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# Thermodynamic and Adsorption studies for corrosion Inhibition of Mild steel in Aqueous Media by *Sargasam swartzii (Brown algae)*

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## Abstract

The Phaeophyceae or brown algae is a large group of marine multicelluar algae and play an important role in marine environments both as food, medicines and industrial purposes. In present study, the inhibition effect of methanolic extract of *Sargassum swartzii* (brown algae) and $Zn^{2+}$ ions (100 ppm) on the corrosion of mild steel in aqueous medium containing 60ppm $Cl^-$ ion was studied by weight loss method at 303 K - 343 K. The energy of activation , adsorption and thermodynamic parameters were evaluated from the results of temperature study. The inhibition efficiency increased with increase in the inhibitor concentration and decreased with rise in temperature. *Sargassum swartzii* (SS) extract is brought about by the increasing its activation energy(Ea) as a result of adsorption is physical adsorption. The adsorption of *Sargassum swartzii* on mild steel surface was found to obey Langmuir , Temkin and Freundlich adsorption isotherms. $\Delta G°_{ads}$ value indicated a strong and spontaneous adsorption of the SS extract components on the metal surface. Thus, it can be concluded that *Sargassum swartzii* – $Zn^{2+}$ inhibitor system acted as a good inhibitor in aqueous medium.

*Keywords*: Seaweeds, *Sargassum swartzii*, mild steel, corrosion, thermodynamic, activation and adsorption studies.

## 1. Introduction

Mild steel finds a variety of applications industrially, for mechanical and structural purposes, like bridge work, building, boiler parts, steam engine parts and automobiles. Mild steel is widely used as an engineering materials for the fabrication of structural and automobile parts due to low cost and tensile strength. Mild steel suffers from severe corrosion in aggressive environment, which needs to be protected. The term “green inhibitor” or “eco friendly inhibitor” refers to the substances that are biocompatibility in nature, environmentally acceptable, readily available and renewable source. Due to bio-degradability, eco-friendliness, low cost and easy availability, the extracts of some plants based chemicals and their by products have been tried as inhibitors for metals under different environments [1-5]. Aquatic plants are incredibly rich naturally synthesized chemical compounds (eg:organic acids, glucosinolates, alkaloids, flavonoids, terpenoids, polyphenols, and tannins) and most of them are known to have corrosion inhibition efficiency. In general, green corrosion inhibitor can be grouped into two categories, namely organic green inhibitor and inorganic green inhibitors. Presence of hetero atoms (S, N and O) with free electron pairs, aromatic rings with delocalized ($\pi$) electrons, high molecular weight alkyl chains, substituent group in general improves inhibition efficiency. For the present study, methanolic extract of *Sargassum swartzii* (SS)(brown algae) was used as corrosion inhibitor for mild steel in aqueous medium containing 60ppm $Cl^-$ ion at 303 K -343 K by weight loss studies.

## 2. Experimental methods

### 2.1. Collection of Aquatic Plant Material

The study was carried out on the seaweeds were collected from Mandapam coastal regions, South East Coast of India. Seaweed sample was picked with hand and immediately washed with sea water to remove the foreign particles, sand particles and epiphytes. Then it was kept in an ice box containing slush ice and immediately transported to the laboratory and washed thoroughly using tap water to remove the salt on the surface of the sample. Then the seaweeds were spread on blotting paper to remove excess water and dried. Further, the seaweed sample was authenticated namely ***Sargassum swartzii***, **C.Agardh** by Dr. P. Palanisamy, Scientist-C, Botanical Survey of India, Coimbatore, Tamilnadu, India.

### *2.2. Preparation of the Sargassam swartzii (SS) extract*

In the present work, the inhibitor was obtained by reflux method from *Sargassum swartzii*(SS). The *Sargassum swartzii* (SS) were cleaned, chopped into small pieces, air dried, and stored at freezer . The 400g of *Sargassum swartzii* material was transferred to 2000ml round bottomed flask, directly heated in a mantle with water condenser for about 6 hrs at room temperature. The resulting solution was concentrated and evaporated to dryness under vacuum using rotatory evaporator. This dried extract of *Sargassum swartzii* was used as corrosion inhibitor.

### *2.3. Preparation of inhibitor solution - Sargassum swartzii (SS)*

The solvent methanol was used to prepare the extract and to get a fine powder of *Sargassum swartzii* (SS). It was used for the corrosion inhibition monitoring techniques. The stock solution of 1g of powdered *Sargassum swartzii* (SS) is dissolved in methanol in 100 ml standard measuring flask as stock solution. Dilution of various desired concentrations (0 to 120 ppm) are made from the above stock solution.

### *2.4. Weight loss method*

Rectangular sample of the dimensional size of 1.0 X 4.0 X 0.2cm have been cut from a same sheet of mild steel. A hole was drilled in the specimen, mechanically polished, degreased with acetone and trichloroethyl amine, washed with double distilled water, dried and stored in desiccators for weight loss study. In the present study, weighed test pieces were immersed, triplicate in aqueous medium with various concentrations of inhibitor. They were removed after a particular period of immersion, washed, dried and reweighed. The specimens were abraded with abrasive emery papers with Grid Numbers: 320, 400, 600, 800 and 1000 grade, washed in acetone, degreased with trichloro ethyl amine, dried at room temperature and stored in the moisture free desiccators before they are used for corrosion studies. The specimens were weighed before immersion in the test solutions and reweighed after immersion. From the initial and final masses of the specimen, the weight loss was calculated. The experiments were performed for evaluating the various parameters;

*Effect of concentration (viz. 0 ppm, 20 ppm, 40 ppm, 60 ppm, 80 ppm, 100 ppm and 120 ppm) of inhibition efficiency on mild steel in aqueous media.

*Effect of temperature (viz. 303K, 313K, 323K, 333K and 343K) of inhibition efficiency on mild steel in aqueous media. (For temperature study, the time of immersion was 1 hour).

## 3. Results and discussion

### ***3.1. Effect of temperature on Corrosion Rate (CR) and Inhibition Efficiency (IE) of mild steelin aqueous medium of inhibitor system***

Temperature has a vital effect on the rate of metal electrochemical reaction. The effect of temperature on inhibition reaction of inhibited aqueous metal surface is highly complex, because many changes may occur on the metal surface, such as rapid etching, rupture, desorption of the inhibitor, decomposition and/ or rearrangement of the inhibitor. At a constant bulk concentration of an adsorptive type inhibitor [6], the temperature variation affects the metal dissolution and the degree of metal surface.

The Corrosion Rate (CR) and Inhibition Efficiency (IE) for mild steel in aqueous media at 303K, 313K, 323K, 333K and 343K in absence and presence of SS extract with $Zn^{2+}$ ions (100 ppm) are given in Table 1. Effect of temperature on CR of SS extract in aqueous medium is represented in Figure 1.

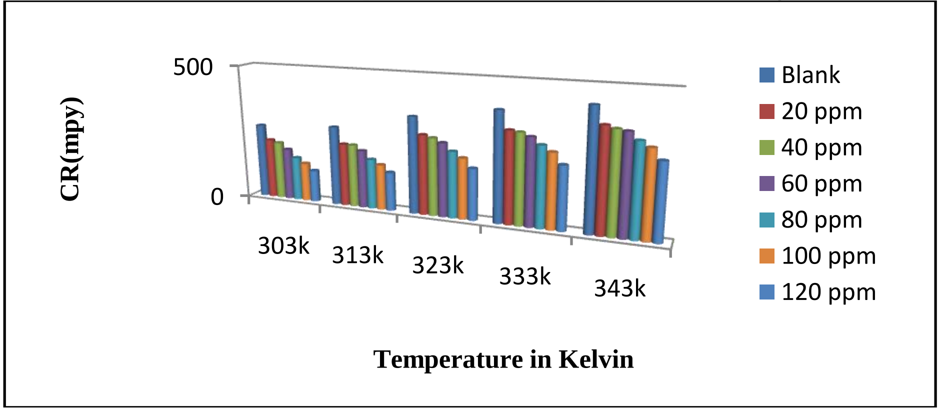

**Figure 1** : Effect of temperature on CR of SS extract in aqueous medium.

The presence of inhibitor leads to decrease in CR. It is noticed that IE of mild steel increases with increase of SS extract concentration upto 57.24% (120 ppm) at 303 K. As a temperature is increases, CR increases and IE decreases. The increase in CR is more pronounced with the rise in temperature for the uninhibited aqueous solution. The result showed that the addition of SS extract concentration decreases the metal dissolution in aqueous medium. This hindrance to dissolution may be due to the formation of Fe - SS complex layer [7]. The nature of adsorption (physical or chemical adsorption) has been confirmed by the thermodynamic parameters analysis as discussed in the forth coming sections.

**Table 1:** Effect of various temperatures on mild steel corrosion in aqueous medium containing 60 ppm $Cl^-$ ion. Inhibitor System: *Sargassum swartzii* (SS) - $Zn^{2+}$ (100ppm). Immersion time: 1hr. $Cl^-$ ion - 60 ppm

| **SS ppm** | **303K** | | **313K** | | **323K** | | **333K** | | **343K** | |
|---|---|---|---|---|---|---|---|---|---|---|
| | **IE (%)** | **CR (mpy)** | **IE (%)** | **CR (mpy)** | **IE (%)** | **CR (mpy)** | **IE (%)** | **CR (mpy)** | **IE (%)** | **CR (mpy)** |
| 0 | _ | 273.72 | _ | 290.31 | _ | 352.52 | _ | 398.14 | - | 435.47 |
| 20 | 19.70 | 219.81 | 20.86 | 229.76 | 17.65 | 290.31 | 16.67 | 331.78 | 14.29 | 373.26 |
| 40 | 22.73 | 211.51 | 21.01 | 229.35 | 20.00 | 282.02 | 17.71 | 327.64 | 16.48 | 363.71 |
| 60 | 31.01 | 189.12 | 27.14 | 211.51 | 24.00 | 267.91 | 20.83 | 315.19 | 17.62 | 358.74 |
| 80 | 41.50 | 160.09 | 37.14 | 182.48 | 31.77 | 240.54 | 27.08 | 290.31 | 23.81 | 331.78 |
| 100 | 48.33 | 141.42 | 42.86 | 165.89 | 37.53 | 220.22 | 32.30 | 269.57 | 28.24 | 312.50 |
| 120 | **57.24** | 117.05 | 51.43 | 141.01 | 47.06 | 186.63 | 42.35 | 229.51 | 37.14 | 273.72 |

### *3.2. Energy of activation (Ea) of metal dissolution and inhibition processes*

Temperature investigations allow the determination of activation energy in the absence and presence of inhibitor. The increase of temperature increases the rate for all electrochemical processes and influences adsorption isotherms and kinetic parameters. The obtained results may lead to elucidate the mechanism of corrosion inhibition. The adsorption mechanism is offered by considering the apparent activation energies (Ea) for mild steel dissolution in aqueous medium in the absence and presence of different concentrations of SS and 100 ppm of $Zn^{2+}$ ion.

The activation parameters play an important role in understanding the inhibitive mechanism of the inhibitors. The apparent activation energy and pre exponential factor for different concentrations of SS extract were calculated from the plot of log CR versus 1/T using the following Arrhenius type equation (1) .

$$CR = A \exp(-Ea/RT) \quad \text{----->} (1)$$

Where, Ea is the apparent activation energy, T is the absolute temperature, A is the Arrhenius pre-exponential constant and R is the universal gas constant [8]. The above equation (1) can be written by taking logarithm as,

$$\text{Log}(CR) = A-(Ea/RT) \quad \text{----->} (2)$$

The Arrhenius plot for SS extract in aqueous medium is shown in Figure 2. The values of $E_a$ at different concentrations of SS are calculated from slopes and intercepts of Arrhenius plot and the results are shown in Table 2. The linear regression co-efficient are close to unity.

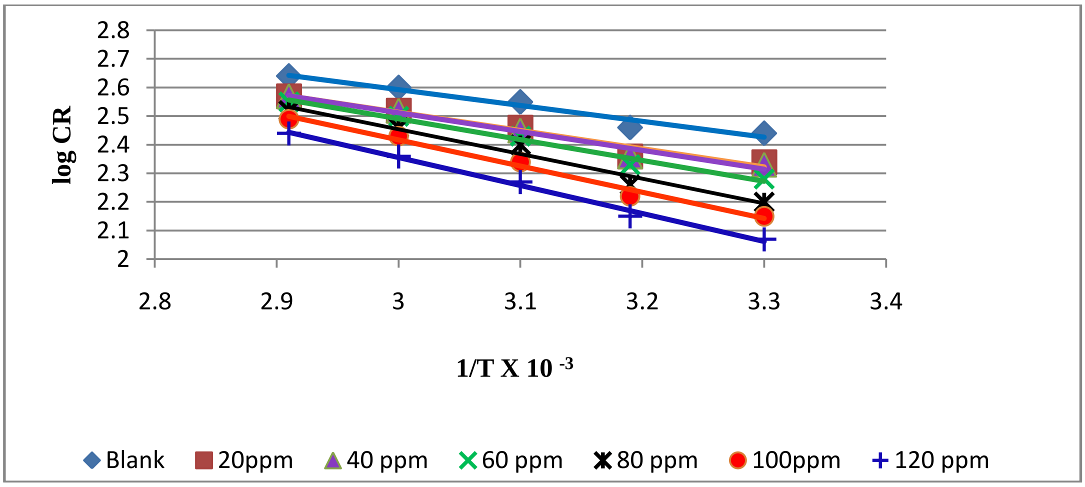

**Figure 2** :Arrhenius plot of log CR Vs 1/T on mild steel corrosion for SS extract in aqueous medium.

**Table 2** : Activation parameters for MS in aqueous medium containing 60 ppm $Cl^-$ ion in absence and presence of different concentration of *Sargassum swartzii* (SS) -$Zn^{2+}$ion.

| **Inhibitor concentration (ppm)** | **$E_a$ (KJ /mol )** | **ΔH ° (KJ /mol )** | **ΔS ° J /mol /K** |
|---|---|---|---|
| 0 | 10.75 | 8.07 | -172.0 |
| 20 | 12.31 | 9.63 | -168.8 |
| 40 | 12.90 | 10.22 | -167.1 |
| 60 | 14.51 | 11.83 | -162.6 |
| 80 | 16.62 | 13.94 | -157.1 |
| 100 | 17.91 | 15.24 | -153.8 |
| 120 | 18.90 | 16.23 | -152.1 |

The value of Ea for the uninhibited aqueous is 10.75 KJ/mol. The activation energy (Ea) for SS extract ranges from 10.75 KJ/mol/ to 18.90 KJ/mol with increasing inhibitor concentration. From Table 2, it is found that Ea values of the inhibited solutions are higher than in uninhibited solutions. It shows that values of Ea enhance with an increase in the inhibitor concentrations from 20 ppm to 120 ppm is due to the deceleration of the corrosion rate of mild steel.

The result (Table 2) suggests that corrosion inhibition by the SS extract is brought about by the increasing its activation energy. There is an increase in Ea as a result of adsorption of the constituents on the mild steel surface making a barrier for mass and charge transfer. The range of Ea values (from 10.75 KJ/mol to 18.90 KJ/ mol ) are lower than the threshold value of 80 KJ/mol required for chemical adsorption. This means that adsorption is physical adsorption [9]. Hence, the fairly high value of activation energy in the present of SS extract suggests strong physical adsorption.

The thermodynamic parameters like enthalpy (ΔH°) and entropy (ΔS°) of corrosion process were calculated using the transition state equation (3).

CR =RT/Nh exp. ΔS°/R exp ( -Δ H°/RT) -----> (3)

Where, h is planck's constant , N is Avagadro number, R is the universal gas constant, ΔH is the enthalpy of activation and ΔS is the entropy of activation. A plot of log (CR/T) Vs 1/T provide straight lines with a slope of (-ΔH°/2.303RT) and an intercept of (log R/Nh) + ΔS°/2.303R) are represented in Figure 3, from which the values of ΔH° and ΔS° are calculated and tabulated in Table 2.

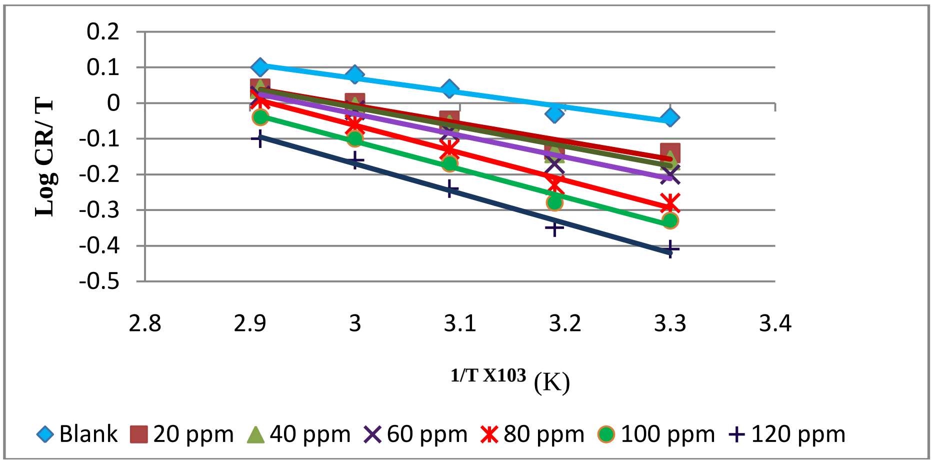

**Figure 3:** Alternative Arrhenius plot for mild steel in aqueous medium in the absence and presence of different concentrations of SS extract

In general , the values of ΔH° lower than 43.2 KJ/mol which attributed the physical adsorption and the value 100KJ/mol indicate chemical adsorption [10]. From Table 2, it was found that the positive sign and values (8.07 KJ/mol to16.23 KJ/mol) of activation of enthalpy ($\Delta H^*$) in the presence of SS extract reflect the endothermic nature of the mild steel dissolution process [11]. The increase in $\Delta H^*$ with inhibitor concentration reveals that decrease in mild steel, CR is mainly controlled by kinetic parameters of activation [ 12 ]. The values of $\Delta S°$ in the absence and presence of inhibitors are negative. This implies that the activation complex is the rate determining step representing association rather than dissociation, indicating that a decrease in disorder takes place on going from reactants to the activated complex [13, 14].

### *3. 3. Adsorption isotherms*

The electrochemical process on the metal surface is likely to be closely related to the adsorption of the inhibitors and the adsorption is known to depend on the structure of the inhibitors. The adsorption of the inhibitor molecules from aqueous solution can be regarded as quasi –substitution process between organic compound in the aqueous phase ($Org_{(aq)}$)and water molecules at the electrode surface ($H2O_{(sol)}$).

$$Org_{(sol)} + xH2O_{(aq)} = Org_{(aq)} + x\,H2O_{(sol)}$$

Where, x (size ratio) is the number of water molecules in the inhibitor.

Corrosion inhibition is a surface phenomenon. The interaction of surface inhibitor can be estimated from the experimental data. The inhibition efficiency depends on the type, number of active sites at the metal surface, charge density, molecular size of inhibitor, metal-inhibitor interactions and the metallic complex formation. Adsorption isotherms give information on the metal inhibitor interactions[15]. Adsorption isotherms are very important in determining the mechanism of Organo-electrochemical reactions, the most frequently used are those of Langmuir, Temkin, Freundlich, Frumkin, Parsons, Flory –Huggins and Bockris – Swinkels. All these isotherms are of the general form :

$$f(\theta ,x) \exp (-2a\, \theta) = kc$$

Where, f (θ ,x) is the configurational factor that depends essentially on the physical model and assumptions underlying the derivation of the isotherm, θ is the degree of surface coverage, c is the inhibitor concentration in the electrolyte, x is the size ratio indicating the number of water molecules displaced by one molecule of organic inhibitor, a is the molecular interaction parameter and k is the equilibrium constant for the adsorption. The mechanism of corrosion inhibition is generally believed to be due to the formation and maintenance of a protective film on the metal surface [16].

The performance of the studied inhibitor as a corrosion may be attributed to the presence of electron donar atoms like N or S or O in the molecular structure of the inhibitor which favours the greater adsorption of it on the metal surface. Several attempts were made to fit various isotherms. In the present study, the experimental data were best fitted by Langmuir, Temkin and Freundlich adsorption isotherms.

The nature of the inhibitor interaction with the corroding surface has been deduced from the adsorption characteristics of the inhibitor. Surface coverage (θ) values are much useful to measure the adsorption characteristics. The surface coverage of an inhibitor at any concentration is calculated using the equation (4 ).

$$\theta = \frac{W_0 - W}{W_0} \quad \text{----->}\ (4)$$

Where , Wo and W are the weight loss without and with inhibitor respectively.The experimental data obtained with the different inhibitor concentrations of *Sargassum swartzii* extract and $Zn^{2+}$ ion (100ppm) in aqueous medium containing 60ppm $Cl^-$ ions at different temperatures from 303 K to 343 K were applied to Langmuir, Temkin and Fruendlich adsorption isotherms.

#### i) Langmuir adsorption isotherm on mild steel corrosion inhibition by SS extract - $Zn^{2+}$ ion inhibitor system

The experimental data were tested graphically to fit a Langmuir, Temkin and Freundlich adsorption isotherms. For all isotherms, the linear regression parameters are listed and tabulated in Table 3. A plot of log (θ /1- θ) against log C (Figure 4) gives a straight line ($R^2$> 0.9) indicating that adsorption follows the Langmuir adsorption isotherm. The strong correlation ($R^2$>0.9) for the Langmuir adsorption isotherm plot confirmed by the validity approach. It is observed that all linear correlation coefficients (R) are almost equal to 1 which indicates the adsorption of *Sargassum swartzii(SS)* extract on mild steel surface obeys Langmuir adsorption isotherm.

Langmuir adsorption isotherm indicated that the SS extract contains organic compounds having polar atom or groups which are adsorbed on the metal surface may interact by mutual repulsion or attraction [17-19].

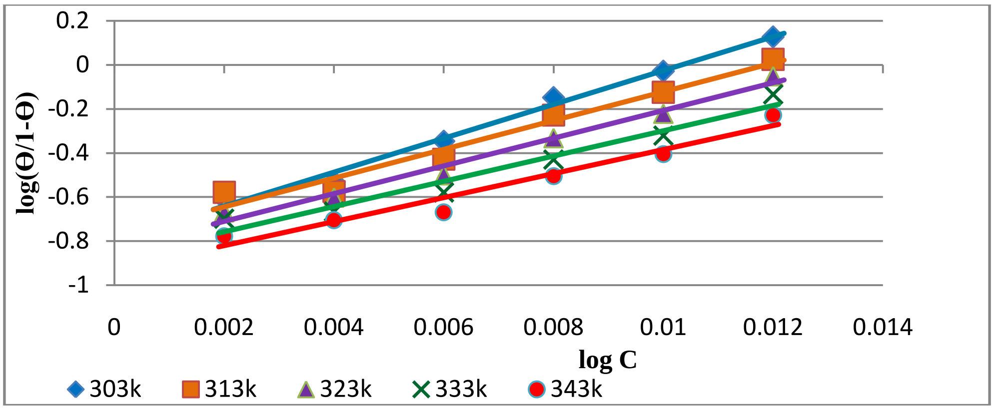

**Figure 4**: Langmuir adsorption isotherm of SS extracts on MS in aqueous medium at different temperatures.

**ii) Temkin adsorption isotherm on mild steel corrosion inhibition by SS extract - $Zn^{2+}$ ion inhibitor system**

According to this isotherm, the plot of surface coverage (θ) obtained from weight loss method versus log C at different concentrations of the inhibitors showed a straight line, which is graphically represented in Figure 5. It indicating that the adsorption of the inhibitor from aqueous medium on mild steel surface follows the Temkin adsorption isotherm. From Temkin datas observed that the corrosion inhibition by inhibitor compounds is being a result of their adsorption on the metal surface [20].

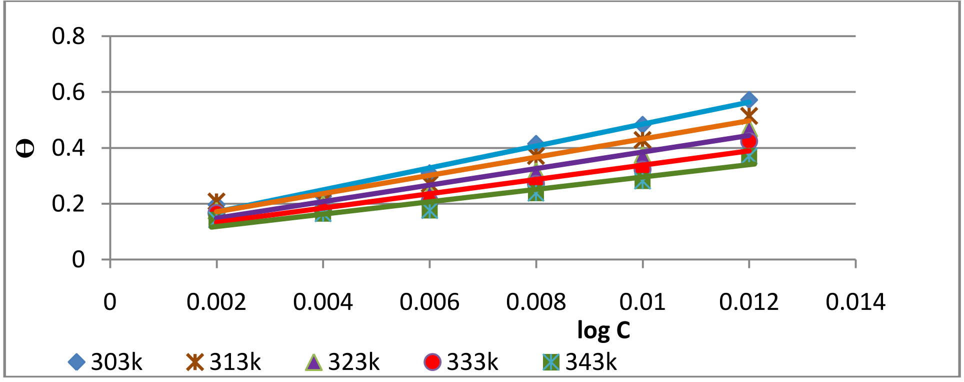

**Figure 5 :** Temkin adsorption isotherm of SS extracts on MS in aqueous medium at different Temperatures.

**iii) Freundlich adsorption isotherm on MS corrosion inhibition by SS extract- $Zn^{2+}$ ion inhibitor system**

A plot of log θ against log C are shown in Figure 6. The linearity shows that the adsorption of the inhibitors on mild steel surface in aqueous medium containing 60ppm $Cl^{-}$ ion follows Feundlich isotherm [ 21]. The adsorption studies clearly indicated that the experimental data fitted the Langmuir, Temkin and Freundlich adsorption isotherm with correlation co-efficient greater than 0.90. The adsorption equilibrium constant ($K_{ads}$) value in( g/L) decreases with increasing temperature, which indicates that, it is easily adsorbed on the mild steel surface for the inhibitor at lower temperature. But when the temperature was higher, the adsorbed inhibitors tended to desorbs from the mild steel surface [22,23].

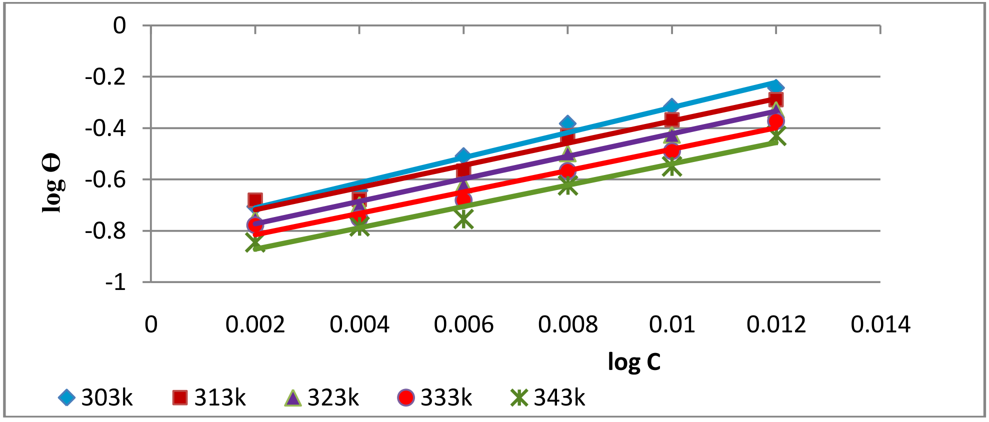

**Figure 6:** Freundlich adsorption isotherm of SS extracts on MS in aqueous medium at different temperatures**.**

**Table 3:** Adsorption parameters on MS corrosion inhibition by SS – $Zn^{2+}$ system obtained from Langmuir, Temkin and Freundlich adsorption isotherms**.**

| **Inhibitor system** | **Temp (K)** | **Adsorption Isotherms** | | | | | |
|---|---|---|---|---|---|---|---|
| | | **Langmuir** | | **Temkin** | | **Freundlich** | |
| | | $\mathbf{K_{ads}}$ (g/L) | $\mathbf{R^2}$ | $\mathbf{K_{ads}}$ ( g/L) | $\mathbf{R^2}$ | $\mathbf{K_{ads}}$ ( g/L) | $\mathbf{R^2}$ |
| *Sargassum swartzii* + $Zn^{2+}$ (100 ppm) | 303 | 6.50 | 0.9516 | 4.21 | 0.9354 | 2.49 | 0.9665 |
| | 313 | 4.21 | 0.9137 | 3.32 | 0.8999 | 1.96 | 0.9248 |
| | 323 | 3.70 | 0.9288 | 2.96 | 0.9026 | 1.92 | 0.9450 |
| | 333 | 2.85 | 0.8979 | 2.52 | 0.8677 | 1.67 | 0.9134 |
| | 343 | 2.47 | 0.9034 | 2.25 | 0.8682 | 1.57 | 0.9170 |

### *3.4. Thermodynamic parameters of adsorption of Sargssum swartzii (SS) in aqueous medium*

Thermodynamic parameters play an important role in understanding the inhibitive mechanism. The free energy of adsorption $\Delta G°_{ads}$, which can characterize the interaction of adsorbed molecules and metal surface, was calculated using the equation (5).

$\Delta G°_{ads} = - RT\ln (55.5 \times k_{ads})$ -----> (5)

Where k is the adsorption equilibrium constant, R is the gas constant (8.314J/K/mol), T is the absolute temperature in kelvin and the value 55.5 is the concentration of water in solution expressed in mol/L[24].The free energy of adsorption is related to the equilibrium constant of adsorption using the following equation,

$K_{ads} = 1/55.5 \exp (\Delta G°_{ads})/RT$-----> (6)

Thermodynamic parameter for adsorption of the SS extract in aqueous medium containing 60 ppm $Cl^-$ ion is given in Table 4. The negative value of $\Delta G°_{ads}$ ensures the adsorption process and stability of the absorbed layer on the electrode surface. The stability of the adsorbed layer decreases with increase in temperature. This is clearly seen from the decrease in the absolute value $\Delta G°_{ads}$ with rise in temperature. This also refers to physical adsorption.

Generally, the values of $\Delta G_{ads}$ upto -20 KJ/mol are constant with the electrostatic interaction between the charged molecules and 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 co-ordinate type of bond (Chemisorption)[25].

Based on the experimental data presented in Table 4, the calculated value of $\Delta G°_{ads}$ was found to be negative less than 40KJ/mol. The values of $\Delta G°_{ads}$ for SS extract are in the range -20.92 KJ/mol to -24.04 KJ/mol, indicating that phyto constituents are adsorbed on the metal surface by a strong physical adsorption process. The relatively high and negative free energy value indicates a strong and spontaneous adsorption of the SS extract components on the metal surface, which explains its high corrosion IE. Thus, the mechanism to be proposed for the SS - $Zn^{2+}$ inhibitor system is most probably based on physical adsorption . In general, the adsorption may be enhanced by the presence of hetero atoms like N / O / S atoms with lone pair of electrons, in the inhibitor molecules that makes it adsorbed electrostatically on the metal surface forming insoluble stable films and thus decreasing metal dissolution. The enthalpy of adsorption $\Delta H°_{ads}$ and entropy of adsorption $\Delta S°_{ads}$ were obtained from Gibbs –Helmholtz equation,

$\Delta G^{\circ}_{ads} = \Delta H^{\circ}_{ads} - T\Delta S^{\circ}_{ads}$ -----> (7)

A plot of $\Delta G^{\circ}_{ads}$ against T gives a straight line with intercept $\Delta H^{\circ}_{ads}$ and slope $\Delta S^{\circ}_{ads}$ are represented in Figure 7. The values of thermodynamic parameters such as $\Delta S^{\circ}_{ads}$, $\Delta H^{\circ}_{ads}$ provide supplementary information about the mechanism of corrosion. Temperature studies showed in aqueous medium for SS extract yield a negative value for enthalpy of adsorption ($\Delta H^{\circ}_{ads}$) . It may be due to adsorption is endothermic which confirms that inhibition performance decreases with temperature. Such behaviour can be interpreted on the basis that increasing temperature resulted in partial desorption of adsorbed inhibitor molecules from the metal surface. Generally, positive values of heat of adsorption indicate an exothermic, (ie. chemical adsorption) where as negative values suggest physical adsorption.

In the study, $\Delta H^{\circ}_{ads}$ values obtained lies in range from -9.163KJ/mol to -17.31 KJ/mol indicates strongly physical adsorption of inhibitor molecules on mild steel surface.The value of $\Delta S_{ads}°$ in SS extract are found to decrease with increasing temperature. This may be due to the fact that predominant desorption of the constituents in the adsorption- desorption equilibrium [26].

**Table 4:** Thermodynamic parameters of adsorption of MS in aqueous medium containing 60 ppm $Cl^-$ ion in the presence of *Sargassum swartzii* (SS) extract**.**

| **Concn (ppm)** | **$\Delta G°_{ads}$ (KJ/ mol)** | | | | | **$\Delta H°_{ads}$ (KJ/ mol)** | **$\Delta S°_{ads}$ (J/ mol/K)** |
|---|---|---|---|---|---|---|---|
| | **303K** | **313 K** | **323 K** | **333 K** | **343 K** | | |
| 20 | -22.21 | -23.13 | -23.32 | -23.85 | -24.04 | -9.163 | -43.8 |
| 40 | -20.92 | -21.35 | -21.87 | -22.13 | -22.55 | -8.715 | -40.4 |
| 60 | -20.97 | -21.17 | -21.47 | -21.56 | -21.62 | -15.887 | -16.9 |
| 80 | -21.40 | -21.63 | -21.68 | -21.72 | -21.88 | -18.271 | -10.5 |
| 100 | -21.53 | -21.67 | -21.76 | -21.85 | -21.90 | -18.922 | -8.7 |
| 120 | -21.97 | -22.09 | -22.32 | -22.49 | -22.54 | -17.31 | -15.4 |

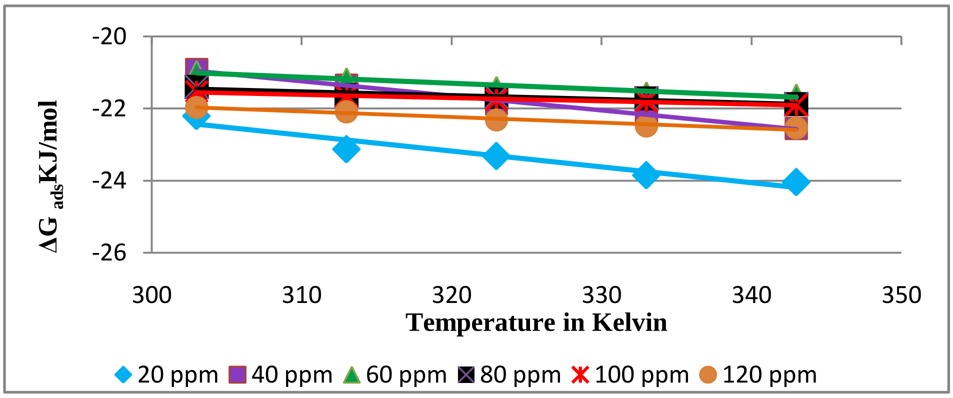

**Figure 7**: A plot of Gibbs free energy versus absolute temperature**.**

Inspection of Table 4, it is noted the negative value of $\Delta S°_{ads}$ mean that the process of adsorption is accompanied by a decrease in entropy. It is explained as : before the adsorption of surfactant on to the mild steel surface, the chaotic degree of corroded mild steel surface is high, but when inhibitor molecules are orderly absorbed onto the mild steel surface, a decrease in entropy was observed [27-29]. $\Delta S°_{ads}$ values have not shown any gradual increase or decrease with respect to inhibitor concentration. It may be due to the fact that the adsorption of phyto constituents is not only dependent on constituents present in the corrosive media, but also depend in the orientation of the consitutents.

## Conclusion

1. The investigated aquatic plant *Sargassum swartzii* are found to perform well as corrosion inhibitors in aqueous solution containing 60ppm $Cl^-$ ion.
2. The inhibition efficiency increases with increase in the concentration, but decreases with rise in temperature.
3. *Sargassum swartzii* extract is brought about by the increasing its activation energy. There is an increase in Ea as a result of adsorption is physical adsorption.
4. The adsorption of *Sargassum swartzii* on mild steel from aqueous medium obey Langmuir , Temkin and Freundlich adsorption isotherms.
5. $\Delta G°_{ads}$ value indicates a strong and spontaneous adsorption of the SS extract components on the metal surface. Thus, it can be concluded that *Sargassum swartzii* - $Zn^{2+}$ inhibitor system were found to be in good agreement with the experimental results.

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