

Polyvinyl Alcohol-Anthranilic Acid Composite as Corrosion Inhibitor for Mild Steel

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The inhibitive nature of polyvinyl alcohol-anthranilic acid (PVAAA) on the corrosion of mild steel in 1 M HCl solution under various conditions has been investigated by means of weight loss, potentiodynamic polarization and AC impedance methods. The studies show that polyvinyl alcohol-anthranilic acid exhibited excellent inhibition property. The potentiodynamic polarization studies reveal that the polyvinyl alcohol-anthranilic acid acts as a mixed type inhibitor. The adsorption of the polymer on the mild steel surface was found to obey Langmuir and Temkin adsorption isotherms.

Key Words: Corrosion, Polymer inhibitor, Weight loss method, Mild steel and electrochemical measurements.

INTRODUCTION

Corrosion of metals in different environment is one of the serious problems facing industry and its prevention has been approached from various angles. Technological and financial considerations favour the addition of certain polymers as inhibitors to reduce the corrosion rate. Aqueous solutions of acids are among the most corrosive medium, especially when soluble corrosion products are formed. Acid media are widely used in industry, the most important field of application being acid pickling, industrial cleaning, acid descaling and oil well acidizing. In order to avoid the corrosion failures, effective additional protective measures are provided by the use of polymer inhibitor.

Recently, the use of polymers as corrosion inhibitors has drawn considerable attention due to their inherent stability and cost effectiveness. Due to presence of functional groups in polymers, they form complexes with metal ions and on the metal surface. These complexes occupy a large surface area thereby blanketing the surface and protecting the metals from corrosive agents present in solution¹. Like other polymeric coatings, these materials can constitute a physical barrier towards corrosive reagents. Moreover as they carry polar groups, they may also act as macromolecular inhibitors and shift the potential of the substrate to a value where its rate of corrosion is reduced. Some research group has investigated the use of polymers as corrosion inhibitors of metals in aggressive medium. Umoren *et al.*² reported the effect of halide ions on the corrosion of mild steel using polyvinyl alcohol

(PVA) in H₂SO₄ at 30-60 °C. Bereket *et al.*³ reported inhibition of the corrosion of low carbon steel in acidic solution by selected polyelectrolytes and polymers using potentiodynamic polarization measurements and impedance measurement techniques over the temperature range of 20-60 °C at different inhibitor concentrations. Inhibition efficiency and adsorption characteristics of two water soluble polymers namely polyvinyl alcohol (PVA) and polyethyleneglycol (PGE) as corrosion inhibitors of mild steel in H₂SO₄ have been reported by Umoren *et al.*⁴. Muralidharans *et al.*⁵ reported a new class of corrosion inhibitors, namely polyamino-benzoquinone has been synthesized and its inhibiting action on the corrosion of mild steel in 1 N HCl and 1 N H₂SO₄ has been investigated by various corrosion monitoring techniques. The corrosion behaviour of mild steel in sulphuric acid solution containing various concentrations of a copolymer formed between maleic anhydride and N-vinyl-2-pyrrolidone was investigated using weight loss, polarization and electrochemical impedance techniques have been reported by Achary *et al.*⁶. The present paper reports a systematic study on the chemical oxidative polymerization of polyvinyl alcohol and *p*-anthranilic acid. The corrosion inhibition efficiency of the resultant polymer composite (polyvinyl alcohol-anthranilic acid) for mild steel in 1 M HCl medium was evaluated by weight loss experiments and electrochemical measurements.

EXPERIMENTAL

Ammonium persulphate (APS), *p*-aminobenzoic acid (*p*-anthranilic acid), polyvinyl alcohol (Mw = 14,000) from merck

chemicals. All other materials were used without further purification.

Polyvinylalcohol-anthranilic acid composite preparation (PVAAA): A standard procedure was adopted to prepare polyvinyl alcohol-anthranilic acid polymer^{7,9}. 1 % *p*-anthranilic acid was well mixed with 10 % polyvinyl alcohol solution. The system was cooled at 0-5 °C followed by the addition of 20 mL of aqueous oxalic acid solution of ammonium persulphate. Anthranilic acid to ammonium persulphate mole ratio was maintained 1:1. Polymerization was allowed to proceed for 3 h and composite was formed as a bright brown stable solution. This was treated with ammonium hydroxide for deprotonation. The pH of this solution was kept around 9 by adding drops of 1 M NH₄OH and kept for 5 h. It was isolated from the medium by precipitation technique using non-polar solvent and dried under vacuum.

Weight loss measurements: Weight loss measurements were carried out using a Denvar balance. The mild steel samples were obtained from a locally available industrial Fe-C steel with very low concentration of carbon. A large sheet of cold rolled mild steel coupons with a chemical composition of carbon 0.106 %, manganese 0.196 %, silicon 0.006 %, phosphorus 0.027 %, sulphur 0.016 %, chromium 0.022 %, molybdenum 0.003 %, nickel 0.012 % and iron 99.612 % was utilized for the study. The mild steel samples, with an active surface of 1 cm × 5 cm were mechanically polished, degreased, washed in double distilled water and dried in warm air.

The experiments were performed in 1 M HCl solution without inhibitor and in the presence of polyvinyl alcohol-anthranilic acid at different concentrations: 600, 1200, 1800, 2400, 3000, 3600, 4200, 4800, 5400 and 6000 ppm at various immersion times: 1/2, 1, 3, 6, 12 and 24 h and at various temperatures 303, 313, 323, 333 and 343 K.

Electrochemical measurements

Polarization and impedance studies: The experiments were performed in a classical three-electrode electrochemical cell. Mild steel specimen of 1 cm² area was used as the working electrode and platinum electrode was used as counter electrode and saturated calomel electrode as reference electrode. Prior to each experiment the working electrode surface was polished with emery paper. Solartron electrochemical analyzer (model 1280B) interface with an IBM computer and corware and z-plot corrosion software were used for data acquisition and analysis for polarization and impedance studies the period of immersion was for 0.5 h. Polarization study was carried out using corware software from a cathodic potential of -0.1 V to an anodic potential of -1 V with respect to corrosion potential at a sweep rate 2 mV s⁻¹, *E* versus log *I* curves were plotted. The linear Tafel segments of the anodic and cathodic curves were extrapolated to corrosion potential to obtain the corrosion current densities. For linear polarization resistance measurements, polarization was done from -0.010 to -0.100 V with respect to corrosion potential at a sweep rate of 2 mV s⁻¹ and the slope of the linear segment at corrosion potential was obtained as polarization resistance *R*_p. AC signals of 10 mV amplitude and a frequency spectrum from 20.0-0.1 Hz were impressed and the Nyquist representation of the impedance data were analyzed with Z view software.

RESULTS AND DISCUSSION

Weight loss method: The results of weight loss measurements are tabulated and discussed below.

Effect of concentration: Effect of polyvinyl alcohol-anthranilic acid on the corrosion of mild steel in 1 M HCl was studied by weight loss measurements at 303 K and the results are tabulated in Table-1. The data revealed that the inhibitor efficiency increased with increasing additive concentration. This behaviour can be attributed to the increase in surface area covered by the adsorbed molecules on the metal surface with the increase in concentration of the inhibitor¹⁰. A maximum efficiency of 91 % was achieved at 6000 ppm.

Concentration (ppm)	Immersion time (h)					
	0.5	1	3	6	12	24
600	75.00	63.9	67.5	65.0	62.8	62.4
1200	85.60	76.3	76.9	73.5	74.3	68.0
1800	86.07	85.6	80.7	78.0	75.9	71.8
2400	87.60	87.7	84.1	80.8	77.1	71.9
3000	87.60	88.4	84.3	81.4	78.5	73.7
3600	88.70	88.7	85.0	84.0	79.8	75.1
4200	89.40	90.2	86.3	84.1	81.5	77.2
4800	89.70	90.3	88.6	84.3	82.0	76.0
5400	90.30	90.3	89.0	84.4	82.8	77.2
6000	90.60	91.0	90.8	86.7	83.8	78.2

Effect of immersion time: Fig. 1 shows the variation of the inhibition efficiency at 6000 ppm with immersion time. Analyzing the graph (Fig. 1) it is clear that inhibition efficiency increases with increasing concentration of polyvinyl alcohol-anthranilic acid. As the time of immersion increases inhibition efficiency increases up to 91 % at 3 h. After that there is a slight decrease in inhibition efficiency at 6 h furnishing 87 % and at 12 and 24 h, inhibition efficiency decreases to 78 % at 6000 ppm. It has been observed that in the presence of a concentration of 6000 ppm polyvinyl alcohol-anthranilic acid in 1 M HCl solution, the inhibition efficiency increased to 91 % (1 h), which proves a good adsorbability on the mild steel surface. One may assume the formation of complexes between polyvinyl alcohol-anthranilic acid and different metal cations, which are found in the mild steel structure. These complexes can form stable passive layer on the surface, so decreasing the corrosion rate¹⁰.

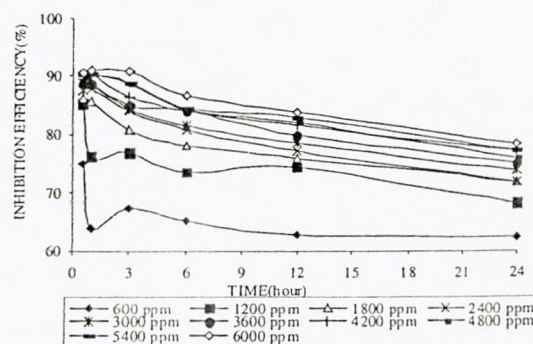


Fig. 1. Role of immersion time on inhibition efficiency of polyvinyl alcohol-anthranilic acid for mild steel in 1 M HCl

Effect of temperature: The influence of temperature on the corrosion behaviour of mild steel in acid medium in the presence of various concentrations of polyvinyl alcohol-anthranilic acid was investigated by weight loss trends in the temperature range 303-343 K. The variation of inhibition efficiency with increasing temperature is shown in Fig. 2.

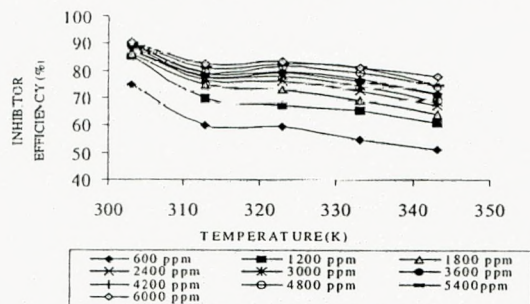


Fig. 2. Variation of inhibition efficiency with temperature at various inhibitor concentration

The behaviour of polyvinyl alcohol-anthranilic acid at 303-343 K may be attributed to the adsorption polyvinyl alcohol-anthranilic acid upto 6000 ppm and further increase in temperature brings about desorption of the polyvinyl alcohol-anthranilic acid under study.

This may be explained as follows, adsorption and desorption of inhibitor molecules continuously occur at the metal surface and the equilibrium exists between these two processes at particular temperature, with the increase of temperature the equilibrium between adsorption and desorption process is shifted leading to a higher desorption rate than adsorption until equilibrium is again established at a different value at equilibrium constant. It explains the lower inhibition efficiency at higher temperature¹¹.

Adsorption isotherm: It is generally assumed that the adsorption of inhibitors on the metal surface is the essential step in the mechanism of inhibition. The surface coverage values (θ) were evaluated using corrosion rate values (CR) obtained from weight loss method. θ Values for different concentrations of inhibitors were tested graphically by fitting into various isotherms. A plot of $\frac{\log \theta}{(1-\theta)}$ versus $\log C$ and θ versus $\log C$ gave straight lines. This confirms that the present system obeys Langmuir and Temkin isotherms (Figs. 3 and 4). This indicates that actual process of inhibition is by adsorption¹⁰.

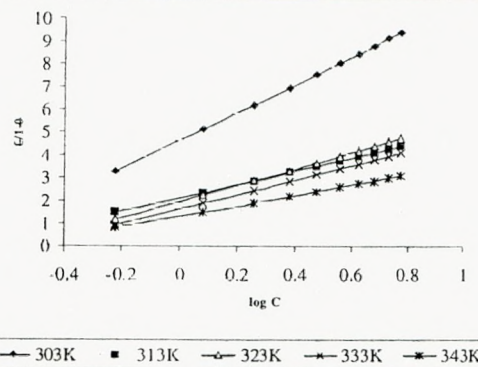


Fig. 3. Plot of Langmuir isotherms

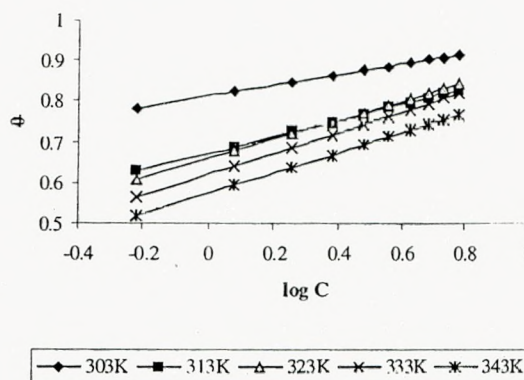


Fig. 4. Plot of Temkin isotherms

Energy of activation and thermodynamic parameters

Activation energy: The kinetic parameter of the system under consideration was evaluated using the data obtained from weight loss method for various concentration of the polyvinyl alcohol-anthranilic acid at different temperature. Activation energy (E_a) of corrosion reaction was calculated from Arrhenius equation.

$$\log K = -\frac{E_a}{2.303RT} + C$$

where K = corrosion rate. The plot of $\log k$ against $1/T$ gave straight lines.

From Table-2, it is understood that the energy of activation changes in the presence of the inhibitor. For adsorption inhibitors the observed rate shows not only the effect of temperature on metal dissolution, but also the variation of surface

TABLE-2
KINETIC AND THERMODYNAMIC PARAMETERS OF MILD STEEL IN THE PRESENCE OF POLYVINYL ALCOHOL-ANTHRANILIC ACID

Concentration of the inhibitor (ppm)	Activation energy E_a (KJ/mol)	Free energy of adsorption $-\Delta G$ (KJ/mol)					Change in enthalpy ΔH (J/mol)	Change in entropy ΔS (J/mol)
		303 K	313 K	323 K	333 K	343 K		
600	66.2	14.14	12.49	13.21	13.05	13.00	-18799.8	17.4
1200	71.8	14.06	12.16	12.22	12.36	12.18	-24093.0	35.6
1800	71.8	13.20	11.76	11.86	11.86	11.39	-23354.8	35.1
2400	71.8	12.82	10.25	11.56	11.57	11.87	-16929.4	15.8
3000	70.6	12.25	10.79	11.19	11.19	10.55	-20887.7	30.0
3600	70.4	12.05	10.79	10.98	10.98	10.03	-21425.7	32.7
4200	71.2	11.85	10.15	10.61	10.61	10.01	-21044.3	32.2
4800	69.2	11.60	9.87	10.57	10.57	10.04	-18330.0	24.2
5400	70.1	11.47	9.53	10.41	10.46	9.74	-18508.2	25.3
6000	69.1	11.29	9.49	10.28	10.18	9.91	-16881.4	20.6

coverage with the temperature at constant concentration. Accordingly the energy of activation changes in the present study the energy of activation decreased in the presence of inhibitor. According to Riggs¹² dissolution process is not determined only by the reaction of the metal from the base surface but involves also the adsorbed inhibitor and consequently the E_a can assume values greater or smaller than those calculated in the absence of the inhibitor. It also suggested that the inhibitor does not change the temperature co-efficient of the reaction and firmly hold on the metal surface¹³⁻¹⁶.

Thermodynamic parameters: With the help of the temperature study results, thermodynamic parameters such as ΔG , ΔH and ΔS were calculated. Standard free energy values of adsorption at different temperatures were derived from Langmuir plot using the relation¹⁷⁻¹⁹,

$$\log C = \log \left(\frac{\theta}{1-\theta} \right) - \log B$$

$$\log B = -1.74 - \frac{\Delta G}{2.303RT}$$

The values of thermodynamic parameters are represented in Table-2. The entropy of adsorption (ΔS) and enthalpy of adsorption (ΔH) can be calculated from the plot of ΔG versus T . ΔS and ΔH were obtained from the slope and intercept, respectively. The negative values of ΔG show that the adsorption of the inhibitor is a spontaneous process, under the experimental conditions. The negative heat of adsorption and positive entropy substantiated the spontaneous adsorption of inhibitor on the metal surface. The change of ΔH and ΔS with concentration of the inhibitor suggests that the process is enthalpic and entropic controlled²⁰⁻²².

Electrochemical measurements

Potentiodynamic polarization studies: Linear polarization method was used to evaluate the corrosion rate of mild steel sample in the presence and absence of the polymer composite inhibitor (polyvinyl alcohol-anthranilic acid). Potentiodynamic polarization curves of mild steel in 1 M HCl solution with and without the polymer composite inhibitor (polyvinyl alcohol-anthranilic acid) are presented in Fig. 5. The electrochemical parameters, corrosion potential (E_{corr}), corrosion current density (I_{corr}), anodic Tafel constant (b_a) and cathodic Tafel constant (b_c) are given in Table-3. In presence of inhibitor the I_{corr} value

decreases, thereby indicating that the inhibitor is corrosion inhibitive in nature. The steady values of E_{corr} indicate that the inhibitor might have predominantly acted as mixed inhibitor to retard both the rates of hydrogen ion reduction and anodic dissolution of mild steel. The values of b_a and b_c have not shifted to any particular direction from the blank values indicating again the mixed mode of inhibition. Tafel slope values b_a and b_c were not much affected and this suggests that inhibitor molecules adsorb on the metal surface by blocking the active sites on the metal surface²³. From the values of inhibition efficiency, it is clear that the corrosion inhibition may be due to the increase in the adsorption of the inhibitor on the metal surface. The adsorption may also be due to the negatively charged metal surface and the protonated species of the polymer inhibitor in the acidic solution on the metal surface. When the content of inhibitor material was increased from 600-6000 ppm, the inhibition efficiency values was found to increase from 42.1 % to 70.6 %.

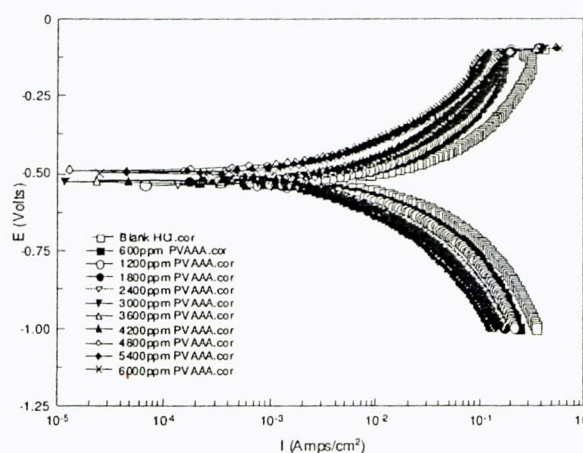


Fig. 5. Potentiodynamic polarization curves for mild steel in 1 M HCl in absence and presence of different concentration of polyvinyl alcohol-anthranilic acid

Electrochemical impedance measurements (EIS): The Nyquist representation of the impedance behaviour of mild steel in 1 M HCl with and without the inhibitor is shown in Fig. 6. The existence of the single semicircle showed the presence of single charge transfer process during corrosion which was unaffected by the presence of inhibitor molecules²⁴. The slightly depressed nature of the semicircle, which has the

TABLE-3
ELECTROCHEMICAL POTENTIODYNAMIC POLARIZATION AND IMPEDANCE STUDIES OF MILD STEEL IN PRESENCE OF POLYVINYL ALCOHOL-ANTHRANILIC ACID IN 1 M HCl

Conc. of inhibitor (ppm)	$-E_{\text{corr}}$ (mV/s)	$I_{\text{corr}} \times 10^{-4}$ (mA/cm ²)	b_a (mV/dec)	b_c (mV/dec)	IE (%)	R_p (Ohm/cm ²)	IE (%)	R_{ct} (Ohm/cm ²)	IE (%)	$C_{dl} \times 10^{-4}$ ($\mu\text{F/cm}^2$)	θ
Blank	524.90	89.50	199.4	153.6	—	2.9	—	6.5	—	3.20	—
600	526.50	51.80	137.1	122.7	42.1	5.0	42.1	22.9	71.7	3.70	-0.14
1200	535.10	45.98	188.5	206.4	48.6	5.7	48.6	28.5	77.2	3.30	-0.02
1800	536.70	46.50	194.3	147.5	48.0	5.6	48.0	51.9	87.4	1.70	0.46
2400	538.90	43.30	153.7	131.7	51.6	6.2	51.6	52.6	87.6	1.50	0.53
3000	541.90	43.50	210.5	148.9	51.4	6.0	51.3	52.0	87.5	1.20	0.64
3600	539.90	37.50	183.3	135.8	58.1	6.9	58.1	65.7	90.1	1.40	0.66
4200	539.80	33.70	214.8	149.0	62.4	7.8	62.4	69.3	90.5	1.00	0.67
4800	508.95	29.40	171.6	116.7	67.1	8.9	67.2	90.0	92.8	0.95	0.70
5400	509.10	27.20	169.3	130.0	69.7	9.6	69.7	136.3	95.2	0.91	0.72
6000	506.60	26.30	95.3	86.4	70.6	9.9	70.6	165.1	96.1	0.80	0.74

centre below the X-axis, is the characteristics for solid electrode and such frequency dispersion has been attributed to roughness and other inhomogenetics of the solid electrode²⁵. The equivalent circuit elements calculated by z view fitting program are given in Table-3. The value of R_{ct} is increased from 71.7 % (600 ppm) to 96.1 % (6000 ppm) ($\Omega \text{ cm}^2$) and the corresponding C_{dl} value decreased from 3.7104 (600 ppm) to 0.81931 (6000 ppm) $\mu\text{F cm}^{-2}$. This indicates that polyvinyl alcohol-anthranilic acid composite was adsorbed on mild steel surface uniformly. Maximum inhibition efficiency was found to be 96.1 % at 6000 ppm concentration of polyvinyl alcohol-anthranilic acid.

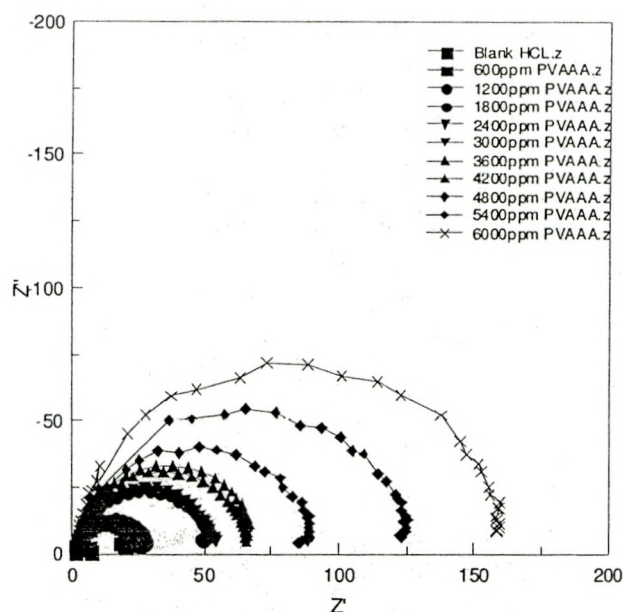


Fig. 6. Nyquist plots for mild steel in 1 M HCl in absence and presence of different concentration of polyvinyl alcohol-anthranilic acid

Comparison of inhibition efficiency obtained by weight loss method and electrochemical measurements: Bar graph obtained using inhibition efficiency obtained by various techniques reveal that the results are quite comparable are shown in Fig. 7.

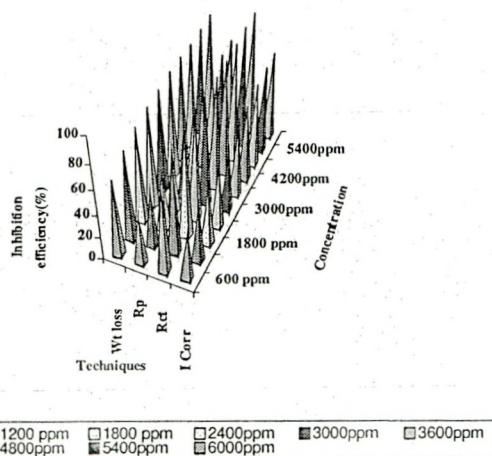


Fig. 7. Comparative graph for electrochemical method and weight loss method

Conclusion

Polyvinyl alcohol-anthranilic acid composite acted as an effective corrosion inhibitor for mild steel in 1 M HCl medium. The inhibition efficiency increases with increasing the concentration and decreases with increasing the temperature and immersion time. Maximum inhibitor efficiency was 91 % at 6000 ppm concentration at 3 h. The adsorption of polyvinyl alcohol-anthranilic acid on the mild steel in 1 M HCl obeys Langmuir and Temkin isotherms. Kinetic and thermodynamic parameters revealed that the inhibition is spontaneous with adsorption of inhibitors on the metal surface. The values of ΔG_{ads}^0 are negative, which suggests that the inhibitor was strongly adsorbed on the mild steel surface. Electrochemical studies confirmed the mixed mode of inhibition for the corrosion of mild steel in 1 M HCl without modifying the mechanism of hydrogen evolution of the inhibitor. Weight loss measurement and electrochemical measurement are in good agreement.

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