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Inhibitory Effect of Anthranilic Acid on Corrosion of Brass in HNO_3 Solution

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Abstract: The inhibition of the corrosion of brass in HNO_3 acid solution by anthranilic acid has been studied using weight loss, Potentiodynamic polarization and Electrochemical Impedance Spectroscopic (EIS techniques. Corrosion rate increases with the increase in acid concentration and temperature. As the inhibitor concentration increases corrosion rate decreases while percentage of inhibition efficiency (I.E.) increases. Maximum I.E. of anthranilic acid was found up to 96.44 % at 20 mM inhibitor concentration in 0.1 M HNO_3 solution. Polarization curve indicates that inhibitor act as mixed type. The results obtained from weight loss and electrochemical techniques were in good agreement.
Keywords: Brass, HNO_3, Corrosion, Anthranilic acid, Polarization, EIS.

I. INTRODUCTION

Corrosion is the deterioration of metal by chemical attack or by reaction with its environment. Brass is extensively used in various industrial operations. Brass alloys are characterized by their excellent thermal conductivity and mechanical workability [1]. They are widely used as tubing material in condensers and as heat exchangers for water cooling systems [2]. Nitric acid is very strong and highly corrosive mono protic acid having ability to dissolve metals, which are inert to most ordinary acids. The main use of nitric acid is for the production of fertilizers. It is primary reagent for nitration. One of the methods used to reduce the rate of metal corrosion is the addition of inhibitors. Many organic compounds, especially those containing polar groups and/or substituted heterocycle including nitrogen, sulphur and oxygen in their structures, have been reported to inhibit the corrosion of metal [3-5]. The inhibiting action of these organic compounds is usually attributed to the formation of donor–acceptor surface complexes between the free or π electrons of an inhibitor and the vacant d-orbital of a metal and adsorption [6,7]. Many researchers [8-16] studied various organic inhibitors to prevent corrosion of Brass in nitric acid solution. Anthranilic acid is an aromatic acid with the formula $C_6H_4(NH_2)$ (CO_2H) and has a sweetish taste. The molecule consists of a benzene ring, ortho-substituted with a carboxylic acid and an amine. As a result of containing both acidic and basic functional groups, the compound is amphoteric. Hebbar et al. [17] studied Anthranilic acid as corrosion inhibitor for mild steel in hydrochloric acid media. Shirazi et al. [18] studied corrosion inhibition of stainless steel in HCl solution using newly aniline and o-anthranilic acid copolymer. The aim of the present study is to investigate the corrosion inhibition effect of anthranilic acid as a corrosion inhibitor for brass in 0.1, 0.25, 0.5 and 1.0 M of HNO_3 by using weight loss, effect of temperature, polarization and EIS techniques. Structure of anthranilic acid is shown in fig.1.

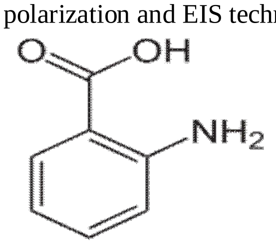

Fig. 1 Structure of anthranilic acid ($C_7H_7O_2N$).

II. EXPERIMENTAL SECTION

A. Preparation of Sample and Solution

The duplex (α β) brass alloy with a chemical composition of 60.73 % Cu, 39.21 % Zn, 0.01 % Fe, 0.02 % Sn and 0.04 % Pb were used in the present study. The brass specimens of the size 4.4 x 2.0 x 0.181 cm having an effective area of 0.206 dm^2 were used. The specimens were cleaned by washing with distilled water, degreased by acetone, washed once more with distilled water and finally dried and weighted by using electronic balance. Nitric acid was used as corrosive solution having concentration of 0.1, 0.25, 0.5 and 1.0 M prepared by diluting analytical grade of HNO_3 purchased from Merck using double distilled water.

B. Weight loss Measurement

For weight-loss measurement, the brass specimens completely suspended in 230 ml of 0.1, 0.25, 0.5 and 1.0 M HNO_3 solution in absence and presence of 5 to 20 mM concentration of anthranilic acid using glass hooks at 301± 1 K for 24h. The coupons are retrieved after 24h washed with distilled water, dried well and reweighed. From the weight loss data, corrosion rates (CR) were calculated.

C.R. (mg/dm^2d) = Weight loss (gm.) x 1000 / Area in dm^2 x day (1)

Inhibition efficiency (I.E.) was calculated by using following equation:

I. E. (%) = $\{(W_u - W_i) / W_u\} \times 100$ (2)

where, W_u= Weight loss in absence of inhibitor, W_i = Weight loss in presence of inhibitor.

The degree of surface coverage (θ) of the brass specimen for different concentration of HNO_3 solution have been evaluated by weight loss experiments using the following equation:

$\Theta = (W_u - W_i) / W_u$ (3)

C. Potentiodynamic Polarization Measurement

Both the potentiodynamic and EIS measurement were carried out using CHI608C-series, U.S. Model with CH- instrument. For polarization study, metal specimens are immersed with and without anthranilic acid in 0.1 M HNO_3 solution. In the electrochemical cell, brass specimens having an area of 1 cm^2 was used as a working electrode, Ag/AgCl electrode as a reference electrode and platinum electrode as an auxiliary electrode and allowed to establish a steady-state open circuit potential (OCP) for approximately 30 min. The polarization curves were plotted with current vs potential. An anodic and cathodic polarization curve gives corresponding anodic and cathodic Tafel lines. The intersect point of Tafel lines gives the corrosion potential (E_{corr}) and corrosion current (i_{corr}) [19].

D. Electrochemical Impedance Spectroscopy (EIS) Measurement

EIS measurements are made at corrosion potentials over a frequency range of 0.1 to 10^5 Hz by a sine wave with potential perturbation amplitude of 5 mV. A graph was drawn by plotting real impedance (Z') versus imaginary impedance (-Z''). From the Nyquest plots of Z' vs -Z'' the charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) were calculated. An experiment was carried out in absence and presence of inhibitor.

III. RESULTS AND DISCUSSION

A. Weight loss Experiments

Effect of acid and concentration- Results showed in Table 1 indicates that as the acid concentration increases corrosion rate increases. Corrosion rate was 1820.39, 6577.67, 9393.20 and 15902.91 mg/dm^2.d corresponding to 0.1, 0.25, 0.5 and 1.0 M HNO_3 respectively for an immersion period of 24 h at 301± 1 K. At constant inhibitor concentration, the I.E. decreases with the increase in acid concentration. At constant acid concentration, as the inhibitor concentration increases corrosion rate decreases while I.E. increases. In 0.1 M HNO_3 the I.E. anthranilic acid was found to be 91.25, 93.05, 95.25 and 96.44 % corresponding to 5, 10, 15 and 25 mM inhibitor concentration respectively (Table 1).

Table 1 Corrosion rate for brass in various concentrations of HNO_3 in the absence and presence of different concentrations of anthranilic acid.

Inhibitior concen tration (mM)	Acid concentration							
	0.1 M		0.25 M		0.5 M		1.0 M	
	CR (mg /dm^2d)	I.E. (%)	CR (mg/dm^2d)	I.E. (%)	CR (mg/dm^2d)	I.E. (%)	CR (mg/dm^2d)	I.E. (%)
Blank	1820.39	-	6577.67	-	9393.20	-	15902.91	-
5	159.27	91.25	888.32	86.49	3038.83	67.65	7271.84	54.27
10	126.58	93.05	490.98	92.54	1410.68	84.98	4286.41	73.05
15	86.54	95.25	394.8	93.99	1116.50	88.11	2907.77	81.72
20	64.83	96.44	289.47	95.60	825.24	91.21	1951.46	87.73

B. Potentiodynamic Polarization Study

Potentiodynamic polarization study was carried out for brass in 0.1 M HNO_3 in absence and presence of 20 mM anthranilic acid. Electrochemical parameters such as corrosion potential (E_{corr}), corrosion current density (i_{corr}), anodic Tafel slope (βa), cathodic Tafel slope (βc) and percentage I.E. are given in Table 2. Inhibition efficiency (I.E.) from polarization study was calculated using following equation: [20]

$$I.E.(\%) = \{(icorr_{(uninh)} - icorr_{(inh)})/icorr_{(uninh)}\} \times 100 \qquad (4)$$

where, $i_{corr\ (uninh)}$ is corrosion current density for uninhibited acid and $i_{corr\ (inh)}$ corrosion current density for inhibited acid.

From Table 2, it was observed that the addition of anthranilic acid in HNO_3 solution indicates the significant decrease in corrosion current density (i_{corr}) and decrease in corrosion rate with respect to blank. In general, an inhibitor is anodic or a cathodic if the variation E_{corr} against the blank is higher or above 85 mV [21,22]. In this study, the displacement of E_{corr} was 67 mV (Table 2) which suggest that the anthranilic acid function as a mixed type of inhibitor. Polarization curves (Tafel plots) were shown in Fig. 2.

Table 2 Potentiodynamic polarization data and I.E. of 20 mM of anthranilic acid as an inhibitor for brass in 0.1 M HNO_3.

System	E_{corr} (V)	I_{corr} (μA/ cm^2)	Tafel slope (V / decade)			I.E. (%) Calculated from	
			Anodic (+βa)	Cathodic (-βc)	β (V)	Polarization method	Weight loss method
Blank	-0.045	1408	6.734	2.986	0.899	-	-
Anthranilic acid	-0.112	51.64	15.284	1.992	0.766	96.33	96.44

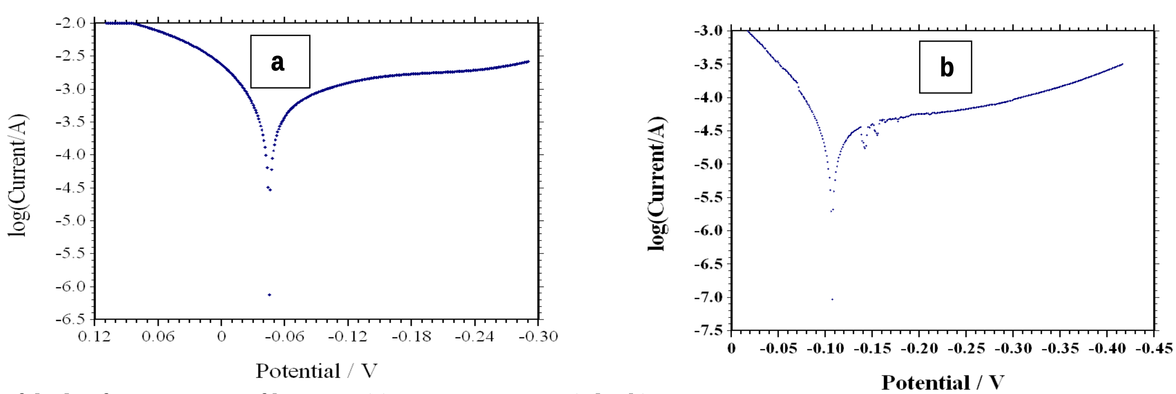

Fig. 2 Tafel Plot for corrosion of brass in (a) in 0.1 M HNO_3 (Blank) (b) in 0.1 M HNO_3 in presence of 20 mM anthranilic acid.

C. Electrochemical Impedance Spectroscopy (EIS) Measurement

Nyquist plots for the corrosion of brass in 0.1 M HNO_3 solution in absence and presence of Anthranilic acid was examined by EIS method at room temperature was shown in Fig. 3 and EIS parameters in Table 3. It is observed from Fig. 3 that the impedance diagram is almost semicircle. The difference has been attributed to frequency dispersion. The semicircle nature of the plots indicates that the corrosion of brass is mainly controlled by charge transfer process.

Table 3 EIS parameters for corrosion of brass in 0.1 M HNO_3 containing 20 mM Anthranilic acid.

System	R_{ct} (Ω cm^2)	C_{dl} (μF / cm^2)	I.E (%) Calculated from	
			EIS method	Weight loss method
Blank	320	4.327	-	-
Anthranilic acid	2800	0.0516	98.80	96.44

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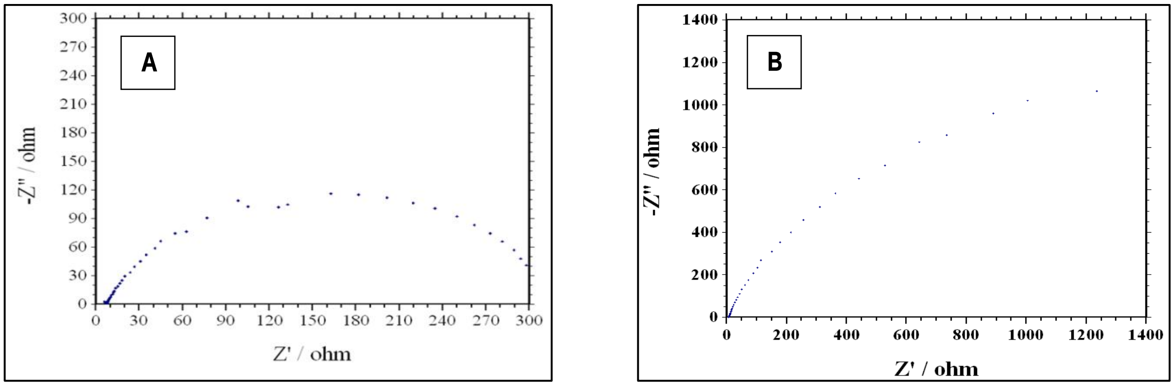

Fig. 3 Nyquist plot for brass in (A) in 0.1 M HNO_3 (Blank) (B) in 0.1 M HNO_3 in presence of 20 mM anthranilic acid.

The diameter of capacitive loop in the presence of inhibitor is bigger than that in the absence of inhibitor. The high frequency capacitive loop is related to the charge transfer resistance (R_{ct}). To calculate the double layer capacitance (C_{dl}), the frequency at which the imaginary component of the impedance is maximum was found as presented in the following equation: [23]

$$C_{dl} = 1/2\pi F_{max} R_{ct} \quad (5)$$

where, ‘f’ is the frequency at the maximum height of the semicircle on the imaginary axis and R_{ct} is the charge transfer resistance [24].

Inhibition efficiency (I.E.) from EIS method was calculated using following equation:

$$\text{I. E. } (\%) = \{Cdl_{(uninh)} - Cdl_{(inh)}/Cdl_{(uninh)}\} \times 100 \quad (6)$$

where, $C_{dl(uninhi)}$ is double layer capacitance for uninhibited acid and $C_{dl(inhi)}$ is double layer capacitance for inhibited acid.

The addition of inhibitor increases R_{ct} value while decreases in C_{dl} values which is due to the adsorption of inhibitor on the metal surface. The results suggest that the inhibitor acts by the formation of a physical protective layer on the surface that retards the charge transfer process and therefore inhibit the corrosion reaction, leading to increase in R_{ct} values. Moreover, the adsorbed inhibitor species decrease the electrical capacity of electrical double layer values at the electrode/solution interface and therefore decrease the value of C_{dl} [25].

D. Mechanism of Corrosion

The behaviour of anodic dissolution of brass in nitric acid consists of dissolution of both zinc and copper. Generally, the anodic reaction for Cu is considered as follows [26,27]:

$$Cu \rightarrow Cu(I)_{ads} + e^- \quad \text{(fast step)} \quad (7)$$

$$Cu(I)_{ads} \rightarrow Cu(II) + e^- \quad \text{(slow step)} \quad (8)$$

Meanwhile, the adsorption of copper ions, Cu (II), on the surface due to its reduction in presence of Zn must be taken into consideration. Also, the anodic dissolution of Zn is considered according to following equation;

$$Zn \rightarrow Zn^{2+} + 2e^- \quad (9)$$

It should be noticed that the cathodic reaction is not hydrogen evolution reaction at all, because the corrosion potential in all experiments is well above the redox potential of hydrogen evolution in this media. In this way, the predominant mechanism of cathodic reaction has been reported according to the following equation-10 [28];

$$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O \quad (10)$$

Also, oxygen reduction in acidic media can be considered to be as another cathodic reaction. Based on Eq. (10), the presence of NO_3^- ions onto cathodic sites is mandatory for reaction.

IV. CONCLUSION

As acid concentration increases corrosion rate increases while I.E. decreases. At constant acid concentration, as inhibitor concentration increases corrosion rate decreases while I.E. increases. The anthranilic acid showed maximum I.E. of 96.44 % at 20 mM inhibitor concentration in 0.1 M HNO_3 solution. A polarization curve indicates that anthranilic acid act as a mixed type of inhibitor. EIS study shows that the charge transfer resistance increases and double layer capacitance decreases with increases in concentration of inhibitor. From this experimental study, it is clear that anthranilic acid can be used as inhibitor for corrosion of brass in HNO_3 solution.

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