

Adsorptive, inhibitive and thermodynamics studies on the corrosion of mild steel in the presence of *Mangifera indica* gums

Habibat F. CHAHUL*, Elijah MAJI, and Tanko B. DANAT

Department of Chemistry, Federal University of Agriculture, P.M.B. 2373 Makurdi, Nigeria

Abstract. The adsorption and inhibitive behavior of gums obtained from *Mangifera indica* tree was investigated at 303-333 K using weight loss and linear polarization measurements. The results obtained from both measurements showed that *Mangifera indica* gums inhibited the corrosion of mild steel in 1.0 M HCl. Linear polarization measurements revealed *Mangifera indica* gums to inhibit both the anodic and cathodic reactions on the surface of the mild steel thereby functioning as a mixed-type inhibitor. Adsorption behavior of the gums were approximated by the isotherm models of Langmuir, Freundlich and Temkin. The adsorption mechanism derived from the trend in inhibition efficiency as a function of temperature as well as kinetic and activation parameters signified *Mangifera indica* gums adsorbed on the surface of the mild steel through the mechanism of physisorption and that the adsorption process was exothermic and spontaneous.

Keywords: mild steel, corrosion inhibition, gums, adsorption isotherm, activation energy.

1. Introduction

Extreme corrosion attack has been reportedly known to take place on the surfaces of steel deployed in service in aqueous acidic environments [1]. A lot of techniques have been engaged in proffering solution to this menace of corrosion. Amid these different techniques, an important one is the use of corrosion inhibitors [2-5].

The rate of corrosion of steel can be notably reduced by the introduction of corrosion inhibitors into the aggressive aqueous environments thereby inhibiting the corrosion process and reducing the corrosion rate. Corrosion inhibitors are chemical substances that when introduced in a little amount to a corrosive environment would significantly lower the corrosion rate of a metal/alloy [3].

Organic compounds possessing polar functions with oxygen, nitrogen, and/or sulfur in a conjugated system have been reportedly used as corrosion inhibitors [6]. Corrosion inhibitors function at the interphase formed by corrosion products involving the metal/alloy and corrosive solution, and their interaction with the corroding metal surface, frequently via adsorption which usually leads to an alteration in either the mechanism of the electrochemical process at the double layer or in the surface available to the corrosion process [6].

The high costs of a good number of corrosion inhibitors albeit the health and environmental hazards that most of them pose necessitates the exploration of a class of inexpensive and eco-friendly inhibitors as substitutes [1-6]. The use of plant products as corrosion inhibitors is a viable field of research because they are inexpensive, renewable and eco-friendly sources of important phytochemicals such as amino acids, alkaloids, flavonoids, tannins, carbohydrates and lignins.

Plants based gums are usually made up of sucrose, arabinogalactan, oligosaccharides, glycoproteins and polysaccharides which possess oxygen and nitrogen atoms which are the centers of adsorption. Most gums of plant origin also possess -COOH functional groups, which can increase the contribution of electron or charge transfer through adsorption of the gums on surface of the metal/alloy thereby inhibiting the corrosion process [7-9].

Mangifera indica (MI) commonly known as mango belongs to the family *Anacardiaceae*. Its gum is a dried gummy exudate polysaccharide obtained from the bark of the mango tree [10]. Gums obtained from plants have been reported as good corrosion inhibitors against the corrosion of steel in acidic environments [7-9].

This study reports on the potential of MI gums as a corrosion inhibitor against the corrosion of mild steel in 1.0 M HCl solution. Weight loss and linear polarization measurements would be employed in this investigation.

2. Experimental

2.1. Materials

Mild steel coupons of dimension 3x2 cm² and percentage composition: Si - 0.03 %, P - 0.04 %, S - 0.04 %, Mn - 0.60 % and the rest Fe, were used for this study. Analar grade reagents were used for the study.

2.2 Methods

2.2.1 Purification of *Mangifera indica* gums. The procedure adopted for the purification of the gums has been reported elsewhere by Femi *et al.* [11, 12]. Pulverized gums were kept in a dry and air tight container. 0.05 g - 0.25 g of the pulverized gums were used to prepare test solutions of 0.2 g/L, 0.4 g/L, 0.6 g/L, 0.8 g/L and 1.0 g/L concentrations by adding the gums to 250 mL of 1.0 M HCl.

* Corresponding author. *E-mail address:* momohbat2007@gmail.com (Habibat F. Chahul)

2.2.2. Weight loss measurement. Weight loss measurements have been comprehensively described elsewhere [13]. Already cleaned and weighed coupons made from steel were suspended in 250 mL of the test solutions. Measurements were carried out in duplicates in order to obtain reproducible results. Effect of exposure time on the corrosion rate of the mild steel was investigated by carrying out the experiment for 24 h, 48 h, 72 h, 96 h, 120 h, 144 h and 168 h. Temperature studies were conducted for three hours at 303 K, 313 K, 323 K and 333 K using a thermostatic water bath. The loss in weight was taken to be the difference in weights of the coupon at a given time and its initial weight.

2.2.3. Linear polarization measurements. Linear polarization studies were carried out using Metrohm Autolab AUT50280 in the potential range of -1500 to 1500 mV with a scan rate of 0.012 v/s at room temperature [14].

Mild steel coupons of 3x2 cm² dimension were covered with epoxy resin in such a way that only 1 cm² surface area was left uncovered. A three-electrode flask containing a mild steel working electrode, saturated calomel electrode (SCE) as reference electrode and platinum (Pt) as an auxiliary electrode, was employed for the measurements.

2.2.4. Optical microscopy. Surface morphologies of mild steel coupons before and after dissolution for 24 hours in the absence and presence 1.0 g/L of MI gums were investigated using a metallurgical microscope (Tsview digital metallurgical microscope, Tucsen 0923502 model) [14].

3. Results and discussion

3.1. Weight loss data

The corrosion rate (CR), inhibition efficiency (% IE) and degree of surface coverage (θ) were calculated using Equations 1 to 3 respectively [13].

$$CR(g \cdot h^{-1} \cdot cm^{-2}) = \frac{\Delta W}{At} \quad (1)$$

$$IE_{exp} = \left(1 - \frac{W_1}{W_2}\right) \times 100 \quad (2)$$

$$\theta = 1 - \frac{W_1}{W_2} \quad (3)$$

where W_1 and W_2 are the weight losses (g) of mild steel in the presence and absence of the inhibitor, $\Delta W = W_2 - W_1$ is the weight loss of mild steel after time, t , A is the area of the metal coupon (in cm²), t is the exposure period (in hours) and θ is the degree of surface coverage of the inhibitor. The presented data are the average of duplicate measurements.

Figure 1 depicts the corrosion rate of mild steel in the test solutions as a function of exposure time. It can be observed from the plot on Figure 1 that the corrosion rate of mild steel decreased with exposure time and increasing concentrations of MI gums while inhibition efficiency increased with increasing concentrations of MI gums up to the exposure time of 72 h before a decrease (Figure 2) to about 70 % at the optimum

concentration of 1.0 g/L at the end of the experiment (168 h).

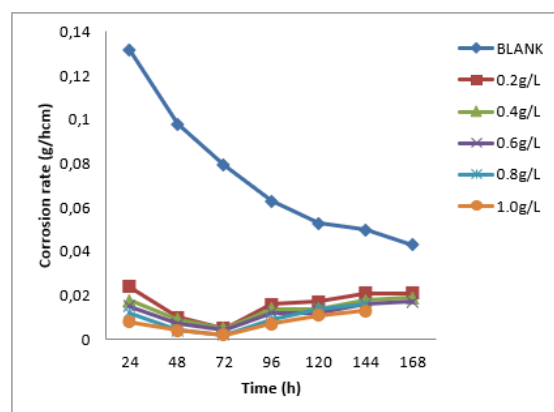


Figure 1. Corrosion rate of mild steel as a function of exposure time.

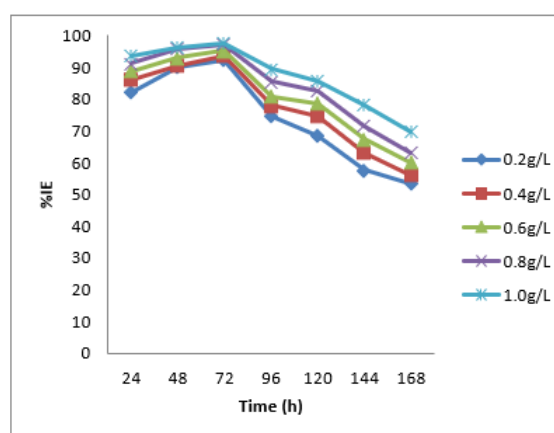


Figure 2. Inhibition efficiency of MI gums as a function of exposure time.

This development has been ascribed to the desorption of the inhibitor from the surface of the steel at longer exposure time leading to lower IE values observed [2, 6, 16].

Table 1. Corrosion rate of mild steel coupons in 1.0 M HCl at 303-333 K.

Concentration (g/L)	Corrosion rate (g·h ⁻¹ ·cm ⁻²)			
	303 K	313 K	323 K	333 K
Blank	0.263	0.505	0.843	1.050
0.2	0.103	0.139	0.200	0.228
0.4	0.086	0.120	0.169	0.214
0.6	0.071	0.107	0.160	0.178
0.8	0.057	0.091	0.123	0.159
1.0	0.049	0.069	0.097	0.121

Table 1 presents the values of the corrosion rate of mild steel in 1.0 M HCl solutions at 303, 313, 323 and 333 K. A closer look at the values of corrosion rates on Table 1, it is evident that the corrosion rates of mild steel generally increased with increase in temperature both in the absence and presence of MI gums. This is because as the temperature increased from 303 to 333 K, the rate of corrosion of the mild steel coupons also increased due to increasing average kinetic energy of the reacting molecules [2, 16]. However, the corrosion rate of mild steel was relatively lower in the presence of MI gums compared with the uninhibited HCl solution. This

signifies the inhibitive effect of MI gums on the corrosion of mild steel in the acid solution.

Figure 3 illustrates the quantitative effect of this inhibitive effect of MI gums with increasing temperature. The plot shows that *IE* decreased with increase in temperature, a phenomenon that has been reportedly associated with the physisorptive kind of adsorption mechanism of an inhibitor to the surface of a metal/alloy [3, 13, 16].

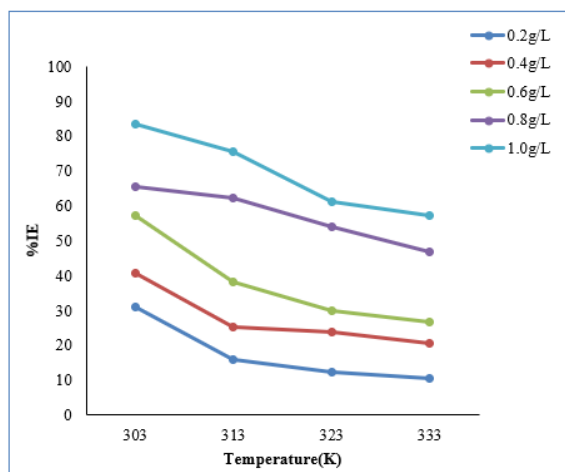


Figure 3. Inhibition efficiency of MI gums as a function of temperature (K).

3.2. Linear polarization

The effect of MI gums on the corrosion of mild steel in 1.0 M solution of HCl was also investigated using linear polarization. Figure 4 shows the linear polarization plots. The linear polarization parameters derived from the polarization plots and inhibition efficiency values quantified using Equation 4 are summarized on Table 2.

$$\%IE = \frac{I_{corr(blank)} - I_{corr(inh)}}{I_{corr(blank)}} \times 100 \quad (4)$$

where $I_{corr(blank)}$ is the corrosion current density of MS without inhibitor and $I_{corr(inh)}$ is the corrosion current density of MS with inhibitor.

The corrosion current density determines the reactivity of a metal in an aqueous environment. The higher the values of I_{corr} , the higher the dissolution of the metal and vice versa. The presence of MI gums was found to influence to both the anodic and cathodic redox reactions, shifting the corrosion potential (E_{corr}) toward more negative (cathodic) values thereby reducing the anodic (b_a) and cathodic (b_c) current densities and the corresponding corrosion current density. This implies that MI gums behaved as a mixed-type inhibitor [16].

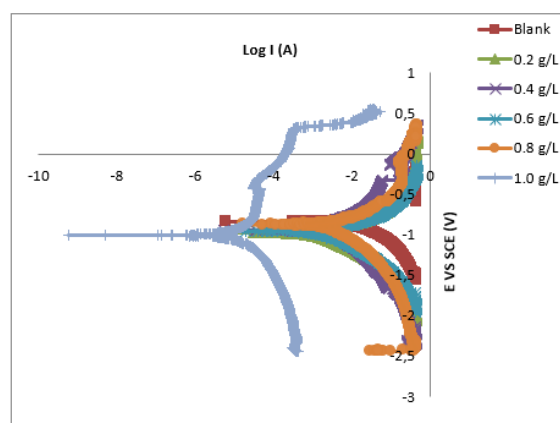


Figure 4. Linear polarization plots of the corrosion of mild steel in 1.0 M HCl in the absence and presence of MI.

Table 2. Linear polarization parameters for the corrosion of mild steel in 1.0 M HCl in the absence and presence of MI.

Conc. (g/L)	E_{corr} (mV)	I_{corr} (μ A/cm)	CR (mm/year)	IE (%)
Blank	-843.79	299.86	348.44	-
0.2	-976.54	68.89	80.044	77.03
0.4	-942.07	29.06	33.768	90.31
0.6	-953.81	56.71	65.80	81.09
0.8	-880.79	58.65	68.149	80.44
1.0	-1010.30	54.50	63.364	99.82

3.3. Optical microscopy

Fig. 5 shows the optical micrograph of the surface of the steel coupon in the free acid, while Fig. 6 is the optical micrograph of the surface of the steel coupon with 1.0 g/L MI gums. Fig. 5 shows a surface morphology that is severely damaged compared to Fig. 6. This is due to the rust formed on it after undergoing acidic attack in 1.0 M solution of HCl. The steel surface in Fig. 6 is absent of cracks and pits except for some polishing lines and the evidence of a very reasonable amount of protective films of MI gums thus confirming the adsorptive and inhibitive properties of MI gums.



Figure 5. Micrograph of steel surface after exposure for 24 h in 1.0 M HCl.

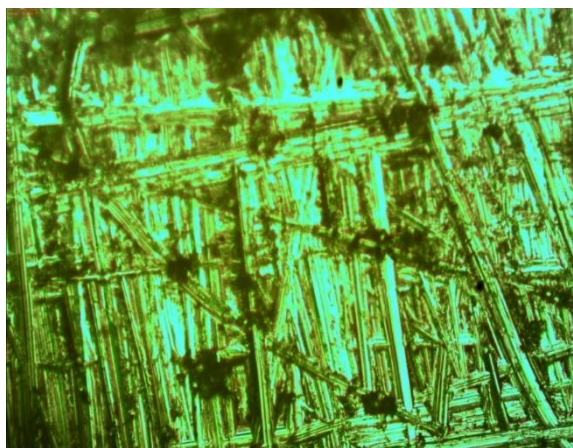


Figure 6. Micrograph of steel surface after exposure for 24 h in 1.0 M HCl with 1.0 g/L MI gums.

3.4. Adsorption mechanism

In trying to identify the adsorption properties of MI gums on the surface of the mild steel, values of θ obtained from weight loss experiments at 303 and 333 K were inserted into different isotherm models, the linearity of the plots and the coefficients of correlation (R^2) were employed in determining the finest fit. The Langmuir, Freundlich and Temkin adsorption isotherms gave the best fit (Figures 7-9).

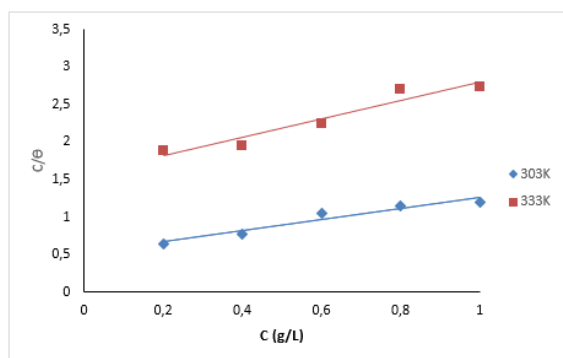


Figure 7. Langmuir isotherm for the adsorption of MI on mild steel surface in 1.0 M HCl.

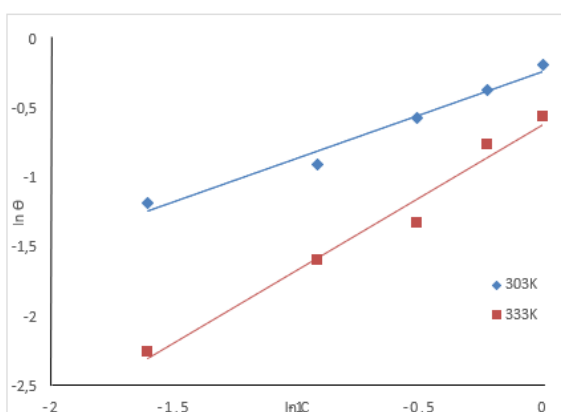


Figure 8. Freundlich isotherm for the adsorption of MI on the mild steel surface in 1.0 M HCl.

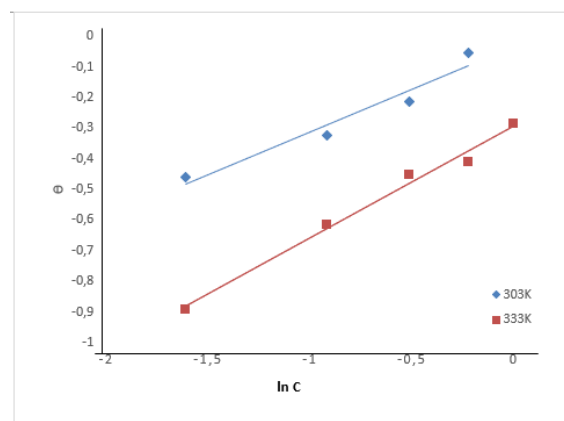


Figure 9. Temkin isotherm for the adsorption of MI on the mild steel surface in 1.0 M HCl.

The isotherm models can be mathematically expressed as [13, 16]:

$$\frac{C}{\theta} = C + \frac{1}{K_{ads}} \quad (5) \text{ Langmuir}$$

$$\log \theta = \log K_{ads} - n \log C \quad (6) \text{ Freundlich}$$

$$-2 \propto \theta = 2.303(\log K_{ads} + \log C) \quad (7) \text{ Temkin}$$

where C is the concentration of MI gums in the bulk electrolyte, K_{ads} is the adsorption equilibrium constant, θ is the degree of surface coverage of MI gums, n is the Freundlich constant and α is the molecular interaction parameter. Table 3 presents the adsorption parameters derived from the plots on Figures 7-9.

The adsorption equilibrium constant, K_{ads} is related to the standard free energy of adsorption, ΔG_{ads}° as shown in Equations 8 and 9 [13]:

$$\log K_{ads} = -1.744 - \frac{\Delta G_{ads}^\circ}{2.303RT} \quad (8)$$

$$\Delta G_{ads} = -2.303 \times RT \log(55.5 K_{ads}) \quad (9)$$

where ΔG_{ads}° is the standard free energy of adsorption of MI gums on the mild steel surface, R is the universal gas constant, 55.5 is the concentration of water in solution in mol/L and K_{ads} is the equilibrium constant of adsorption.

The values of the standard free energy of adsorption were negative and less than $-20 \text{ kJ} \cdot \text{mol}^{-1}$ for all the three isotherms. This shows that the adsorption of MI gums on the surface of the mild steel coupon is spontaneous and aligns with physisorption [2-5].

Table 3. Adsorption parameters of MI on mild steel surface in 1.0 M HCl.

Isotherm	T (K)	Slope	R^2	K_{ads}	α	ΔG_{ads}° (kJ mol ⁻¹)
Langmuir						
	303	0.904	0.991	5.917		-14.60
	333	1.076	0.990	3.623		-21.07
Freundlich						
	303	0.280	0.945	0.924		-9.921
	333	0.366	0.990	0.509		-9.250
Temkin						
	303	0.150	0.975	0.150	37.70	-25.07
	333	0.204	0.985	0.204	36.34	-21.07

3.5. Thermodynamics

Using the values of the corrosion rates of the steel coupons at different temperatures (Table 1) and the Arrhenius equation (Equation 10), the activation energies of the corrosion of mild steel in 1.0 M HCl in the absence and presence of MI gums was evaluated.

$$CR = A \cdot \exp^{-E_a/RT} \quad (10)$$

Taking the logarithm of both sides of equation 10, Equation 11 is obtained.

$$\log CR = \log A - \frac{E_a}{2.303RT} \quad (11)$$

where CR is the corrosion rate of the mild steel, A is the Arrhenius constant, E_a is the activation energy, R is the universal gas constant and T is the absolute temperature of the system in Kelvin (K). A plot of $\log CR$ versus $1/T$ represented on Figure 10 gave a straight line graph with a slope of $(-\frac{E_a}{2.303R})$ and an intercept of $[\log A]$ from which the values of the apparent activation energy (E_a) were evaluated.

Table 4 presents E_a values obtained from the plot. From Table 4, it can be observed that the value of E_a in the uninhibited system increased when MI gums were introduced into the acid solutions. This behavior is suggestive of a physisorptive kind of adsorption mechanism whereby increase in temperature results in the desorption of the adsorbed inhibitor from the surface of the steel thereby exposing the steel surface to the acid solution and leading to an increase in the corrosion rate of the steel [13].

The values of enthalpy (ΔH^*) and entropy (ΔS^*) of activation of the corrosion inhibition process were evaluated from the Eyring equation:

$$\log CR/T = \left[\log(R/nh) + \frac{\Delta S^*}{2.303R} \right] - \frac{\Delta H^*}{2.303RT} \quad (12)$$

where CR is the corrosion rate at temperature T , R is the molar gas constant, n is Avogadro's constant 6.0225×10^{23} and h is the Planck's constant ($6.6261 \times 10^{-34} \text{Js}$). A plot of $\log CR/T$ versus $1/T$ as shown on Figure 11 is a straight line graph with a slope of $(-\Delta H^*/2.303R)$ and an intercept of $[\log(R/nh) + \Delta S^*/2.303R]$ from which the values of ΔH^* and ΔS^* were calculated [13, 17-19].

The results presented on Table 4 show that the enthalpies of activation are all negative which signifies that the process of the dissolution of the mild steel was exothermic. Also, the entropies of activation were negative for the gums. Negative values of ΔS^* have been reported to characterize the association mechanism of the corrosion process whereby a decrease in disorder takes place on going from the reactants to the activated complex [17-20].

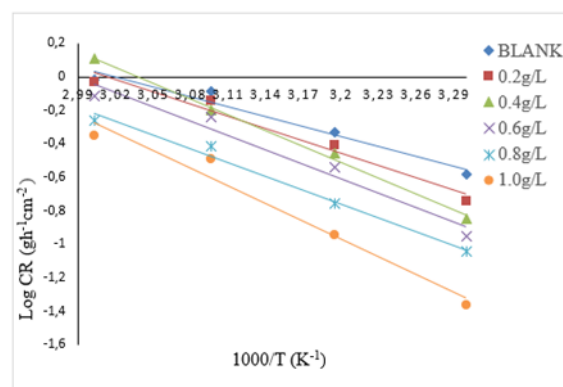


Figure 10. Arrhenius plot of the temperature-dependence of the corrosion rate of mild steel in 1.0 M HCl.

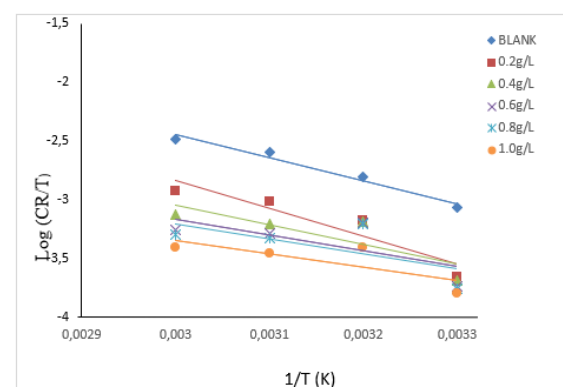


Figure 11. Eyring plot of the temperature-dependence of the corrosion rate of mild steel in 1.0 M HCl.

Table 4. Activation parameters for the corrosion of mild steel in 1.0 M HCl with and without MI gums.

Concentration (g/L)	E_a ($\text{kJ}\cdot\text{mol}^{-1}$)	ΔH^* ($\text{kJ}\cdot\text{mol}^{-1}$)	ΔS^* ($\text{kJ}\cdot\text{mol}^{-1}$)
Blank	16.28	37.49	-131.9
0.2	18.27	45.06	-116.4
0.4	18.56	31.92	-159.6
0.6	19.56	25.95	-180.4
0.8	20.84	24.07	-186.9
1.0	22.52	21.92	-195.9

4. Conclusion

MI gums suppressed the corrosion of mild steel in 1.0 M solution of HCl. Linear polarization measurements revealed MI gums to inhibit both the rates of the cathodic hydrogen ion reduction and anodic metal dissolution reactions on the surface of the mild steel thereby functioning as a mixed-type inhibitor. Adsorption behavior of the gums were approximated by the isotherm models of Langmuir, Freundlich and Temkin. Thermodynamics considerations showed that MI gums adsorbed on the surface of the mild steel through the mechanism of physisorption and that the adsorption process was exothermic and spontaneous.

Conflict of interest

The interests of the authors do not conflict.

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