CORROSION INHIBITORS FOR MILD STEEL IN SULPHURIC ACID

[1]A. Gilbert Sunderraj & [2]R. Sethupathi

[1]Assistant Professor , Department of Chemistry,
Vinayaka Mission's Kirupananda Variyar Engineering College,
Vinayaka Mission's Research Foundation (Deemed to be University), Salem.

[2]Associate Professor, Department of Physics,
Vinayaka Mission's Kirupananda Variyar Engineering College,
Vinayaka Mission's Research Foundation (Deemed to be University), Salem.

Abstract:

The corrosion inhibition of mild steel in 1M H_2SO_4 by the Calophyllum inophyllum oil has been studied using weight loss method, adsorption isotherm methods and thermodynamic calculation. The results show that the inhibition efficiency increases with the increase of the extract concentration. The effect of temperature on the corrosion behavior of mild steel in 1M H_2SO_4 with addition of the extract was also studied. The adsorption of the extract molecules on the steel surface obeys Langmuir adsorption isotherm and occurs spontaneously. The activation energy as well as other thermodynamic parameters for the inhibition process was calculated. These thermodynamic parameters show strong interaction between inhibitor and mild steel surface.

Keywords: - corrosion, inhibition, thermodynamic, molecules

I. Introduction

1.1 Corrosion and Its Importance

Corrosion is one of the naturally occurring processes generally defined as the deterioration of a metal or its properties because of a reaction with its environment. Corrosion can also be defined as the destructive attack of a metal by chemical or electrochemical reaction with the environment. The interaction between the material and their environment sometimes give beneficial effects such as passivation, pickling of steel, storage of electrical energy in dry cells, etc., But most of the time it leads to destructive results. The environment under which the metals undergo corrosion is termed as corrosive or aggressive environment. Corrosion degrades useful properties of materials and structures including strength, appearance and permeability to liquids and gases. Corrosion can cause more economic loss like the earthquake, forest fire, flood and severe weather disturbance.

Inhibitors:

Inhibitors are chemical compounds added in small quantities in order to reduce the corrosion rate. The presence of such compounds retards the corrosion process and keeps its rate to a minimum and, thus, prevents economic losses due to metallic corrosion. The chemicals that can act as corrosion inhibitors may be inorganic or organic.

Inhibitor efficiency (%)

$$= \frac{\text{Uninhibited corrosion rate} - \text{Inhibited corrosion rate}}{\text{Uninhibited corrosion rate}}$$

Inhibitors slow corrosion processes by:

- Reducing the anodic and cathodic reaction speed;
- Reducing the movement or diffusion of ions to and from the metallic surface;
- Increasing the electrical resistance of the metal surface.

1.2 Importance of Inhibitors

An inhibitor is a chemical substance which when added in small amount to an environment effectively checks, decrease or prevent the reaction of the metal with the environment. In a sense, an inhibitor can be considered as a retarding catalyst. Corrosion inhibitors are added to many systems including cleaning pads, cooling systems, various refinery units, chemical operations, steam generators, ballast tank, oil and gas production units. Inhibitors function by

i) Adsorption as a film on to the surface of the corroding medium.

ii) Inducing the formation of a thick product.

iii) Changing the characteristics of the environment either by producing protecting precipitates or by inactivating an aggressive constituent.

So that it prevent or arrest the corrosion processes. It can also interface with the cathodic, anodic or both reactions.

- ❖ Mild steel (MS) has been extensively used under different conditions here Chloride, sulphate and nitrate ions in aqueous media are particularly aggressive and accelerate corrosion.
- ❖ The aim of the present work is to find naturally occurring cheap and environmentally safe non-edible oil that could be used for inhibiting the corrosion of mild steel.
- ❖ In present study non-edible Calophyllum inophyllum oil is used as green corrosion inhibitor for Mild steel in 1N Sulphuric acid environment.

2. Proposed Methodology

Methods and Instrumentation

There are many corrosion monitoring techniques like Tafel linear extrapolation method (potentiodynamic), cyclic voltametric, A.C. impedance and weight loss method can be used to find the corrosion rate. In this present investigation, weight loss method is used to find the corrosion rate. The procedures for the above said technique are described as follows.

2.1instruments used:

1. Experimental setup for Weight loss measurements
2. Single pan electronic balance

2.2preparation of Specimen

All the test specimens of mild steel were cut to an overall apparent size of 2.5 cm × 1 cm. The specimens were polished with different grades of emery papers namely 150, 650, 400, 800, 1200 and 2000 and these were decreased with trichloroethylene, dried and finally weighed.

2.3Preparation of Solutions

The solutions required for carrying out the experiments were prepared as follows.

2.4sulphuric Acid

1N Sulphuric acid solution was prepared by mixing 28 ml of H_2SO_4 (AR) in 1000 ml double distilled water.

2.5preparation of Stock Solution

The fruits of ripe and non-germinating Calophyllum inophyllum(CIM) seed are collected to crack the shells without damaging the kernels and it is exposed to the sun directly. The kernels become brownish in colour with an aromatic odour and increase their oil content. This process is completed within 55 to 65 days and it can be stored for a long period. The oil can be easily extracted from the dark kernels using only by mechanical pressing. The resulting oil has a rich texture and greenish amber in colour. This resulting oil is used as an inhibitor in the present study.

2.6weight loss method

Mild steel specimens were weighed using electronic balance. After initial weighing, the specimens in triplicate were immersed in 50 mL of 1N H2SO4 in the absence and presence of different concentrations (1%, 2%, 3%, 4% and 5% v/v) of the plant extracts (CIM) at 303K. Then coupons were removed washed, dried and weighed. The experiment was carried out at different immersion periods (3 and 5 Hrs). Weight loss was measured for all the above mentioned timings at 303K. Corrosion inhibition studies were also carried out at different temperatures (303 and 323K). The thermostat was set to the appropriate temperature.

2.7Measurements Of Corrosion Rate

The corrosion rates were calculated in millimiles per year (mmpy) using the relation.

$$\text{Corrosion Rate} = \frac{87.6 \times W}{A \times T \times D}$$

Where W = Weight loss in milligrams, A = Area of specimen in cm2, D = Density of the specimen in gms/cm3 and T = Time for which the specimens were exposed to the corroding medium (in hours).

2.8Determination of inhibitor efficiency

Weight losses in the presence and absence of inhibitor were determined by weight loss method. The inhibitor efficiencies were obtained from the relationship.

$$\text{Inhibitor Efficiency } (I\%) = \frac{W_b - W_i}{W_b} \times 100$$

Where, W_b = weight loss without inhibitor in gms and W_i = weight loss with inhibitor in gms.

Where T_1 = low temperature in Kelvin, T_2 = High temperature in Kelvin, R = Gas constant (8.314), P_1 = Corrosion rate for low temperature and P_2 = Corrosion rate for high temperature.

Where T = Temperature in Kelvin, R = Gas constant (8.314), K = equilibrium constant = $\theta / C(1- \theta)$ and θ = Surface coverage.

2.9adsorption isotherms

These relationships were investigated to cover all the data related to adsorption of inhibitors. The isotherms are

a) Langmuir adsorption isotherm: Plots log (θ/1-θ) Vs log conc.

b) Tempkin adsorption isotherm: Plots θ Vs log conc.

3. Results And Discussion

weight loss method

3.1 Time Variation

There is a significance difference in corrosion behavior of the mild steel after using the eco friendly inhibitor. The differences have been calculated to find out the corrosion rate, surface coverage and from that the inhibition efficiency of the oil. The results of weight loss experiments of corrosion of mild steel in 1 N H2SO4 containing various concentration of inhibitor in different intervals of time. The IE was found to increase with increase in the concentration of the inhibitor with maximum IE of 91.62 % at 5% concentration.

From the figure 3.1, it is seen that the rate of corrosion are found to be decreased compared with the blank solution. This is due to the presence of phytochemical constituents present in the inhibitor molecules adsorbed on the metal surface through ring oxygen atom and π electron. The adsorption of the phyto constituents on the metal surface makes a barrier for mass and charge transfers thus protecting the metal surface from corrosion. The degree of protection increases with the increasing surface fraction occupied by the adsorbed molecules.

The maximum inhibition efficiency is found to be 86.73 % (3hrs) and 91.62 % (5hrs) for 5 % of CIM. It is assumed that the surface coverage is equal to inhibition efficiency.

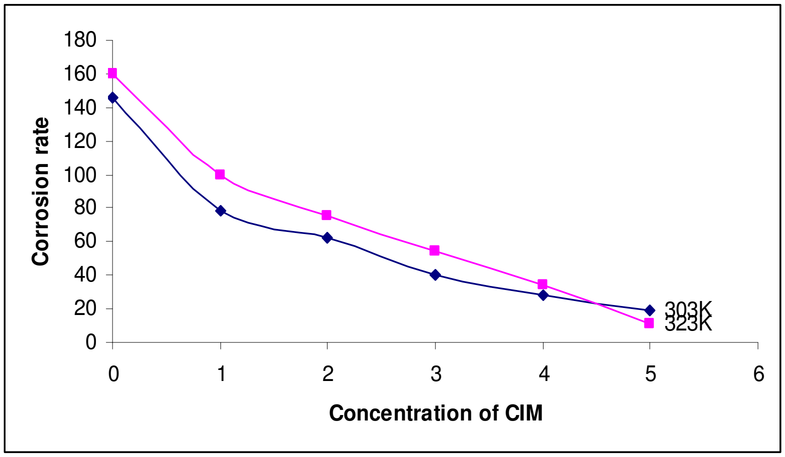

Figure 3.1 (a): Corrosion behavior of Mild Steel in 1N H2SO4 with CIM at 303K

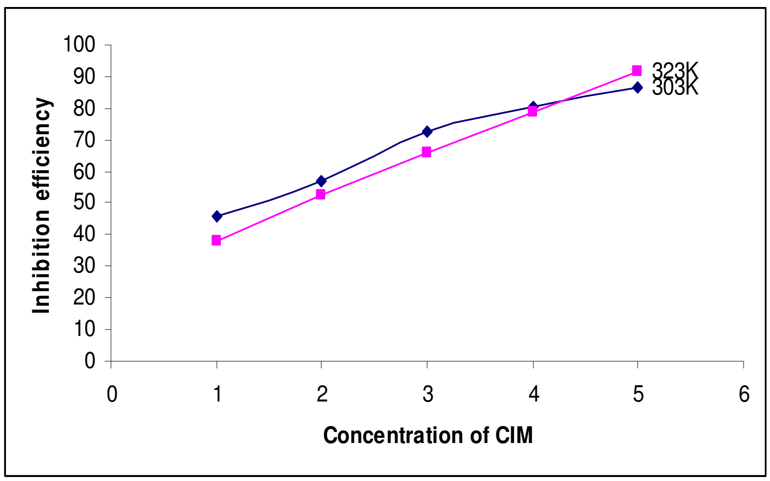

Figure 3.1 (b): Corrosion behavior of Mild Steel in 1N H2SO4 CIM at 303 K

Temperature Effect

There is a significance difference in corrosion behavior of the mild steel when the temperature varies.

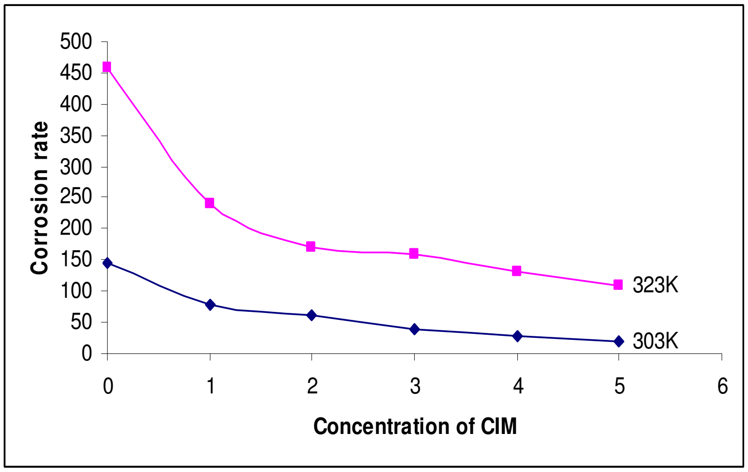

Figure 3.2 (a): Corrosion behavior of Mild Steel in 1N H_2SO_4 with CIM at various temperatures

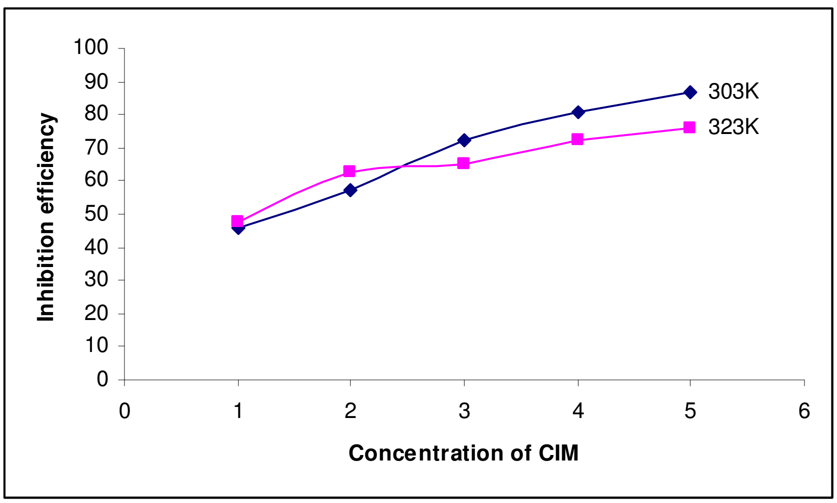

Figure 3.2(b): Corrosion behavior of Mild Steel in 1N H_2SO_4 with CIM at various temperatures

The effect of temperature on inhibition of mild steel in 1N H2SO4 with various concentration of CIM between the temperature ranges from 303 to323 K has been studied and the data were calculated. From the figure 3.2(a) and (b), it is observed that the rate of corrosion and percentage of inhibition efficiency of CIM inhibitor on mild steel is significantly reduced with raise in temperature form 303-323K. This is due to the adsorption and desorption of inhibitor molecules continuously occur at the metal surface and equilibrium exists between two processes at a particular temperature, when increase of temperature the equilibrium is shifted to higher desorption rate than adsorption until equilibrium is again established at a different value of equilibrium constant 37. The decrease of inhibition efficiency with rise in temperature is suggestive of physical adsorption mechanism.

Adsorption Isotherms

One of the most convenient ways of expressing adsorption quantitatively is by applying an adsorption isotherm that gives the relationship between the coverage of an interface with an adsorbed species (the amount adsorbed) and the concentration of the species in solution. This allows the inhibition efficiency to be expressed as a function of the inhibitor concentration at a constant temperature, the inhibition efficiency of the studied inhibitor is related to their adsorption on the surface.

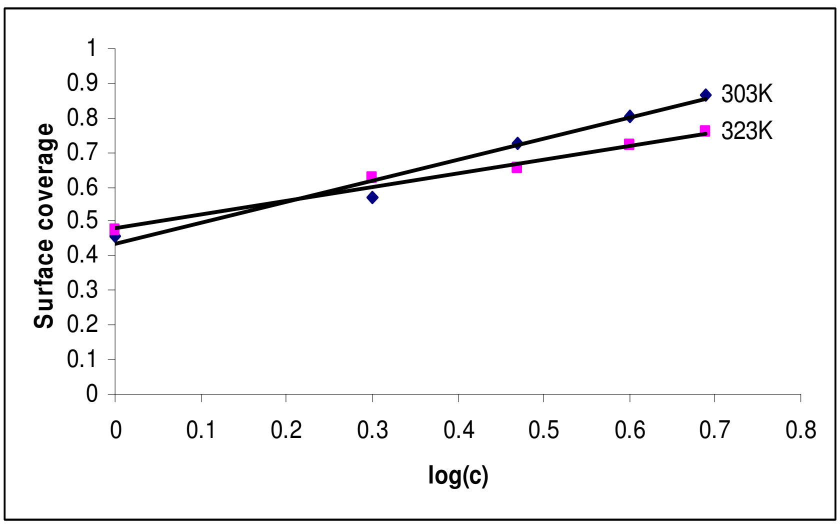

Figure 3.3: Tempkin isotherm for Mild Steel corrosion in 1N H_2SO_4 with CIM at various temperatures.

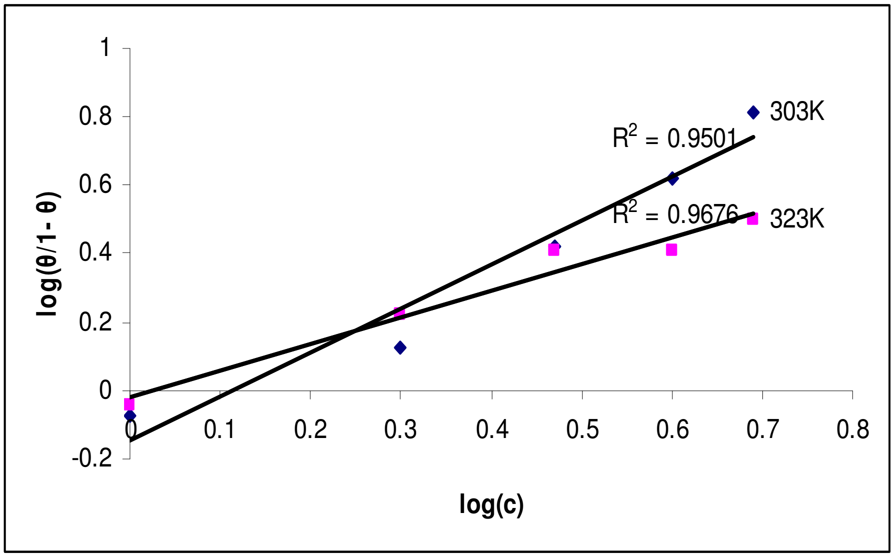

Figure 3.4: Langmuir adsorption isotherm for Mild steel corrosion in 1N H_2SO_4 with CIM at various temperatures

The Langmuir and Tempkin adsorption isotherm for Mild steel in 1N sulphuric acid with CIM were studied at the temperature range (303-323K). The values are shown Fig 3.3 and 3.4. The experimental data fits the Langmuir and Tempkin adsorption isotherm.

Thermodynamic Studies

The calculated values of activation energy (Ea) obtained from Arrhenius equation and free energy of adsorption (ΔGads) are given in table 4.1.

The values of ΔGads calculated are in the range -9.09 to -10.70 kJ/mol indicating that the plant constituents are adsorbed on the metal surface by a strong physical adsorption process. Negative sign indicates that the adsorption of the plant constituents on to the metal surface is a spontaneous process[56]. The change in ΔGads, may be due to the predominant desorption of the constituents in the adsorption-desorption equilibrium as the temperature increases. It was also found that value of activation energy of the inhibited system was greater than that of uninhibited system at higher temperatures.

Concentration of CIM (%)	Energy of Activation(Ea) KJ/mole	Free Energy Change(ΔGads) KJ/mole	
	303 - 323K	303K	323K
0	46.47	-	-
1	45.27	-9.70	-10.50
2	40.98	-9.09	-10.29
3	56.03	-9.78	-9.50
4	62.83	-10.21	-9.59
5	70.77	-10.79	-9.53

Table 4.1: Calculated Values of Energy of Activation (Ea) and Free Energy Change (ΔGads) for Mild Steel in 1N H_2SO_4 with CIM

4. Conclusion

The following conclusions were made from the studies, Corrosion rates of Mild steel in 1N H_2SO_4 are found to be decreased with increasing concentration of inhibitor CIM. The inhibition efficiency increases with respect to the concentration of CIM as it is assumed that the inhibition efficiency is equal to surface coverage. The maximum inhibition efficiency is found to be 91.62 % at 303 K for 5 % CIM in 1N H_2SO_4. The inhibition efficiency of CIM in H_2SO_4 decreases with raise in temperature. Inhibition efficiency of the CIM is temperature dependent. The low and negative value of ΔG_{ads} indicated that the CIM is physically adsorbed and also the adsorption is spontaneous process and is consistent with the mechanism of physical adsorption. Langmuir and Frumkin isotherms are best described the adsorption characteristics of the inhibitor.

References:

[1] Jamiu K. Odusote and Olorunfemi M. Ajayi, “Corrosion Inhibition of Mild Steel in Acidic Medium by Jathropha Curcas Leaves Extract” Journal of Electrochemical Science and Technology Vol. 4, No. 2, 2013.

[2] E. Dharmaraja, C. Pragathiswaranb, P. Govindhanb, P. Arockia Sahayarajb, A. John Amalrajb, V. Dharmalingamb, “Corrosion Inhibition Of Mild Steel By Plant Extracts In Acid Media” International journal of nano corrosion science and engineering.

[3] Ahmed A. Al-Amiery, Abdul Amir H. Kadhum, Abdulhadi Kadihum, Abu Bakar Mohamad1, Chong K. How and Sutiana Junaedi, “Inhibition of Mild Steel Corrosion in Sulfuric Acid Solution by New Schiff Base” Materials 2014, 7, 787-804.

[4] Mohamed Tezeghdenti, Leila Dhouibi & Naceur Etteyeb, “Corrosion Inhibition of Carbon Steel in 1 M Sulphuric Acid Solution by Extract of Eucalyptus globulus Leaves Cultivated in Tunisia Arid Zones” springer J Bio Tribo Corros (2015).

[5] Xingwen Zheng, Min Gong, Qiang Li & Lei Guo, “Corrosion inhibition of mild steel in sulfuric acid solution by loquat (Eriobotrya japonica Lindl.) leaves extract” SCientifiC REPOrTS | (2018) 8:9140 | DOI:10.1038/s41598-018-27257-9.

[6]T. U. Onuegbu, E.T.Umoh and U.A.Onuigbo , Inter. J. Scienti. Tech. Res., 2, 2013

[7]J. Buchweishaija, G. S. Mhinzi. Electrochim. Acta, 26, 2008, 257-265.

[8]R.Saratha and V.G. vasudha, E.J. Chem., 7, 2010, 677-684

[9]A.Y. El-Etre and Z. El-Tantawi, Electrochim. Acta, 24, 2006, 347-356.

[10]M. Sangeetha, S. Rajendran, Sathiyabama and P. Prabhakar, J. Nat. Prod. Plant Resour., 2 (5), 2012, 601-610