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Anthranilic Acid as Corrosion Inhibitor for Mild Steel in Hydrochloric Acid Media

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Abstract

The inhibition effect of Anthranilic acid on corrosion of mild steel in 1M HCl solution was investigated by using traditional weight loss method, Polarization measurements and Electrochemical Impedance Spectroscopy (EIS) measurements. Small amount such as500 ppm of the Inhibitor shows good inhibition efficiency. Polarisation measurements infer inhibitor acts as mixed type inhibitor. Weight loss, Polarisation and Electrochemical impedance results are gives same order of inhibition efficiency

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Keywords:

1. Introduction

Corrosion phenomena, control and prevention are unavoidable major scientific issues that must be addressed daily as far as there are increasing needs of metallic materials in all facets of technological development. The protection of metals against electrochemical corrosion mainly depends on the isolation of metals from corrosive media. Inhibitors are applied in these processes to control the metal dissolution and it is the most effective and economic method Olivera W X et al. (1992), Vendrame Z B et al. (1998), Most of the inhibitors used in industry are

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organic compounds containing multiple bonds in their molecules that mainly contain nitrogen, sulphur, and/or oxygen atoms through which they get adsorbed on the metal surface Bentiss F et al. (2000), Fouda A S et al. (2000). However, most of these substances are toxic and using them is harmful for both human health and environment.

This is led to consider pharmaceutical ingredients are used as corrosion inhibitors. Ketoconazole Obot I B et al. (2010), Antifungal drugs Obot I B et al. (2009), Meclizine hydrochloride Ishwara Bhat J et al. (2011) and some antimalarian drugs Fouda A S et al. (2009) have been reported as good inhibitors. Thus drugs with planar structure can be a promising inhibitor which encouraged us to choose a drug Anthranilic acid is a class of non steroidal anti-inflammatory drug used for the treatment of inflammatory disorders. The IUPAC name of Anthranilic acid is 1-[N-[8-(trifluoromethyl)-4-quinolyl] anthranilate] (www.drugbank.com)..The presence of electron rich N, O, F atoms and π- bonds in its structure might be in favour of its adsorption on the metal surface which gives a scope for its study as a potential corrosion inhibitor. The aim of the present investigation is to study the effect of Anthranilic acid as a corrosion inhibitor for mild steel in 1M HCl.

2. Experimental

2.1 Material

Steel strips having compositions 0.04% C, 0.35% Mn, 0.022% P, 0.036% S and the rest being Fe (99.55%) were used for all experiments. The stripes were polished by emery papers from 80 – 1500 grade, washed thoroughly with distilled water, degreased with acetone and dried at room temperature. Weight loss method is carried out in 1M HCl media. Strips with an exposed area of 1 cm^2 (rest is covered) for electrochemical measurements were used. The corrosive media 1M HCl solutions were prepared using AR grade HCl and distilled water.

2.2 Test solution

Anthranilic acid structure is shown in Figure 1. It is procured from Hangzhou Zhenghan Biological Technology Co., Ltd. China, It is water insoluble but soluble in 1M HCl. Different weight of Anthranilic acid was dissolved in 1M HCl solution. The prepared stock solutions were used to the experiments including of the blank solution (1M HCl).

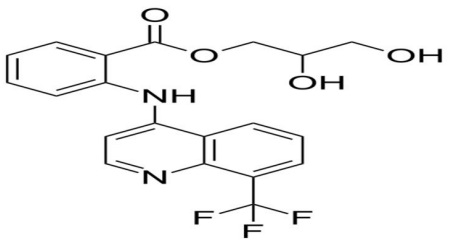

Figure 1: Structure of Anthranilic acid.

2.3 Methods

2.3.1 Weight loss Measurements

Weight loss measurements were performed by immersing steel plates in glass beaker containing 100 cm^3 of corrosive media (1M HCl) with different concentration of inhibitor at 303K.. After an immersion time of 4 h, steel

plate was taken out and washed well with plenty of tap water followed by distilled water, dried and weighed accurately using digital balance (accuracy: ±0.1 mg). All experiments were carried out in static and aerated condition. Each measurement was repeated thrice for reproducibility and an average value was reported.

2.3.2 Electrochemical Measurements

The electrochemical measurements were carried out in CHI 608D electrochemical work station (manufactured by CH Instruments, Austin, USA) at 303K. The cell consists of three electrodes namely, the working electrode (steel), counter electrode (platinum) and reference electrode (Ag/AgCl electrode). Before each electrochemical measurement, the working electrode was allowed to stand for 30 min in test solution to establish steady state open circuit potential (OCP). All reported potentials were with respect to Ag/AgCl electrode. For Tafel measurements, potential-current curves were recorded at a scan rate of 0.01 V s^{-1} in the potential range obtained by adding -0.2 and +0.2 V to the open circuit potential (OCP) value. The corrosion parameters such as corrosion potential (Ecorr), corrosion current (icorr) cathodic Tafel slope (bc) and anodic Tafel slope (ba) were calculated from the software installed in the instrument. Impedance measurements were carried out using AC signal with amplitude of 5 mV at OCP in the frequency range from 0.1 Hz to 1 KHz . The impedance data were fitted to most appropriate equivalent circuit by using Z_{Simp} Win 3.21 software. The impedance parameters were obtained from Nyquist plots.

3. Result and Discussion

3.1 Weight loss method

The weight loss method is probably the most widely used method of initial inhibition assessment. In our study, different mild steel samples were used which were immersed in 1 M HCl solutions containing different inhibitor concentrations at 303 K temperature for 4hrs.The investigations were carried out in aerated solutions. The mass of each steel specimen before and after immersion was determined using an analytical balance.

The value of percentage inhibition efficiency (η_w) was calculated from following relation:

$$\eta_w = \frac{W^o - W}{W^o} \times 100 \quad (1)$$

Where, W° and W are weight loss of steel in absence and presence of inhibitor.

The rate of corrosion ρ (mg cm^{-2} h^{-1}) was calculated from equation

$$\rho = \frac{W^o - W}{ST} \times 100 \quad (2)$$

Here, *S* is the surface area of the steel specimen and *T* is the immersion time in hours. Corrosion parameters for mild steel in 1M HCl in presence of different concentrations of the Anthranilic acid is provided in **Table 1**

Table 1. Corrosion parameters obtained from weight loss measurements for steel in 1M HCl in Presence of various concentrations of

Anthranilic Acid at 303K.

Corrosive medium of Anthranilic Acid (ppm)	Corrosion value (gm/cm^2 hr)	Inhibition Efficiency η_w
1M HCl	0.365	-
100	0.175	52.0
200	0.157	56.9
300	0.136	62.7
400	0.131	64.1
500	0.129	64.6

η_w is increased with increase in concentration up to 500 ppm and above this concentration almost same trend was observed. The increase in η_w with increase in concentration of Anthranilic acid is due to the strong adsorption of the of Anthranilic acid on the steel metal surface. So 500 ppm is considered as optimum concentration for achieving the maximum inhibition efficiency.

3.2 Electrochemical measurements

3.2.1 Polarization measurements

The polarization behavior of steel immersed in 1 M HCl in presence of different concentration of Anthranilic acid at 303K is shown in **Figure 2**.

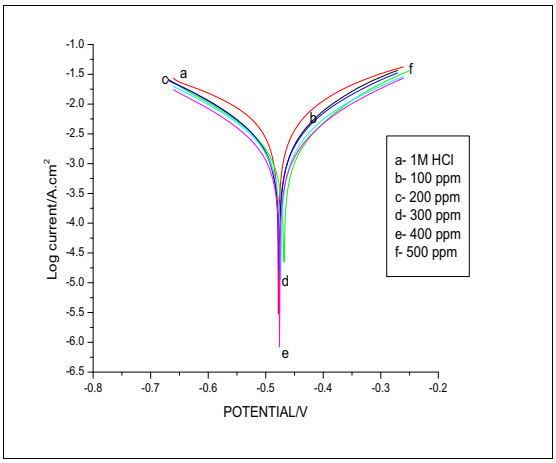

Fig. 2. Tafel Plots for mild steel in 1 M HCl in presence of different Concentration of Inhibitor at 303K

Electrochemical parameters like corrosion potential (E_{corr}), corrosion current density (i_{corr}), cathodic Tafel slope (β_c), anodic Tafel slope (β_a) and inhibition efficiency according to polarization studies (η_p) are listed in Table 2. The η_p was calculated from following relation.

$$\eta_P = \frac{i^{o}_{corr} - i_{corr}}{i^{o}_{corr}} \times 100 \quad (3)$$

Where i_{corr} and i^{0}_{corr} are the corrosion current densities in absence and presence of the corrosion inhibitor respectively. The presence of Anthranilic acid shifts both anodic and cathodic branches to the lower values of current densities and thus causes a remarkable decrease in the corrosion rate. Oxygen is reduced in low cathodic over potentials, but the main cathodic reaction in acidic solution is the discharge of hydrogen ions to produce hydrogen gas. It can be clearly seen from **Figure 2** that both anodic metal dissolution and cathodic reactions were inhibited after the addition of inhibitor to the aggressive solution. This result is indicative of the adsorption of inhibitor molecules on the active sites of mild steel surface. The inhibition of both anodic and cathodic reactions is more pronounced with the increasing in inhibitor concentration Saleh M M et al.(2006). i_{corr} values are decreased with increase in the concentration of Anthranilic acid. The inhibition efficiencies of Anthranilic acid were determined through electrochemical experiments **(Table 2)**. The values of the corrosion current density (i_{corr}) and corrosion potential (E_{corr}), as well as the cathodic and anodic Tafel slopes (β_c, β_a), were obtained by the linear extrapolation of the Tafel slopes. The figures show the influence of inhibitor and its concentration. The corrosion current density decreased with increase in inhibitor concentration and it indicates the corrosion rate was mitigated. Inhibition was reached by a blocking mechanism on the anodic and cathodic sites as polarization curves are displaced downward on the whole potential range. These results indicated that the presence of Anthranilic Acid inhibited iron oxidation and in a lower extent cathodic reduction reaction; consequently this compound can be treated as mixed type corrosion inhibitor, as electrode potential displacement is lower than 85 mV in any direction Hojatollah Jafari et al.(2013).

3.2.2 Electrochemical Impedance Spectroscopy (EIS) measurements:

Electrochemical impedance spectra for steel in 1 M HCl with different concentration of inhibitor is presented as Nyquist plot in **Fig. 3**. Nyquist plots were analyzed by fitting the experimental data to a simple circuit model (Figure **4**). The fitted values of R_{ct} and C_{dl} are listed in **Table 2**. It is clear that by increasing the inhibitor concentration, the C_{dl} values decreases, R_{ct} values increase and thus inhibition efficiency values increases. The addition of inhibitors provide lower C_{dl} values, this situation was the result of an increase in the thickness of the electrical double layer and decrease in local dielectric constant Pongsak Lowmunkhong et al. (2010). The increase in size of the semicircle and R_{ct} values with increasing inhibitor concentration, indicating the charge transfer process is the main controlling factor of the corrosion of mild steel. Considering the impedance diagram at 303 K**(Figure 3),** the size of the capacitive loop increased by increasing the, concentration of Anthranilic Acid, indicated that Anthranilic acid increased the charge transfer resistance and hence have inhibiting effect on mild steel corrosion in acidic medium. All impedance plots contain a depressed semicircle which can be attributed to the frequency dispersion effect as a result of the roughness and inhomogeneous of electrode surface Singh A K. et al (2010).

Popova et al. [27] said that sum of charge transfer resistance (R_{ct}) and adsorption resistance (R_{ad}) is equivalent to polarization resistance (R_p). Inhibition efficiency (η_z) was calculated using following equation

$$\eta_Z = \frac{R_p - R^{o}_{p}}{R_p} \times 100 \quad (4)$$

where, R_p and R_p^o are polarization resistance values in presence and absence of inhibitor.

The values of η_p and ηz at 303K is given in **Table 2**.

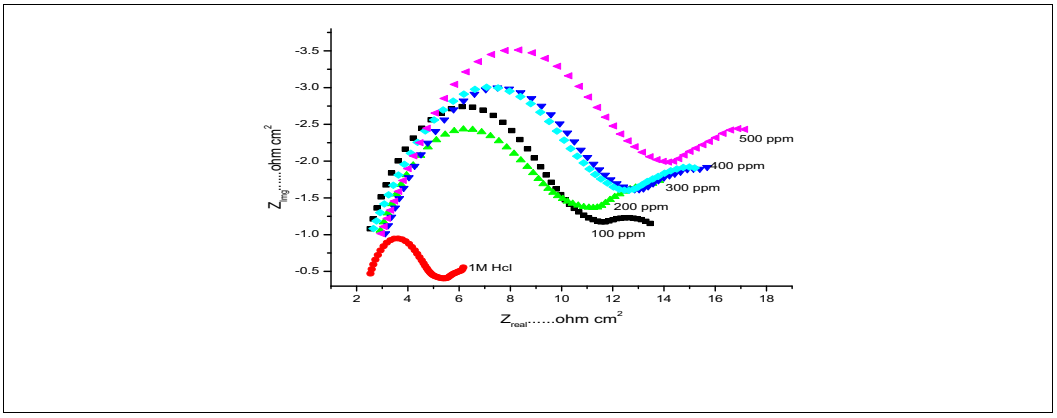

Fig.3. Nyquist Plots for steel in 1M HCl in the absence and presence of different Inhibitor concentrations at 303K .

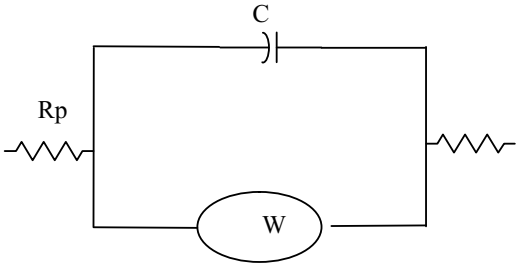

Fig. 4. Electrical Equivalent circuit model used to fit impedance data.

Table 2. Tafel and AC impedence results for the corrosion of mild steel in 1 M HCl in the presence different weights of Anthranilic acid at 303 K.

Inhibit or con^n (ppm)	E_{corr} (V)	I_{corr} A cm^{-2}	Corrosion rate(mpy)	βc mV/decade	Ba mV/decade	% η_p	R_p Ωcm^2	C_{dl} (µF cm^{-2})	% η_z
Blank	-0.478	0.237	46.53	5.27	6.00	-	1.855	6230	-
100	-0.477	0.108	21.20	6.73	7.16	**54.43**	4.026	4100	**53.92**
200	-0.477	0.104	20.50	6.80	6.90	**56.10**	4.453	1410	**58.34**
300	-0.474	0.091	18.00	6.62	6.83	**61.60**	5.763	1350	**67.80**
400	-0.476	0.076	15.20	6.80	7.20	**67.70**	6.093	410	**69.50**
500	-0.472	0.071	13.50	7.57	8.94	**69.90**	6.867	113	**73.00**

4. Conclusions

- There is a good agreement between weight loss methods and electrochemical measurements at 303K.
- Anthranilic Acid was found to be a good inhibitor for mild steel in 1M HCl.
- Tafel polarization studies have shown that Anthranilic Acid acts as mixed type inhibitor.

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