Gum Tragacanth Powder as A Green Corrosion Inhibitor for Mild Steel in 1N Sulphuric Acid Solution

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Abstract:-The effect of Gum Tragacanth powder on corrosion inhibition of mild steel in sulphuric acid was investigated by weight-loss method, potentiodynamic polarization and electrochemical impedance spectroscopy studies. The inhibition efficiency is found to increase with temperature as well as with increase in concentration of the inhibitor. The activation energy and thermodynamic parameters for inhibition process were calculated. These thermodynamic parameters indicate a strong interaction between the inhibitor and the mild steel surface. The inhibition is assumed to occur via adsorption of inhibitor molecules on the mild steel surface, which obeys Langmuir adsorption isotherm. The polarization measurements showed that the inhibitor behaves as a mixed type inhibitor and the higher inhibition surface coverage on the mild steel was predicted. Inhibition efficiency values were found to show good trend with weight-loss method, potentiodynamic polarization and electrochemical impedance spectroscopy studies.

Keywords: Mildsteel, Sulphuric acid, Gum Tragacanth powder, Inhibition, Isotherm.

I.   INTRODUCTION

The industrial and domestic applications of mild steel and alloys cannot be exaggerated; they are applied in several manufacturing processes as well as kitchen utensils. Hospitals and laboratory equipment are mostly shaped with these metals. However, mild steel and alloy applications are prone to corrosion when deployed in service in acidic or alkaline environments. To save our industries the huge amount of money is wasted on metal maintenance and repair. Innovations have been made to use corrosion inhibitors to Salvage the situation. In recent times there has been a lot of developments and search to discover natural inhibitors that are environmentally friendly. The use of natural inhibitors of plant origin is fast replacing the use of toxic compounds which are hazardous to man and his environment. These plant inhibitors are not just eco-friendly but cheap and affordable which adds

to their sustainability. Research has proved that plant extracts constitute several organic compounds which have corrosion inhibiting properties[1-6].Some gums have also been found to be good corrosion inhibitors for the corrosion of metals in acidic solutions[7].

Natural gums are indispensable recipient in pharmaceutical, food and cosmetic industries [8]. Several corrosion 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 [9]. Natural guar gum is also employed as a binder of water-insoluble, ultrafine minerals in the froth flotation of potash ores [10]. According to Eddy[11], gums have been found to be good corrosion inhibitors .

In view of the numerous advantages offered by some gums for corrosion inhibition systems, Umoren *et al*.,reported the potential of *Gum Arabic* as corrosion inhibitor for aluminum in alkaline medium[12]. The effect of naturally occurring exudates gum from *Raphia hookeri* on the corrosion of mild steel in H_2SO_4 in the temperature range 30-60 °C was investigated by Moran *et al*.,[13] .*Guar gum* has been shown to be an effective corrosion inhibitor for metal in aggressive acid environment by Abdallah [14].The present work investigates the corrosion inhibition and thermodynamic adsorption study of Gum Tragacanth powder(GTP) on mild steel in 1 mol L^{-1} H_2SO_4.The inhibition efficiency has been tested by weight loss, potentiodynamic polarization and electrochemical impedance spectroscopic methods. The effect of acid concentration, temperature and immersion time on the corrosion behavior of mild steel was studied using weight loss measurements. The kinetic and thermodynamic adsorption studies for mild steel corrosion and inhibitor adsorption .were determined and discussed in detail.

II.   MATERIALS AND METHODS

A.   Corrosion Study

Materials used for the study were mild steel sheet of composition 0.07 wt. % C, 0.008 wt. % P, 0.34wt. % Mn,

remaining Fe. The sheets were mechanically pressed cut into different coupons, with a dimension of 25 x 10 x 1 mm for each sheet. Each coupon was degreased by washing with ethanol, cleaned with acetone and allowed to dry in the air before preservation in a desiccators. Laboratory grade sulphuric acid solution was used as an aggressive medium and double distilled water was used for their preparation. The Gum Tragacanth Powder (GTP) used for the study was purified and concentrations of 10 to 60 ppm were used.

B.   Methods

The gravimetric experiments were carried out according to the ASTM practice standard G-31 [15]. Corrosion rate, Inhibition efficiency and Surface coverage were calculated using the formulae given in equation (1), (2) and (3).

$$\text{Corrosion rate (mmpy)} = 87.6 \times \frac{W}{\rho At} \quad \text{--- (1)}$$

where, W is the weight loss (g), 'ρ' the density of the mild steel specimen (g cm^{-3}), 'A' the area of specimen (cm^2) and t is the time of exposure (h).

$$\text{Inhibition efficiency (\%)} = \frac{W_o - W_i}{W_o} \times 100 \quad \text{--- (2)}$$

$$\theta = 1 - \frac{W_i}{W_o} \quad \text{--- (3)}$$

where, θ, W_i and W_o are the surface coverage, weight losses of mild steel in inhibited and uninhibited solution respectively.

The electrochemical experiments were performed using three electrode cell assembly. The cell consisted of a platinum counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The working electrode was immersed in the acid solution and the constant steady-state (open circuit) potential was recorded as a function of time, when it became virtually constant.

The polarization studies were carried out over a potential of + 200 to − 200 mV with respect to the open circuit potential at a scan rate of 1 mV s^{-1}. The linear Tafel segments of the cathodic curves and the calculated anodic Tafel lines were extrapolated to the point of intersection to obtain the corrosion potential (E_{corr}) and corrosion current density (i_{corr}). The inhibition efficiency was evaluated from the measured I_{corr} values using equation (4)

$$\text{Inhibition efficiency} = (i^\circ_{corr} - i_{corr} / i_{corr}) \text{ x } 100 \text{ -- (4)}$$

where, i_{corr} is the corrosion current density without inhibitor and i_{corr} is the corrosion current density with inhibitor.

The electrochemical impedance spectroscopic (EIS) measurements were carried out using AC signals of 10mV amplitude over the frequency range of 10 KHz to 0.01 Hz. The electrode was immersed in the solution for half an hour before starting the impedance measurements. All the impedance data were automatically controlled by Z_{view} software. The charge transfer resistance (R_{ct}) values were obtained from the diameter of the semicircles of the Nyquist plots. The inhibition efficiency of the inhibitor has been found out from the charge transfer resistance values according to the following equation (5)

$$\text{Inhibition efficiency (\%)} = (R_{ct} - R^\circ_{ct} / R_{ct}) \text{ x } 100 \quad \text{--- (5)}$$

where, R_{ct} and R^o_{ct} are the charge transfer resistance with and without inhibitors respectively.

III.   RESULTS AND DISCUSSION

A.   Weight Loss Measurements

a).   *Corrosion Inhibition Performance of GTP*

The effect of addition of Gum Tragacanth powder (GTP) at different concentrations on the corrosion of mild steel in 1 N Sulphuric acid was investigated using weight loss technique for different immersion periods (1-6 hours) at a temperature range of 303K -323K. The inhibition efficiency, surface coverage and corrosion rates of the mild steel coupons in 1N H_2SO_4 with and without different concentrations of the inhibitor were determined. The results presented in Table 1 shows that there is increase in inhibition efficiency of the metal coupons in the presence of the inhibitor (GTP) compared to the free acid solution (blank). Inspection of the table further revealed that the loss in weight of the coupons decreases as the concentration of the inhibitor increases. It has been observed that 40 ppm of GTP serves as an optimum concentration that exhibit higher inhibition efficiency. This behavior could be attributed to the increase in adsorption of the inhibitor at the metal-solution interface [16] and reduces the surface area that is available for direct attack on the metal surface. Above 40 ppm, the corrosion rate approximately remained constant. The constant rate obtained could be attributed to the competitive adsorption effect between inhibitor molecules and the metal surface which is already covered with initial layers of molecules [17]. Further the inhibition efficiency increasing with increase of temperature implies that constituents of the inhibitor adsorb chemically on the MS surface, form a protective layer and screen the metal from corrosion [18].

b).   *Effect of Immersion Period*

In order to assess the stability of the inhibitor on MS surface, weight loss measurements were performed in sulphuric acid medium in the absence and presence of GTP for 1–6hours of immersion time at 303K. From the Table 1, it can be observed that the inhibition efficiency of GTP increased with immersion time and stabilized after 6hours.This increase in inhibition of GTP with immersion time reflects strong adsorption on the mild steel surface resulting in a more protective layer. When the immersion time and the concentration of the tested inhibitor increase, more inhibitor molecules are expected to adsorb chemically [23]. However, when more inhibitor molecules adsorb, the adsorption density of the inhibitor becomes so that cause decrease of the effective area covered by the inhibitor molecule to some extent. This may explain why the efficiency of the tested surfactants first increases with the immersion time, reaching a maximum at certain time, and then decreases with further increasing the immersion time.

c). Effect of Temperature

Analysis of temperature dependence of inhibition efficiency and comparison of corrosion activation energies in the absence and presence of GTP give some insight into the possible mechanism of inhibitor adsorption. The weight loss measurements were carried out as a function of temperature (303 to 323 K) and concentration (10 to 60 ppm) at 1 h immersion time.The percentage inhibition efficiencies (IE %) and corrosion rates (CR) are summarized in Table 2. It was found that increase in temperature leads to a decrease in the corrosion rate in the absence and presence of GTP in sulphuric acid medium. The dependence of corrosion rate on temperature can be expressed by the following Arrhenius equation:

$$\log \text{CR} = \log \text{A} - \frac{E_a^*}{2.303RT} \quad \text{----------- (6)}$$

where, E_a^* is the apparent activation energy, R is the universal gas constant, T is the absolute temperature and A is the frequency factor. In general,a decrease in inhibition efficiency with the rise in temperature with analogous increase in corrosion activation energy in the presence of inhibitor compared to its absence is frequently interpreted as being suggestive of formation of an adsorption film of physical (electrostatic) nature. The reverse effect, corresponding to an increase in inhibition efficiency with rise in temperature and lower activation energy in the presence of inhibitor, suggests a chemisorption mechanism.

The apparent activation energy for GTP was determined by the linear regression between log CR and 1/T and the represented plots are given in Figure 1. Plots of log CR versus 1/T gave straight line with slope $(- E_a^*/2.303R)$ and intercept A. The linear regression coefficients were

close to unity for all the systems studied. The calculated values of apparent activation energy are given in Table 3.

Other kinetics data (enthalpy and entropy of corrosion process) are accessible using the alternative formulation of the Arrhenius equation.

$$\text{CR} = \left(\frac{RT}{Nh}\right)\exp\left(\frac{\Delta S^*}{R}\right)\exp\left(\frac{-\Delta H^*}{RT}\right) \text{---} \quad (7)$$

where, h is Planck's constant, N the Avogadro's number, R is the universal gas constant, T the absolute temperature, ΔS^* the entropy of activation and ΔH^* the enthalpy of activation. Figure 2 shows the plot of log (CR/ T) versus 1/ T gives straight line with slope $(-\Delta H^*/2.303 \text{ R})$ and an intercept (log (R/ Nh) + ΔS^*/ 2.303 R), from which ΔH^* and ΔS^* are calculated (Table 3). The value of E_a^* determined in 1 mol L^{-1} H_2SO_4 (blank) solution was 65.71 kJ mol^{-1}. E_a^* for the inhibited system increases with increases in the concentration of the inhibitor. It is clear that activation energies for the inhibited solution are lower than the blank.

It is found that the Ea value in the inhibited system is lower than that in the uninhibited system. The reduction of Ea in the presence of inhibitor may be attributed to the chemisorption of inhibitor on the steel surface [24-26]. With the increase of temperature, some chemical changes occur in the inhibitor molecules, leading to an increment in the electron densities at the adsorption centre of inhibitor molecules and then an improvement in inhibition efficiency.

The change in enthalpy (ΔH^*) for the inhibited solution containing various concentrations of GTP are lower than the blank again supports the chemical mode of adsorption. Also, the positive values of ΔH^* in the uninhibited and inhibited solutions reflects the endothermic nature of mild steel dissolution. The values of ΔS^* for the uninhibited solution was -13.99J K^{-1} mol^{-1} and it decreases towards more negative side with increase in concentration of GTP upto maximum of -45.5 J K^{-1} mol^{-1}. The negative value of ΔS^*in the absence and presence implies that the activated complex is the rate determining step, which represents an association step rather than dissociation step. In the presence of the inhibitor, the values of ΔS^*increases and is generally interpreted as an increase in disorder as the reactants are converted to the activated complexes [27].

d). *Adsorption Isotherm*

The surface coverage (θ) of corrosion inhibitor on MS is the most useful parameter for the study of the adsorption behavior

of the inhibitor. A direct relationship between inhibition efficiency and the degree of surface coverage can be assumed for different concentrations of the inhibitor. Data obtained from mass loss measurements were tested graphically for fitting various isotherms including Langmuir, Frumkin, Freundlich, El-Awady and Temkin are presented in table 4. However, the best fit is obtained from Langmuir isotherm (Figure 4). This isotherm assumes that the adsorbed molecules occupy only one site, and there are no interactions with other adsorbed species [28]. According to this isotherm surface coverage is related to inhibitor concentration as

$$C/\theta = 1/K_{ads} + C \qquad \text{---- (8)}$$

where K_{ads} is the equilibrium constant for adsorption, C is the concentration of the inhibitor, and θ is the surface coverage. The strong correlation ($R^2 > 0.97$) suggests that the adsorption of inhibitor on the MS surface obeyed this isotherm. The K_{ads} is related to the free energy of adsorption (ΔG_{ads}) using the following equation:

$$K = -\log C_{H_2O} - \left(\frac{\Delta G^o_{ads}}{2.303\ RT} \right) \qquad \text{---- (9)}$$

where R is the universal gas constant, T is the absolute temperature, and 55.5 is the concentration of H_2O in solution (mol L^{-1}). The values of free energy change of adsorption for GTP are calculated as -24.6, -77.3 and -101.1KJ/mol for 303,313 and 323 K respectively. The negative values of ΔG_{ads} means that the adsorption of GTP on MS surface is a spontaneous process and shows the strong interaction of the inhibitor onto the MS surface [29]. Analyses of the experimental results suggests that the inhibitor GTP inhibited corrosion of mild steel by being chemically adsorbed to the metal surface at higher temperatures .

B. Electrochemical Polarization Method

Figure 4 shows the polarization curves for mild steel in 1N H_2SO_4 solution in the absence and presence of various concentrations of GTP. The anodic and cathodic current potential curves are extrapolated up to their intersection at the point where corrosion current density ($I corr$) and corrosion potential ($E corr$) are obtained. The electrochemical polarization parameters Ecorr, Icorr, anodic and cathodic Tafel slopes (ba and bc) obtained from polarization measurement are listed in Table 5. The inhibition efficiency was calculated from the expression

$$IE(\%) = \frac{Icorr(0) - Icorr(i)}{Icorr(0)} \times 100 \qquad \text{--- (10)}$$

where $I corr(0)$ and $I corr$ are corrosion current densities obtained in the absence and presence of inhibitors, respectively.

It is clear from Table 5 and Figure 5 that the addition of inhibitors to 1N H_2SO_4 solution brings about a change in both the anodic and cathodic Tafel slopes. These results suggested that the addition of the studied inhibitors reduces the anodic dissolution and also retards the cathodic hydrogen evolution reaction, indicating that these inhibitors influence both cathodic and anodic inhibition reactions. Further the addition of inhibitors decreased the corrosion current density (I_{corr}) significantly, which further decreases with increase in concentration of the inhibitors. It can be seen from the table that the corrosion potential was not shifted significantly in presence of extract suggesting that the GTP control both anodic and cathodic reactions to inhibit the corrosion of mild steel by blocking active sites on the surface of mild steel . This showed that the inhibition action is of mixed type [30]. According to Li et al. [31], if the displacement in E_{corr} is >85mV with respect to E_{corr} (blank), the inhibitor can be viewed as a cathodic or anodic type. In our study the maximum displacement was found to be 7mV, which indicates that the inhibitors could be considered as mixed type [32].The behavior of Tafel slopes b_a and b_c also suggested mixed type of behavior for the inhibitor. Therefore, the studied inhibitor GTP can be classified as mixed type inhibitor for mild steel in 1N H_2SO_4 solution. The inhibition efficiency was found to increase with increase in concentration of the inhibitors.

C. Electrochemical Impedance Measurements

The corrosion behavior of mild steel in sulphuric acid in the absence and presence of various concentrations of the inhibitor was investigated by the electrochemical impedance spectroscopy method at 300 K and the impedance parameters R_{ct} and C_{dl} derived from these investigations are given in Table 6. Nyquist plots of mild steel in the presence and absence of different concentrations of the inhibitor 10 ppm, 20 ppm and 40 ppm are shown in Figure 5. The semicircular nature of impedance diagrams indicates that the corrosion of mild steel is mainly controlled by a charge transfer process, and the presence of the inhibitor does not affect the dissolution mechanism of mild steel [33]. The impedance spectra of the Nyquist plots were investigated by fitting the experimental data to a simple equivalent circuit model as shown in Figure 6, which includes the solution resistance R_s and the double layer capacitance C_{dl} which is placed in parallel to the charge transfer resistance $R_{ct.}$.The charge transfer resistance $\square_{ct}$ values are calculated from the difference in impedance at low and high frequencies. The $\square_{ct}$ value is a measure of electron transfer across the mild steel surface and it is inversely proportional to the corrosion rate. The double layer capacitance $\square_{dl}$ was calculated at the frequency $\square_{max}$ at which the imaginary component of the impedance is maximal using the equation [34]

$$C_{dl} = 1 / 2\ \pi\ f_{max}\ R_{ct} \text{ ---- (11)}$$

Analysis of the data presented in Table 6 indicates that the magnitude of $\square_{ct}$ value increased while that of $\square_{dl}$ decreased with the addition of inhibitor to 1N H_2SO_4 medium. The decrease in $\square dl$ values results from the adsorption of the inhibitor molecules at the metal surface. The double layer between the charged metal surface and the solution is considered as an electrical capacitor. The adsorption of inhibitors on the mild steel surface decreases its electrical capacity as they displace the water molecules and other ions originally adsorbed on the surface leading to the formation of a protective adsorption layer on the electrode surface which increases the thickness of the electrical double layer. The thickness of this protective layer ($\square$) is related to $\square_{dl}$ in accordance with Helmholtz model, given by the following equation :

$$\square dl = \frac{\square\square o\square}{\square} \quad \text{------ (12)}$$

where $\square$ is the dielectric constant of the medium and $\square\square$ is the permittivity of free space (8.854×10^{-14} F/cm) and $\square$ is the effective surface area of the electrode.

From (11), it is clear that as the thickness of the protective layer, that is, the film formed by inhibitor molecules, increases, the $\square_{dl}$ should decrease. In our present studies $\square_{dl}$ value was found to be highest for uninhibited solution. Addition of inhibitor to the aggressive medium is found to decrease the $\square_{dl}$ .The inhibition efficiency of inhibitors for the corrosion of mild steel in 1N H_2SO_4 medium is calculated using $\square_{ct}$ values as follows:

$$IE\ (\%) = \frac{R\ ct(i) - Rct(0)}{R\ ct(i)} * 100 \quad \text{---- (13)}$$

where $\square_{ct(0)}$ and $\square_{ct(\square)}$ are the charge-transfer resistance values in absence and presence of inhibitor, respectively. The $\square_{ct}$ value was found to be the highest for the inhibitor of 40 ppm concentration of GTP.

IV. CONCLUSION

- GTP acts as good inhibitor for mild steel in 1 N HCl solution.
- The inhibition efficiency increased with concentration as well as temperature.
- The calculated values of activation energy, enthalpy of activation and   standard free energy of adsorption conclude a chemisorptions mechanism.
- The adsorption behavior of GTP on mild steel surface is confirmed by the   Langmuir adsorption isotherm.
- The polarization measurements show the gum act as mixed type inhibitor.

	Concentration ppm	corrosion rate mmpy (*10 -3)	Inhibition Efficiency (%)	Surface Coverage (θ)
	Blank	57.8620		
	5	50.6293	12.50	0.1250
	10	42.4924	26.56	0.2656
	20	31.6433	45.31	0.4531
	40	22.6024	60.94	0.6094
	60	23.5065	59.38	0.5938
	80	25.3146	56.25	0.5625
	100	24.8626	57.03	0.5703
	150	25.7667	55.47	0.5547
1 hr	200	24.4105	57.81	0.5781
	Blank	51.9854		
	5	37.9720	26.96	0.2696
	10	21.2462	59.13	0.5913
	20	18.0819	65.22	0.6522
	40	16.9518	67.39	0.6739
	60	18.5339	64.35	0.6435
	80	18.7600	63.91	0.6391
	100	18.5339	64.35	0.6435
	150	18.3079	64.78	0.6478
2 hrs	200	16.9518	67.39	0.6739
	Blank	56.5059		
	5	27.0098	52.20	0.5220
	10	17.5168	69.00	0.6900
	20	15.0306	73.40	0.7340
	40	15.8216	72.00	0.7200
4 hrs	60	17.8559	68.40	0.6840
	Blank	51.6087		
	5	25.9927	49.64	0.4964
	10	18.1572	64.82	0.6482
6 hrs	20	13.1847	74.45	0.7445
	40	15.2943	70.36	0.7036
	60	15.9723	69.05	0.6905

Table 1 : Corrosion Parameters for Ms in 1N H_2so_4 Containing Various Concentrations of Tragacanth.

Temperature	Concentration ppm	corrosion rate mmpy (*10 -3)	Inhibition Efficiency (%)	Surface Coverage (θ)
	Blank	57.1352		
	10	41.9587	21.67	0.2167
	20	31.2459	41.67	0.4167
	40	22.3185	58.33	0.5833
303 K	60	23.2112	56.67	0.5667
	Blank	160.4767		
	10	85.8890	46.48	0.4648
	20	64.1907	60.00	0.6000
	40	60.5743	62.25	0.6225
313 K	60	65.0948	59.44	0.5944
	Blank	277.5569		
	10	112.5597	59.45	0.5945
	20	98.0942	64.66	0.6466
	40	84.0808	69.71	0.6971
323 K	60	94.4779	65.96	0.6596

Table 2: Corrosion Parameters for MS In 1N H_2SO_4 Solution Containing Various Concentrations of Tragacanth At Different Temperatures.

C ppm	Pre -Exponential factor A	Ea	ΔH	ΔS
B	1.3134 x 10^13	65.71	63.06	-13.9996
10	5.3247 x 10^9	41.02	38.37	-98.0947
20	5.179 x 10^9	47.56	44.90	-79.1792
40	7.9749 x 10^10	55.14	52.48	-56.4424
60	2.966 x 10^11	58.36	55.70	-45.5175

Table 3: Activation Parameters for MS in 1N H_2SO_4 Solution Containing Various Concentrations of Tragacanth.

Isotherm	Temperature K	R^2	Slope
	303	0.970	1.2695
	313	0.994	1.5981
Langmuir	323	0.996	1.4690
	303	0.999	0.4628
	313	0.973	0.1365
Freundlich	323	0.842	0.0693
	303	0.999	0.8224
	313	0.994	0.2944
El-Awady	323	0.858	0.1917
	303	0.856	2.7059
	313	0.5557	2.0841
Frumkin	323	1	4.7116
	303	0.999	0.4476
	313	0.997	0.1674
Temkin	323	0.854	0.1016

Table 4: R^2 Values For Different Isotherms .

Concentration (ppm)	-Ecorr (V vs SCE)	Icorr (mA/cm²)	Tafel Slope (mV/decade)		Inhibition Efficiency (%)
			ba	bc	
Blank	488.1	410	85	137	-
10	505	195	67	156	52.43
20	488.4	119	60	144	72.68
40	499.8	112	60	144	70.97

Table 5: Electrochemical Polarization Parameters for MS in 1N H_2SO_4 in the Absence And Presence of Various Concentrations of GTP .

Concentration ppm	R_{ct} (Ω cm⁻²)	C_{dl} (µF cm⁻²)	IE (%)
Blank	9.19	35.1	-
10	59.46	15.3	84.54
20	62.73	14.2	85.34
40	70.15	13.5	86.89

Table 6: AC Impedance Parameters For MS in 1N H_2SO_4 in the Absence and Presence of Various Concentrations of GTP.
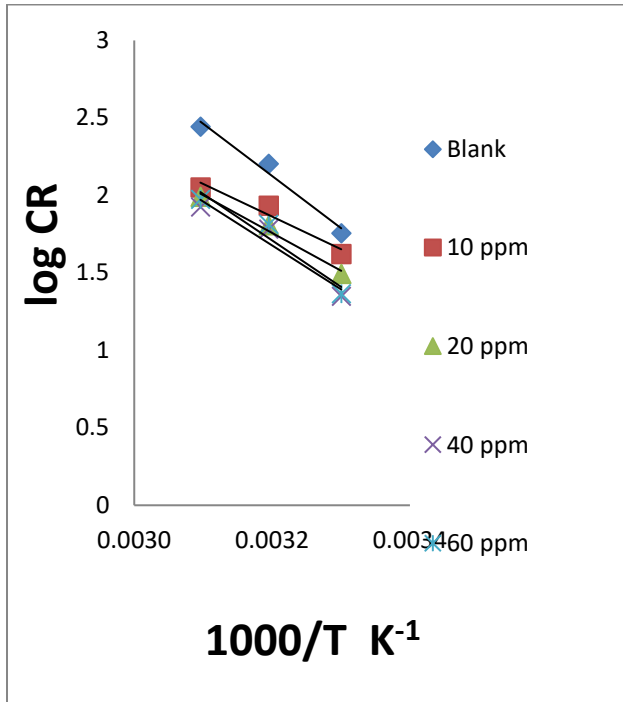
Fig.1 Arrhenius Plots For GTP on Mild Steel In 1N H2SO4.
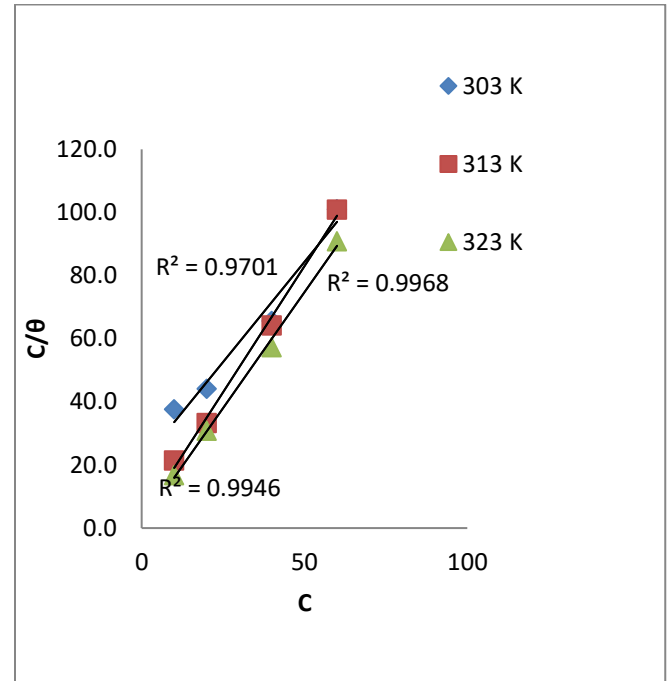

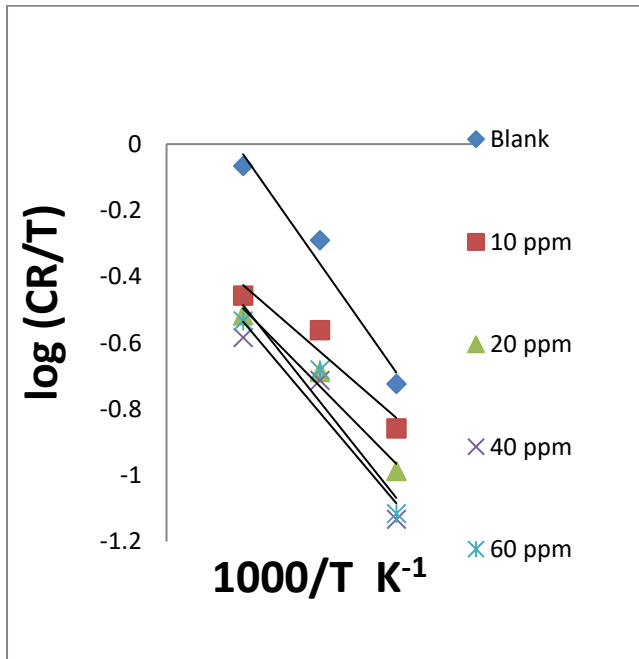Fig. 3 Langmuir Isotherm For the Adsorption of GTP on the MS Surface In 1N H_2SO_4 At Different Temperatures.

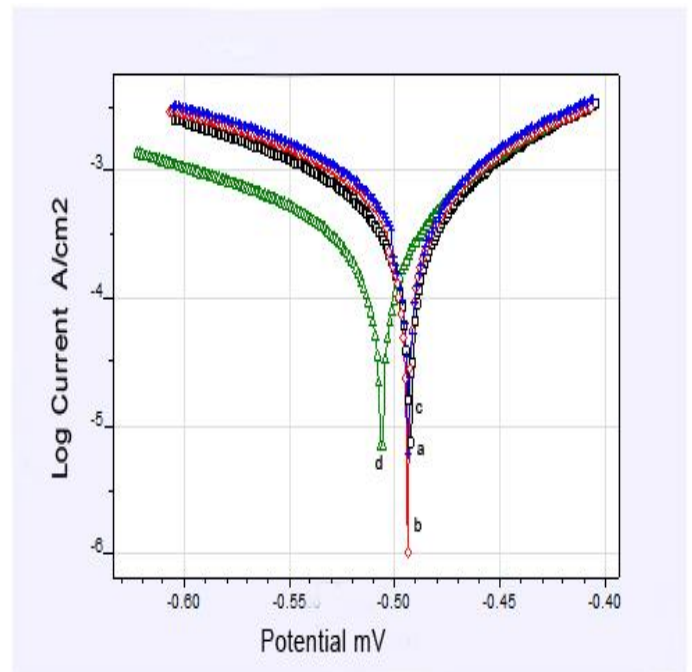Fig. 2 Transistion State Plots For GTP on Mild Steel In 1N H_2SO_4..

Fig.4 Potentiodynamic Polarization Curves
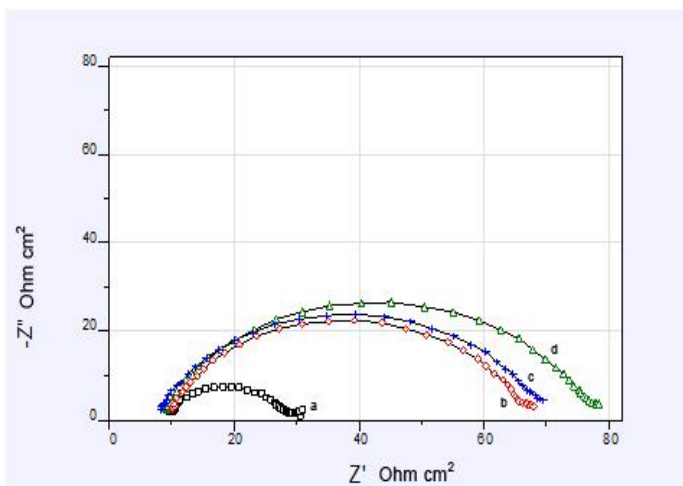(a) blank (b)10 ppm (c)20 ppm (d) 40 ppm

Fig.5 Nyquist plots.
(a) blank (b) 10 ppm (c)20 ppm (d) 40 ppm.

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