used. It is evaluated here by taking the reference of the molar concentration of α – *solanine* (M. Wt. 868). The data best suited for the adsorption isotherm is Langmuir adsorption isotherm with the linear regression coefficient of 0.996 with a slope equal to 1.115 (Fig. 2). Adsorption constant K_{ads} is calculated from the intercept of straight-line figure 4. This value is used to calculate the value of the free energy of adsorption (ΔGº). The relation between the free energy of adsorption and adsorption constant is,

$$\Delta G^o = -RT \ \text{In} \left(55.5K_{ads}\right) \qquad \ldots (3)$$

Where 55.5 is a concentration of water in solution in mol/L. From the intercept of Fig. 2, the value of the adsorption constant is obtained and is equal to 200000 (Calculation See SF1). This value is used to calculate the free energy (-ΔGº), which is found to be 17.46 kJ/mol. The computed value of ΔGº is less than the standard upper limit of the physical adsorption, i.e. <20 kJ/mol. It indicates that the adsorption of α-solanine molecule on the MS surface is physical adsorption. The value of ΔGº is negative that implies the adsorption of α-solanine on the MS surface is spontaneous [6, 26, 29]. Freundlich adsorption isotherms (Figure See SF2) for these three inhibitors were checked. In the plot, $\ln\theta \ \ VS \ln C$ [6], the linear regression coefficients are found 0.97, 0.75, and 0.05 for RR, AV, and ST respectively, indicating this inhibitor system does not obey Freundlich isotherm.

Effect of Temperature

The temperature has a great influence on corrosion. To find the effect of temperature on corrosion, weight loss measurement in MS samples was carried out in the presence of 600 ppm inhibitor solution and in the absence of inhibitor too at different temperatures. There is good inhibition by inhibitor at low temperature, but inhibition gradually decreased at high temperature. At high temperatures, inhibition may be lost so that there is high weight loss even in the presence of an inhibitor.

As in Fig. 3, the inhibition efficiency of these three different inhibitors is different. For AV, inhibition efficiency is more than 80 % and is almost constant up to 318 K, which drastically decreases on increasing the temperature from that point. The remaining two inhibitors RR and ST, have inhibition efficiency of more than 70 % at 298 K and gradually decrease on increasing temperature. It shows that the inhibitor molecules are attached by feeble attraction forces so that on the increasing temperature, they get detached or there may be a chance of decomposition of alkaloids molecules. In comparison, alkaloids inhibitors obtained from AV have quite more stability than others. It gives the idea that these inhibitors can be useful at low temperatures.

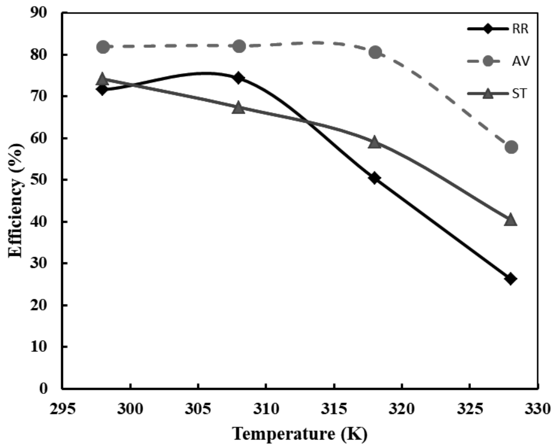

Fig. 3: *Variation in inhibition efficiency of inhibitor in mild steel sample with temperature*

At higher temperatures, the adsorbed inhibitors may detach from the surface or may lose their properties, resulting in a decrease in inhibition efficiency. It gives the basic idea that the interaction between inhibitor molecules with the MS surface is physical adsorption. This result is also following free energy.

Activation energy and thermodynamic parameters

The activation energy of the reaction, in the presence and absence of inhibitor in an electrochemical cell, can be explained by rearranging the Arrhenius equation. The activation energy of the reaction is related to corrosion rate as,

$$\log (CRT) = \log A - \frac{E_a}{2.303RT} \qquad \dots (4)$$

Where A is the Arrhenius pre-exponential constant, T is the absolute temperature, and the log is the base 10 log. Equation (4) reveals that the activation energy of the reaction is equal to the slope of the Arrhenius plot, i.e. a plot obtained between logarithms of corrosion rate with $\frac{1}{2.303RT}$ along axes. Enthalpy and entropy of the system calculated by using transition state equation, an alternative form of Arrhenius equation,

$$\log\left(\frac{C.R.}{T}\right) = \log\left(\frac{R}{nN}\right) + \left(\frac{\Delta H^*}{2.303R}\right) - \frac{\Delta H^*}{2.303RT} \qquad \dots (5)$$

Where **h** is Plank's constant (6.6261×10^{-34} Js), and N is the Avogadro's number (6.0225×10^{23} mol^{-1}). Enthalpy of activation (ΔH^*) is measured as the slope of a straight line by plotting $\log\left(\frac{C.R.}{T}\right) = VS \ \frac{1}{2.303RT}$ in equation (5), and the entropy of activation (ΔS^*) can be calculated from its intercept.

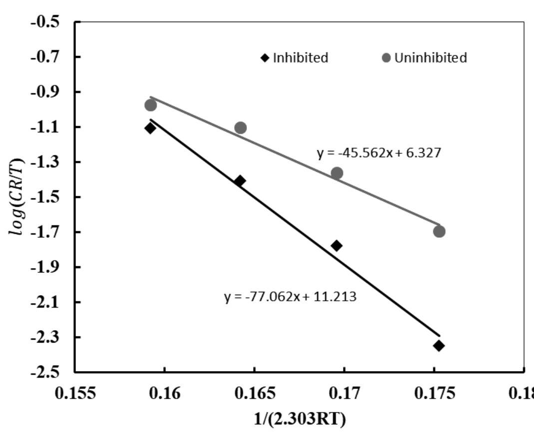

Fig. 4: *Arrhenius plot for MS in 1M H_2SO_4 with and without inhibitor RR*

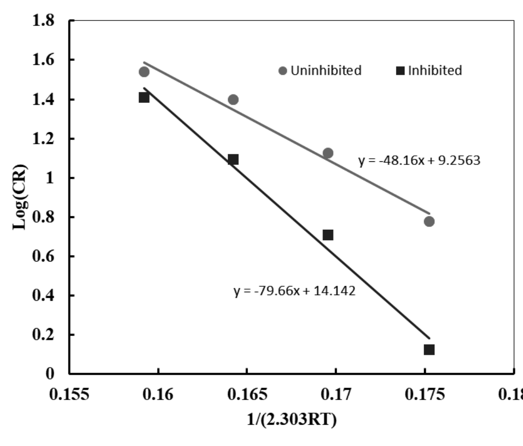

Fig. 5: *Transition state plot for mild steel in 1M H_2SO_4 with and without inhibitor RR*

Arrhenius plot (Fig. 4) shows that the energy of activation of the reaction between MS and acid in the absence of inhibitor is 48.16 kJ/mol and in the presence of inhibitor is 79.66 kJ/mol. In the presence of an inhibitor, the energy of activation increased by 31.5 kJ/mol. This increase in activation energy reveals that the addition of inhibitor molecules suppresses the reaction rate between acid and MS, resulting in a decrease in corrosion rate. From the transition state plot (Fig. 5), the enthalpy of the system in the absence and presence of inhibitor is 45.56 kJ/mol and 76.76 kJ/mol, respectively. Enthalpy is increased by 31.2 kJ/mol on the addition of inhibitor in the corrosion cell. This increase in enthalpy indicates a decrease in the corrosion rate. Similarly, the entropies of these systems have been determined from the intercept of the transition state plot and are equal to -76.39 kJ/K and 17.23 kJ/K in the absence and presence of inhibitors. In acid solution, the entropy is negative, but with the addition of inhibitor, entropy increased to positive.

The Arrhenius plot (Fig. 6) shows that the energy of activation of the reaction between MS and acid in the absence and presence of inhibitor is 49.30 kJ/mol and 70.14 kJ/mol, respectively. In the presence of an inhibitor, the energy of activation increased by 20.84 kJ/mol. This increase in activation energy reveals that with the addition of inhibitors, inhibitor molecules suppress the reaction rate between acid and MS resulting in the decrease in corrosion rate.

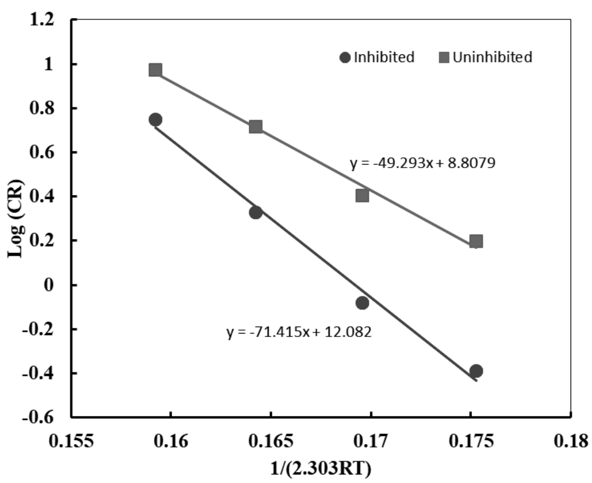

Fig. 8: *Arrhenius plot for MS in 1M H_2SO_4 with and without inhibitor ST*

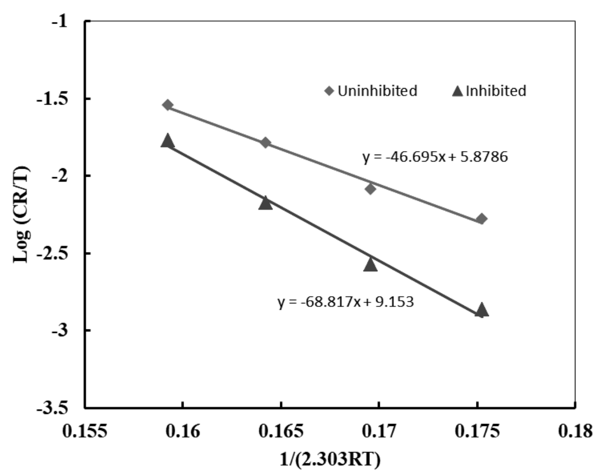

Fig. 9: *Transition state plot for mild steel in 1M H_2SO_4 with and without inhibitor ST*

From the transition state plot (Fig. 7) the enthalpy of the system in the absence and presence of inhibitor is 46.70 kJ/mol and 67.54 kJ/mol respectively. With adding inhibitors, the enthalpy of the system is increased by 20.8 kJ/mol. This increase in enthalpy indicates a decrease in the corrosion rate. Similarly, the entropy of these systems has been calculated from the intercept of the transition state plot and found -85.01 kJ/K and -30.63 kJ/K in the absence and presence of inhibitor respectively. In acid solution, the entropy is negative but with the addition of inhibitor, entropy increased by 54.39 kJ/K.

Arrhenius plot (Fig. 8) shows that energy of activation of the reaction between MS and acid in the absence of inhibitor is 49.29 kJ/mol which on the addition of inhibitor is increased by 22.12 kJ/mol and reached 71.41 kJ/mol. This increase in activation energy reveals that the addition of inhibitor molecules suppresses the reaction rate between acid and MS, resulting in a decrease in corrosion rate. From the transition state plot (Fig. 9) the enthalpy of the system in the absence and presence of inhibitor is 46.69 kJ/mol and 68.81 kJ/mol respectively, and the enthalpy increased by 22.12 kJ/mol in the presence of the inhibitors. This increase in enthalpy indicates a decrease in the corrosion rate. Similarly, the entropies of these systems were calculated from the intercept of the transition state plot and found -85.01 kJ/K and -22.15 kJ/K in the absence and presence of inhibitors. In acid solution, the entropy is negative but increased with the addition of inhibitor.

***Table 1:** Activation parameters of the MS dissolution in 1M H_2SO_4 without and with inhibitor*

Plant Species	Electrolyte	**E_a**	**ΔH***	**E_a-ΔH***	**ΔS***
RR	1M H_2SO_4	48.16	45.56	2.60	-76.39
	Acid with inhibitor (1000 ppm)	79.66	77.06	2.60	17.23
AV	1M H_2SO_4	49.30	46.70	2.60	-85.01
	Acid with inhibitor (1000 ppm)	70.14	67.54	2.60	-30.63
ST	1M H_2SO_4	49.29	46.69	2.60	-85.01
	Acid with inhibitor (1000 ppm)	71.41	68.81	2.60	-22.15

Calculated values of E_a, ΔH^*, and ΔS^* for acid without and with inhibitor are tabulated in table 1. The activation energy of the system has increased with the addition of three different inhibitors. An increase in activation energy reduces the reaction rate resulting in the suppression in corrosion rate. An increase in E_a with the addition of inhibitor shows the strong adsorption of inhibitor molecules on the metal surface with complete or nearly complete coverage so that acid molecules have the least or almost no chance to react with metal [6, 25, 26].

The metal dissolution process is endothermic as the value of ΔH^* is positive. An increase in the value of ΔH^* with the addition of inhibitor shows the decrease in corrosion rate is controlled by kinetic parameters of activation [26, 29]. It is found that E_a is higher than that of ΔH^*, indicating the involvement of a gaseous reaction, simply the hydrogen evolution reactions, resulting in the decrease in the total reaction volume [27, 30]. Here, the value of $E_a - \Delta H^*$ is 2.60 kJ/mol, which is very close to the value of RT for all three inhibitor systems, obeys the relation $E_a - \Delta H^* = RT$. Value of E_a and ΔH^* shows that adsorption of inhibitor on mild steel surface is both physical and chemical adsorption.

In acid, a high negative value for the ΔS^* is obtained. But, in the presence of an inhibitor, the value of ΔS^* is increased. The increase in the value of ΔS^* with the addition of inhibitor implies an increase in disorder or randomness. It is due to the formation of activated complex, i.e. associative mechanism. This behavior is expected to be quasi-substitution, i.e. replacement of water molecules during adsorption of alkaloids on the metal surface [26, 28, 29].

Conclusions

Alkaloids from three different plants have been extracted successfully and used as green inhibitors for MS samples. Temperature effect and concentration-effect have been studied for those inhibitors by weight loss measurement. The activation energy of the system increased with the addition of inhibitors, which implies the adsorption of inhibitor molecules on the MS surface and acts as a barrier. The structure of the adsorbed inhibitor layer is checked by testing Freundlich and Langmuir adsorption isotherms and concluded that the adsorption of those inhibitors on the MS surface obeys Langmuir adsorption isotherm. It suggests that there is monolayer adsorption on the MS surface and no interaction among the inhibitor molecules. Calculated free energy of the system indicates the adsorption process is spontaneous and the adsorption is physical. The enthalpy and entropy of the system also increase in the presence of inhibitors, indicating an association of molecules with MS surface increasing the degree of randomness. It seems all green inhibitors adsorbed physically on the MS surface and reduce corrosion rate, and the inhibitors can only be used at low temperatures.

Acknowledgements

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