

# NATURAL POLYELECTROLYTE FOR THE CORROSION PROTECTION OF MILD STEEL IN PHOSPHORIC ACID SOLUTION

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## ABSTRACT

*The inhibition of corrosion on mild steel in 1 mol L<sup>-1</sup> H<sub>3</sub>PO<sub>4</sub> by gum exudates of Araucaria heterophylla has been studied by weight loss, potentiodynamic polarization and electrochemical impedance spectroscopic methods. The effect of temperature on corrosion inhibition was also studied using weight loss measurements. Various adsorption isotherms were tested and finally it was confirmed that it obeys Langmuir adsorption isotherm. From the potentiodynamic polarization studies, the studied gum was found to behave as mixed type inhibitor.*

**Keywords:** Corrosion, mild steel, Phosphoric acid, natural gums.

## I. Introduction

Green corrosion inhibitors are bio degradable, eco-friendly and rich source of ingredients with high efficacy and environmentally acceptable [Ma, X, and Pawlik, M, 2007 & N.O.Eddy,2011]. Studies have shown that organic compounds especially those having hetero atoms such as N, S, O in their aromatic are long chain carbon system shows significant inhibition efficiency. However most of these compounds are not just expensive but also toxic to environment. Therefore, need for cheap and eco-friendly corrosion inhibitor prompted the recent research for green corrosion inhibitors. The extracts of plant parts like root, stem, leaves ,bark and exudates gums behaves as good inhibitors. The gums exudated from plant bodies also act as good inhibitors. Several studies have been carried out and reported for some plant gums and it is generally accepted that industrial utilization of a given gum depends on its physiochemical and rheological properties [Mothe, C.G. and Roa, M.A, 1999] Structurally, the gum exudates consists of surface active units such as amino (-NH<sub>2</sub>), hydroxyl (-OH) and carboxyl (-COOH), which suggest them to be electro chemically active and they can therefore interact with metallic surfaces through these units and inhibit corrosion.

In this present work we introduced the gum exudate from *Araucaria heterophylla* (AH gum)(Christmas tree) for the corrosion inhibition of mild steel in 1 mol L<sup>-1</sup> phosphoric acid solution.

## II. Materials and methods

### 2.1. Mild Steel Specimens

Mild steel sheets cut into rectangular coupons of size 5 X 1cm<sup>2</sup> provided with holes to enable suspension in test solutions were used for the study. These steel pieces were mechanically polished to remove any rust on it. The metal pieces were then degreased with acetone washed with distilled water and polished with emery paper, cleaned, dried and stored in desiccator.

### 2.2. Preparation of aggressive medium

Laboratory grade concentrated phosphoric acid was used as corrosive environment. The acid solution was standardized before use.

### 2.3. Preparation of inhibitors solutions

The inhibitor is prepared by weighing 5 g of dried gum exudates from AH and dissolved in mixture of ethanol – water.

### 2.4. Weight loss method

For weight loss measurements, well cleaned mild steel specimens were weighed using shimadzu AY62 model were immersed completely in 100ml of the test solutions using glass hooks for 1 hour period. The experiments were carried out 300 ± 1K. The test solutions contained 1N acid with and without various concentrations (100 ppm, 200 ppm, 400 ppm, 600ppm, 800ppm) of the AH gum. After immersion for one hour period, the specimens were taken out, rinsed with double distilled water and dried. The dried

specimens were weighed and from this the loss in weight of the specimen was determined. Same procedure was repeated for different temperatures.

### 2.5. Electrochemical Studies

The mild steel specimen (working electrode) used for the electro chemical studies were made from cylindrical mild steel rod bearing the same composition as that of the specimen used for weight loss measurements. The mild steel electrode was embedded in Teflon with an exposed area of 1.0cm<sup>2</sup>. The exposed area of the specimen was polished using 1/0, 2/0, 3/0 and 4/0 emery papers, washed with double distilled water, dried and degreased with acetone and immersed in the solution under study. A conventional three electrode glass cell assembly with 100ml cell capacity was used. A platinum mesh electrode and a saturated calomel electrode along with a Lugg in capillary were used as the counter electrode and reference electrode respectively. The mild steel electrode was then placed in the test solution for 10 – 15 minutes before commencement of the electro chemical measurements. Both polarization and impedance measurements were conducted at the open circuit potential. The electro chemical measurements were carried out for mild steel specimen is 1N H<sub>3</sub>PO<sub>4</sub> in the absence and presence of selected concentrations of AH gum at 300 ± K.

## III. Results and discussion

### 3.1 Weight loss measurements

The corrosion inhibition of mild steel in 1 mol L<sup>-1</sup> H<sub>3</sub>PO<sub>4</sub> by *Araucaria heterophylla gum* (AH gum) has been studied by weight loss method with different concentrations (50 ppm to 600 ppm) and the results are summarized in Table 1.

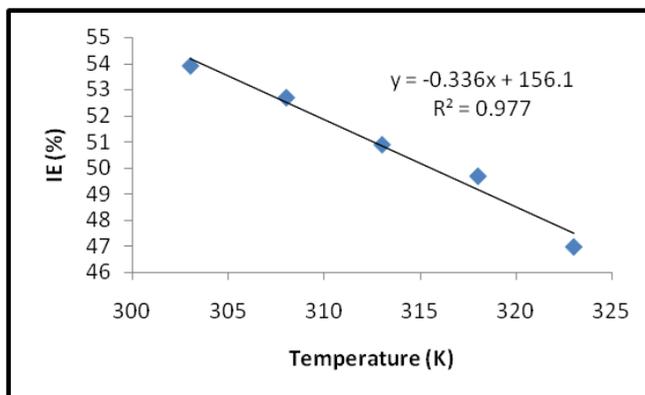
**Table 4.1 Corrosion parameters of AH gum on carbon steel in 1mol L<sup>-1</sup> H<sub>3</sub>PO<sub>4</sub> from weight loss measurement at room temperature**

S. No	Inhibitor Concentration (ppm)	Weight Loss (g)	Inhibition Efficiency (%)	Corrosion Rate (mmpy)	Degree of Coverage (θ)	-ΔG <sub>ads</sub> (KJ/Mol)
1.	Blank	0.1150	-	0.0445	-	-
2.	50	0.0061	46.95	0.0235	0.4695	17.356
3.	100	0.0059	48.69	0.0228	0.4869	15.762
4.	200	0.0058	49.56	0.0224	0.4956	14.121
5.	400	0.0053	53.91	0.0205	0.5391	12.302
6.	600	0.0057	50.43	0.0220	0.5043	11.301

Analysis of table indicates that the inhibition efficiency increases with increase in the concentration of the inhibitor whereas the rate of corrosion decreases. The adsorption of AH gum on the mild steel surface may take place through any one of the process:

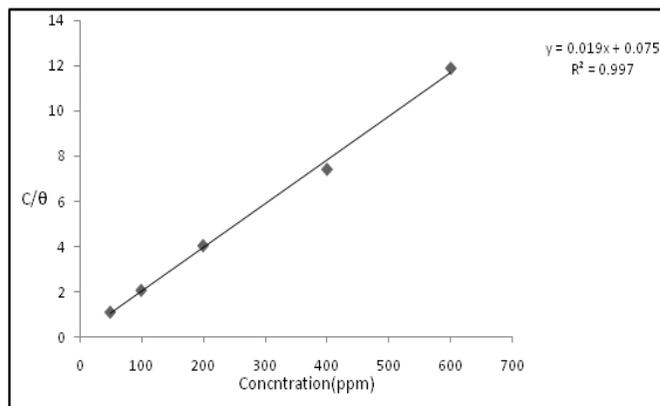
- Due to the interaction between the lone pair of electrons of oxygen atom (polysaccharides) and the vacant d, π orbitals of iron atom of the mild steel surface
- Ion-pair interactions between organic cations and phosphate ions of the phosphoric acid solution [Noor, E.A, 2007 & Quraishi, M.A, 2003].

To verify the nature of adsorption, the effect of temperature (303 – 328 K) on the corrosion behavior of mild steel in presence of optimum concentration of AH gum (400 ppm) was also studied using weight loss technique.



**Figure 1 Plot of IE Vs different temperatures for AH gum on mild steel**

Figure 1 indicates that the IE depends on temperature and it decreases with the rise in temperature. Generally, organic molecules are used to inhibit corrosion as they are adsorbed on the metal solution interface. The adsorption depends on the chemical structure of the inhibitor, chemical composition of the solution, nature of the metal surface, temperature and electrochemical potential at the metal-solution interface. The values of surface coverage ( $\theta$ ) corresponding to different concentrations of inhibitor ( $C$ ) are used to obtain the best adsorption isotherm. The  $\theta$  values have been calculated using the following relationships.



**Figure 2 Langmuir adsorption isotherm for the AH gum on mild steel in 1 mol L<sup>-1</sup> H<sub>3</sub>PO<sub>4</sub> at room temperature**

Various adsorption isotherm were tested for the present experimental data and the Fig 2 reveals that the data follows the Langmuir adsorption isotherm. The Langmuir adsorption isotherm is expression as [Putilova, I.N, 1980]

$$\theta = \frac{KC}{(1+KC)} \quad (1)$$

where  $K$  is the equilibrium constant for the adsorption process and  $C$  is the concentration.

The above equation may be modified as

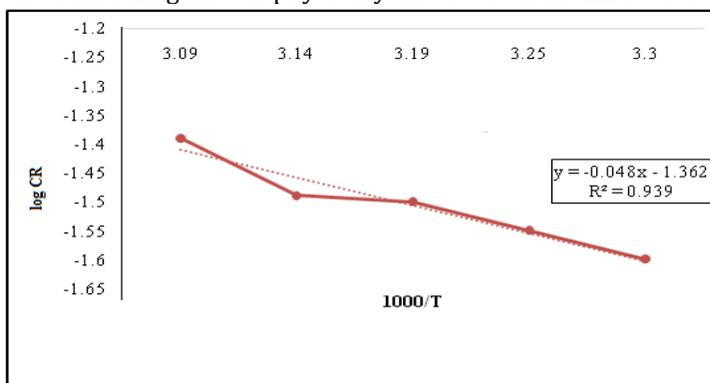
$$\frac{C}{\theta} = \frac{1}{K} + C \quad (2)$$

A straight line with slope equal to unity should be obtained when plotting  $C/\theta$  vs.  $C$  when the experimental data follow Langmuir adsorption isotherm. In the present study, Langmuir adsorption behavior was observed for AH gum. Free energy of adsorption ( $\Delta G_{ads}$ ) was calculated using the equation and the values are included in Table 1.

$$\Delta G_{ads} = -RT \ln (55.5K) \quad (3)$$

$$K = \frac{\theta}{C(1-\theta)} \quad (4)$$

The obtained value of  $\Delta G_{ads}$  indicates that the spontaneity of the adsorption process in the experimental conditions used. Generally, values of  $\Delta G_{ads}$  until  $-20$  kJ/mol are consistent with the electrostatic charged metal surface (physical adsorption). In the present study,  $\Delta G_{ads}$  values lies below  $-20$  kJ/Mol, indicating that the added AH gum was physically adsorbed on the mild steel surface



**Figure 3 Arrhenius plot for inhibition of AH gum on mild steel in 1N H<sub>3</sub>PO<sub>4</sub>**

The activation energy ( $E_a$ ) was calculated from the plot of  $\log$  (corrosion rate) versus  $1000 / T$  by using the formula and its representative curve is given (Fig 3).

$$\log CR = - \frac{E_a}{2.303R} + \log A \tag{5}$$

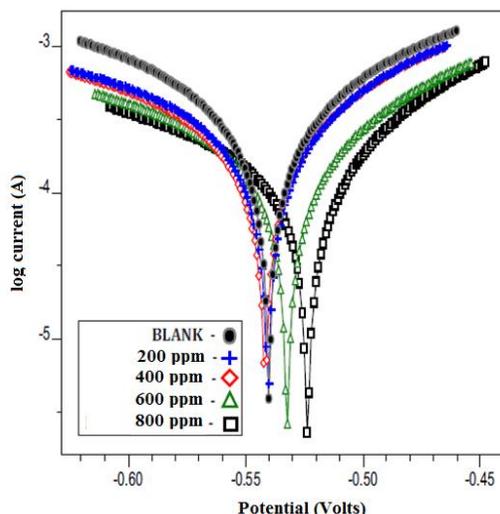
The value of activation energy ( $E_a$ ) in the inhibited solution is greater than that in the uninhibited (blank) solution, for the inhibitors whose inhibition efficiency decreases with increase in temperature. Again the higher values of  $E_a$  in inhibited solution supports the physisorption mechanism.

**3.2. Potentiodynamic polarization studies**

Polarization curves for mild steel in  $1 \text{ mol L}^{-1} \text{ H}_3\text{PO}_4$  with the addition of selected concentrations of AH gum are shown in Figure 4. The anodic and cathodic current-potential curves are extrapolated up to their intersection at the point where corrosion current density ( $i_{\text{corr}}$ ) and corrosion potential ( $E_{\text{corr}}$ ) are obtained. The electrochemical parameters  $i_{\text{corr}}$ ,  $E_{\text{corr}}$ , anodic and cathodic Tafel slopes ( $b_a$  and  $b_c$ ) obtained from the polarization measurements are listed in Table 2. It can be seen from the table that corrosion current density decreases with increase in the concentration of AH gum, indicating its inhibiting effect towards corrosion of mild steel in acid solution. The addition of 200 and 400 ppm of AH gum the corrosive medium shifts its  $E_{\text{corr}}$  towards negative direction compared to free acid solution. However, it exhibits a positive shift for 600 and 800 ppm of AH gum. The changes observed in the polarization curves after addition of the inhibitor are usually used as criteria to classify inhibitors as cathodic, anodic or mixed [Rosliza, R, 2010]. These results imply that AH gum functions as a mixed-type inhibitor. This means that the AH gum have significant effects on retarding both the anodic dissolution of mild steel and inhibiting the cathodic hydrogen evolution.

**Table 2 Potentiodynamic polarization parameters for the corrosion inhibition of mild steel in  $1 \text{ mol L}^{-1} \text{ H}_3\text{PO}_4$  with and without AH gum**

S.NO	Inhibitor Concentration (ppm)	$I_{\text{corr}}$ ( $\text{mV}/\text{cm}^2$ ) $\times 10^{-3}$	$E_{\text{corr}}$ (mV/SCE)	$b_a$ (mv/dec)	$b_c$ (mv/dec)	Corrosion rate (mppy)	Inhibition efficiency (%)
1.	$\text{H}_3\text{PO}_4$ (blank)	0.27	-0.54	0.091	0.102	4.42	
2.	200	0.12	-0.52	0.074	0.129	1.994	55.55
3.	400	0.20	-0.539	0.082	0.121	3.186	25.94
4.	600	0.21	-0.538	0.083	0.123	3.375	22.25
5.	800	0.11	-0.531	0.082	0.119	2.317	59.25



**Figure 4 Potentiodynamic Polarization curves for different concentrations of AH gum on mild steel in  $1 \text{ mol L}^{-1} \text{ H}_3\text{PO}_4$**

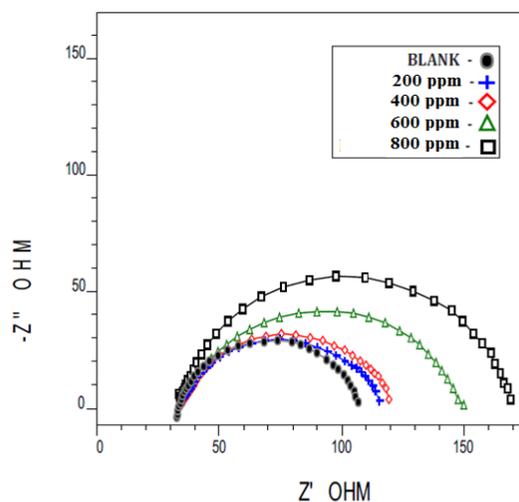
**3.3. Electrochemical impedance spectroscopic studies**

The corrosion behaviour of mild steel in various acidic solution in presence of and absence of AH gum has been investigated by EIS method at  $30^\circ\text{C}$ . Nyquist plots were recorded and typical plot is given in Figure 5. Impedance parameters like charge transfer resistance ( $R_t$ ), double layer capacitance ( $C_{dl}$ ) are given in Table 3. The impedance diagrams are almost semi-circular. The charge transfer resistance values are calculated from the differences in impedance at lower and higher frequencies. The double layer capacitance values are

obtained from the frequency at which imaginary  $Z''$  component of the impedance ( $-Z''_{max}$ ) is maximum. It is evident from the table that  $R_{ct}$  value increases while  $C_{dl}$  value decreases with the addition of AH gum (400 ppm). This is due to the increase in the surface coverage by AIG, which leads to an increase in the inhibition efficiency. The decrease in  $C_{dl}$  value may result due to the decrease in local dielectric constant and/or an increase in the thickness of the electric double layer, suggested that the AH gum gets adsorbed onto the mild steel surface. The increase in  $R_{ct}$  value indicates that the corrosion of mild steel is mainly controlled by charge transfer process. It means that the faradic process take place on the surface uncovered by the inhibitor film decreases with increasing inhibitor concentration.

**Table 3 AC Impedance parameters for the corrosion inhibition of mild steel in 1 mol L<sup>-1</sup> H<sub>3</sub>PO<sub>4</sub> with AH gum**

S. No	Inhibitor concentration (ppm)	$R_{ct}$ (ohms)	$C_{dl}$ ( $\mu$ F)	Inhibition efficiency (%)
1.	Blank	2.95	0.302	-
2.	200	8.74	0.239	66.24
3.	400	3.55	0.261	16.90
4.	600	3.24	0.256	08.91
5.	800	5.81	0.232	49.13



**Figure 5 Nyquist plots for the corrosion inhibition of AH gum on mild steel in presence of halide ions in 1 mol L<sup>-1</sup> H<sub>3</sub>PO<sub>4</sub>**

#### IV. CONCLUSION

The maximum inhibition efficiency of AH gum in 1 mol L<sup>-1</sup> Phosphoric acid solution on mild steel was achieved at very low concentration (400 ppm). The rate of corrosion does not significantly change, appreciably up to 60°C indicating the efficient inhibiting nature of the gum in the temperature range studied. It obeys Langmuir adsorption isotherm. From the potentiodynamic polarization studies, it can be concluded that AH gum has significant effects on retarding both the anodic dissolution of mild steel and inhibiting the cathodic hydrogen evolution reaction.

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