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Veratraldehyde as Corrosion Inhibitor for Zinc in Different Acid Medium

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ABSTRACT

The corrosion inhibition of zinc in 0.1 M HCl and 0.05 M H₂SO₄ was studied separately by using Veratraldehyde as a corrosion inhibitor. Mass loss and electrochemical studies were part of the investigations. The Inhibition efficiencies were evaluated at different concentrations of the inhibitor at different temperature. The inhibition efficiency increased with increase in inhibitor concentration and decreased with increase in temperature in both the medium. The inhibitor was more active in HCl than in H₂SO₄. The maximum inhibition efficiency approached at 1000 ppm in both HCl and H₂SO₄ medium. Electrochemical studies show that inhibitor acts a mixed type inhibitor. The inhibitor was found to adsorb on the zinc surface according to the Langmuir adsorption isotherm.

Key words: vertraldehyde; Langmuir isotherm; mass loss; Impedance; polarization

INTRODUCTION

Zinc play a major role in corrosion protection of steel structures and it acts as sacrificial anode. In order to increase the corrosion resistance property of the zinc layer applied for steel protection, a thin conversion coating is usually formed by reacting the metal with an aqueous solution of chromic acid and mineral acids. Generally these formed compounds are toxic and carcinogenic in nature [1] of the hexavalent chromate corrosion inhibitor, considerable effort has been directed towards developing alternative, environmentally acceptable inhibitors in order to satisfy with substance restriction legislation such as RoHS (Restriction of Hazardous Substances Directive, 2002/95/EC).

The earlier research works revealed the use of a large number of organic compounds of different nature as corrosion inhibitors for zinc [2-7]. Most of these organic compounds are adsorbed on the metal surface and provide a barrier between metal and environment, thereby reducing the rate of corrosion. The effectiveness of inhibition depends on the nature and surface charge of the

metal, the nature of the medium, the nature and chemical structure of the inhibitor molecule such as functional groups, aromaticity, the π orbital character of the donating electron, steric factor, and electron density at the donor atoms [8-10].

In the present investigation an attempt has been made to evaluate the inhibiting action of veratraldehyde on the corrosion of zinc in 0.1 M HCl and 0.05 M H₂SO₄ solution. Chemical and electrochemical methods were used to determine the rate of corrosion and corrosion inhibition efficiencies.

MATERIALS AND METHODS

The inhibitor used in this experiment was Veratraldehyde. The structure was shown in Fig. 1. The treatment solution is different concentration of inhibitor in 0.1 M HCl and 0.05 M H₂SO₄. All the chemicals used were of AR grade (sd. fine chemicals Ltd., Mumbai) and doubly distilled water was used for the preparation of solutions. All the tests have been conducted in an aerated and unstirred solution. The pure zinc plate (Cu=0.185%, Al=0.006%, Fe=0.004%, Mn=0.3%, Sn=0.003%, Pb=0.002%, Cd=0.002% and the rest zinc) were used. Zinc sheets having rectangular shape with an exposed area of 2 cm x 4 cm x 1 cm were used for the corrosion rate measurements. The samples were first degreased with trichloroethylene, grounded with different grades of emery papers, washed with water and rinsed with alcohol. The dried and weighed samples were placed in 50cm³ of 0.1M HCl and 0.05 M H₂SO₄ solutions with and without inhibitors for a period of 2 hours at 298 K. Runs were also done at different temperatures (308 & 318 K). Duplicate experiments were performed in each case and the mean value of the weight loss was noted. inhibition efficiency (IE %) were calculated.

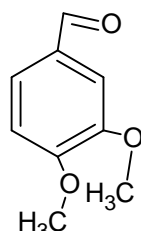


Fig . 1 Structure of Veratraldehyde (Inhibitor)

The polarization studies were carried out for zinc strips having an exposed area of 1 cm². The specimens were mechanically polished using different grades of emery paper and washed thoroughly with distilled water and degreased with acetone. Polarization experiments were performed using different concentration of inhibitor in different corrosive medium. A conventional three-electrode compartment consisting of zinc specimen, saturated calomel and platinum as the working, reference and counter electrodes respectively were selected. Electrochemical measurements were carried out using CHI 660C electrochemical analyzer (USA make). The polarization curves were potentiodynamically obtained at open circuit potential (OCP) with a scan rate of 1mVs⁻¹. Initially the potentials were scanned in the cathodic direction from the corrosion potential and consequently in the anodic direction.

The impedance measurements were carried at OCP in the frequency range 1 mHz to 100 kHz with 5 mV sine wave as the excitation signal. The interfacial double layer capacitance (C_{dl}) and charge transfer resistance (R_{ct}) values were calculated from Nyquist plots

RESULTS AND DISCUSSIONS

Mass loss measurements

The Table 1 shows the inhibition efficiencies and surface coverage (θ) obtained from mass loss method at different concentrations of inhibitors in different corrosive medium at different temperature. The inhibition efficiency was calculated from the following relationship.

$$\text{Inhibition efficiency (IE), } \eta_{ML} = \frac{W_u - W_i}{W_u} \times 100$$

where, W_u and W_i are the average weight-losses of test sample after immersion in corrosive solutions with and without inhibitor, respectively.

It is clear that IE values increases with increase in the inhibitor concentration and decreases with increase in temperature in both the acid media. Further it is found that IE of the inhibitor is comparatively higher in HCl than in H_2SO_4 under similar experimental conditions. In both the acids, the optimum concentration of the inhibitor was found to be 1000 ppm and above this concentration almost same IE values were observed and below 500 ppm of the inhibitor concentration not shows good inhibition values. Also in addition, the mass loss measurement revealed the excellent stability of the inhibitors in the acid medium. To see the stability, the experiments were conducted by taking acid solution containing inhibitor which was kept for 10 days under air agitation and no change in IE values were observed.

Table 1 corrosion parameters and surface coverage for zinc in different acid media at different temperature obtained from mass loss measurements

Medium	Concentration (ppm)	Inhibition efficiency ($\eta_{ML}\%$) 298 K	Surface coverage (θ)	Inhibition efficiency ($\eta_{ML}\%$) 308 K	Surface coverage (θ)	Inhibition efficiency ($\eta_{ML}\%$) 318 K	Surface coverage (θ)
HCl	none						
	700	80	0.80	70	0.70	64	0.64
	800	83	0.83	73	0.73	65	0.65
	900	87	0.87	77	0.77	67	0.67
	1000	90	0.90	80	0.80	70	0.70
H_2SO_4	none						
	700	50	0.50	45	0.45	39	0.39
	800	67	0.67	59	0.59	52	0.52
	900	73	0.73	62	0.62	56	0.56
	1000	83	0.83	67	0.67	60	0.60

Polarization studies

The polarization studies of zinc specimens were carried out in 0.1 M HCl and 0.05 M H_2SO_4 solutions separately in absence and presence of different concentrations of inhibitor and those are given in Fig. 2 and 3. The inhibition efficiency (η_{pol}) was calculated using the relationship:

$$\eta = \frac{I_{corr}^0 - I_{corr}}{I_{corr}^0} \times 100$$

Where I_{corr}^0 and I_{corr} are the corrosion current densities in absence and presence of inhibitor respectively. The data obtained from polarization and weight loss studies were in good

agreement with each other. In both methods same order of % IE was observed. The inhibition of corrosion was due to the blockage of cathodic and anodic sites of the corroding surface. The effect of inhibitor concentration on free corrosion potential (E_{corr}) and corrosion current density indicated that the free corrosion potential did not get affected in the presence of inhibitors, but the corrosion current density decreased with inhibitor concentration. The anodic as well as cathodic polarization curves shifted towards lower current density values in the presence of inhibitors. This indicated that the inhibitors acted in such a manner that both anodic as well as cathodic reactions were influenced by it simultaneously almost to the same extent showing mixed nature of inhibitors [11]. This was also confirmed from the Tafel slopes. The polarization parameters such as corrosion potential (E_{corr}) and corrosion current density (I_{corr}) obtained by extrapolation of the Tafel lines are listed in Table 2.

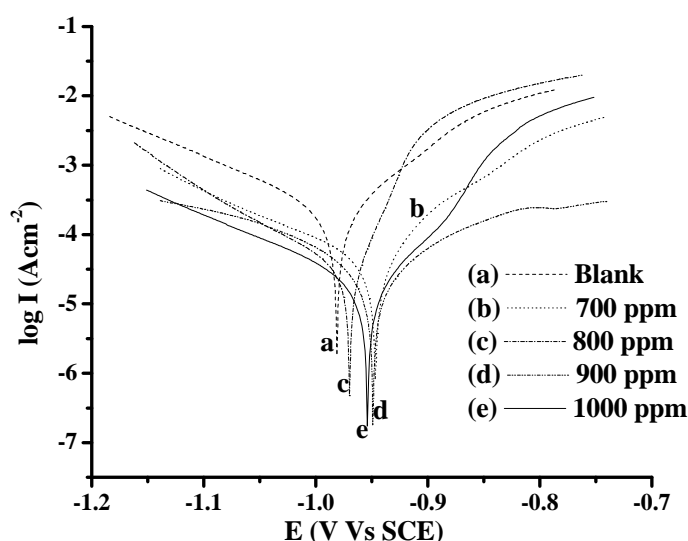


Fig. 2 Polarization profile of zinc in HCl in Presence of different concentration of inhibitor

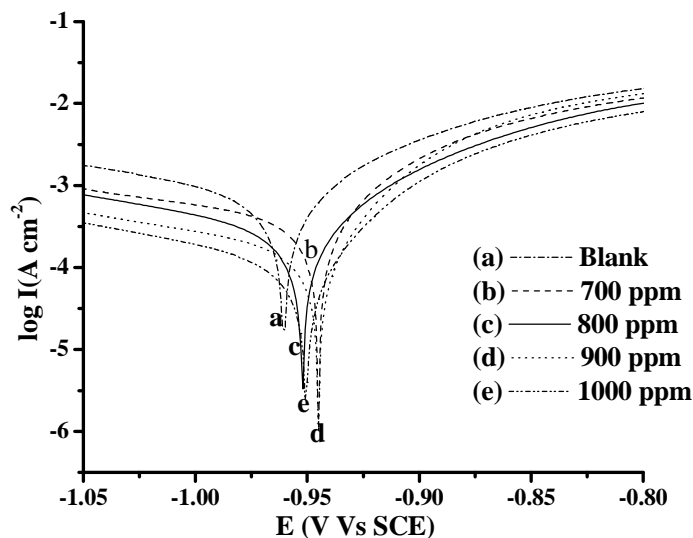


Fig. 3 Polarization profile of zinc in HCl in Presence of different concentration of inhibitor

Table 2 Electrochemical corrosion parameters for zinc in different acid media obtained from polarization method

Medium	Concentration of inhibitor (ppm)	$-E_{\text{corr}}$ (mV)	β_c (mV dec ⁻¹)	β_a (mV dec ⁻¹)	I_{corr} (μAcm^{-2})	R_p (Ωcm^2)	%IE
HCl	None	981	149.6	81.7	224.8	102	
	700	947	155.5	99.6	59.48	388	73.5
	800	970	112.2	99.9	59.32	444	73.6
	900	949	165.8	150.8	41.46	829	81.55
	1000	954	153.9	43.0	14.23	1028	93.66
H ₂ SO ₄	None	960	221.4	132.2	1269	28	
	700	945	246.0	138.5	880.4	44	30.6
	800	952	207.0	112.0	477.5	66	62.3
	900	945	213.4	119.2	371.9	89	70.69
	1000	951	191.5	109.3	199.6	152	84.2

Electrochemical impedance spectroscopy (EIS)

Nyquist plots for zinc in 0.1 M HCl and 0.05 M H₂SO₄ with different concentration of inhibitor are shown in Fig. 4 and 5. It was evident from these plots that the impedance response of zinc containing inhibitor in both the acid media has significantly altered.

Charge transfer resistance is unequivocally correlated to the corrosion current density in relatively simple corrosion systems characterized by a charge transfer controlled process. The results show that R_{ct} values increased with increase of inhibitor concentration. Inhibition efficiency η was calculated from the relationship

where R_{ct} and R_{ct}^I are the charge transfer resistances in the presence and absence of inhibitors. The electrochemical impedance parameter derived from the Nyquist plots and the inhibition efficiencies η_{EIS} are shown in Table 3. The trend of IE values was same like mass loss and polarization measurements. Maximum IE was obtained at 1000 ppm and these values are high in HCl medium. It was clear from the table 3 that R_{ct} values were increased with increasing inhibitor concentration. Increase in the resistance with increase in the concentration indicates the formation of electrical double layer and also shows the adsorption of the inhibitor molecules at the metal/solution interface.

$$\eta_{EIS} = \frac{R_{ct} - R_{ct}^I}{R_{ct}^I} \times 100$$

The mechanism of inhibition of corrosion is generally believed to be due to the formation and maintenance of a protective film on the metal surface. The corrosion inhibition of zinc in acidic solution by the inhibitor molecules can be explained on the basis of adsorption on the metal surface.

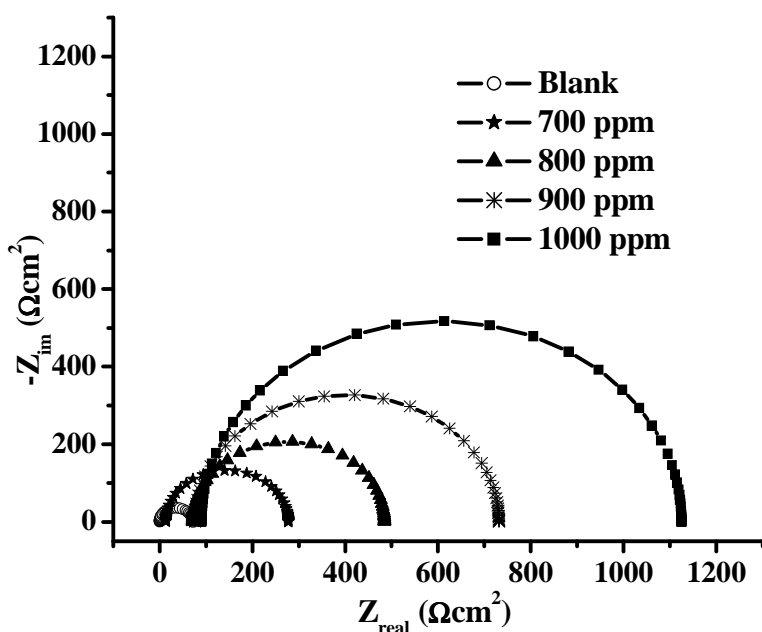


Fig . 4 Nyquist plots for zinc in HCl containing different concentrations of inhibitor at 298 K

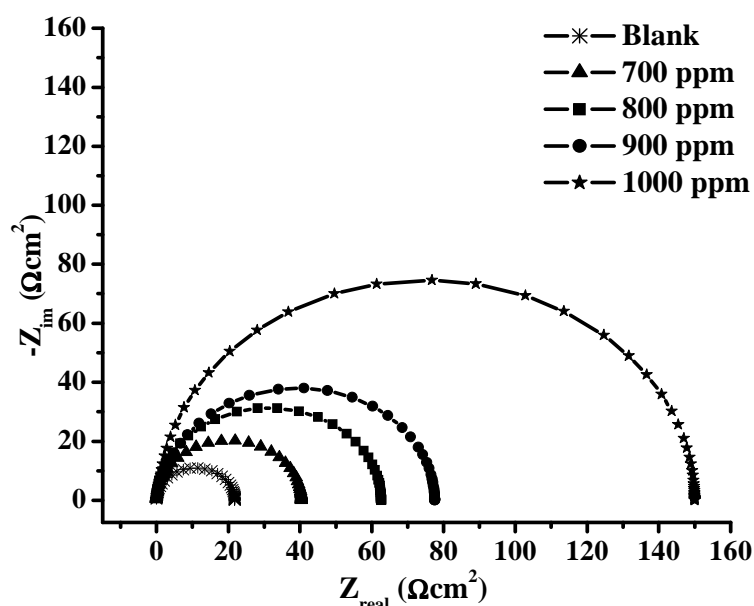


Fig . 5 Nyquist plots for zinc in H₂SO₄ containing different concentrations of inhibitor at 298 K.

The protection action of the inhibitor can be attributed to the presence of methoxy group and carbonyl group in the benzene ring and which interacts with metal effectively adsorbed on the metal surface. It is also confirmed by adsorption isotherms

Adsorption isotherm

Table 3 Corrosion parameters for zinc in different acid media obtained using electrochemical impedance method

Medium	Concentration of inhibitor (ppm)	$R_{ct}(\Omega\text{cm}^2)$	$C_{dl}(\mu\text{Fcm}^{-2})$	$\eta_{(EIS)}$
HCl	none	71.48	2.188	
	700	264.2	2.461	72.9
	800	413.2	11.74	82.7
	900	655	8.976	89.08
	1000	1035	5.912	93.09
H ₂ SO ₄	none	21.8	3.906	
	700	40.4	7.778	46.03
	800	62.61	2.912	65.18
	900	76.07	2.072	71.34
	1000	149.2	0.4122	85.3

The plot of $\log[\theta/(1-\theta)]$ vs. $\log C$ for the inhibitor at temperatures 298K, 308K and 318K in both HCl and H₂SO₄ media were straight lines (Fig. 6 and 7). These observations indicate that the inhibitor obeys Langmuir adsorption Isotherm in both acid media. Langmuir adsorption Isotherm formulae are given below.

$$\log [\theta / (1 - \theta)] = \log K + \log C$$

where θ is surface coverage, K is equilibrium adsorption constant and C is the concentration of the inhibitor. The values of surface coverage θ were evaluated by mass loss measurements using the equation

$$\theta = \frac{W_u - W_i}{W_u}$$

where w_u and w_i are mass loss in the absence and presence of the inhibitor, respectively.

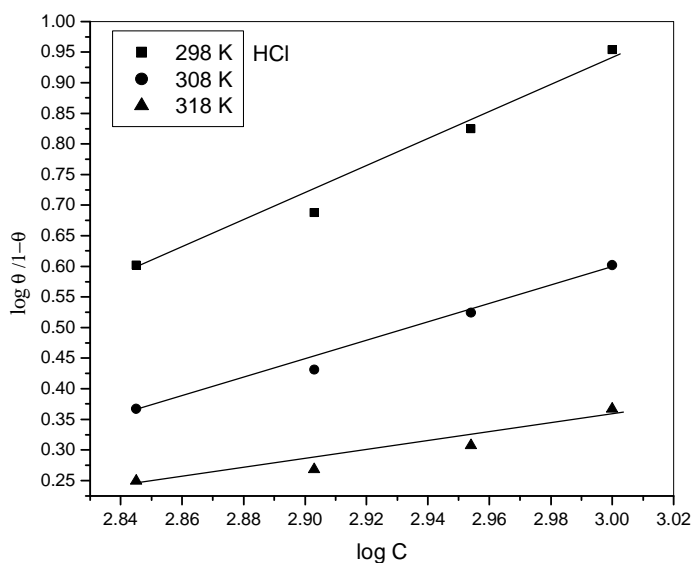


Fig. 6 Langmuir adsorption isotherm for inhibitor on the zinc surface at different temperature in HCl

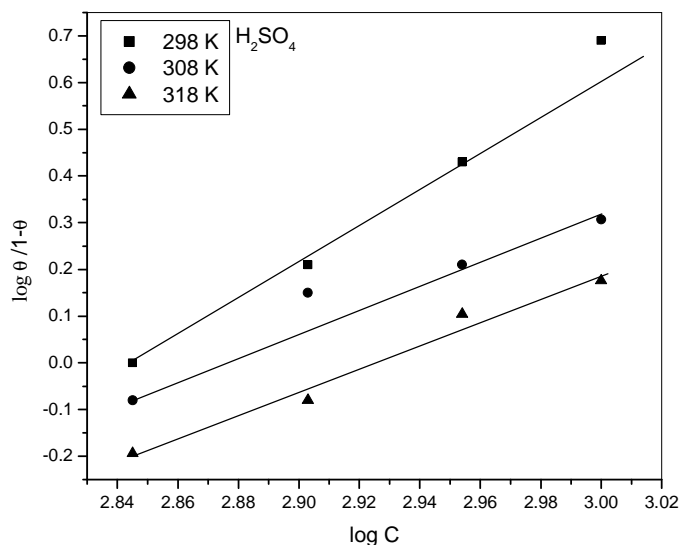


Fig. 7 Langmuir adsorption isotherm for inhibitor on the zinc surface at different temperature in H₂SO₄.

CONCLUSION

Veratraldehyde reduced the corrosion rate of zinc considerably in both HCl and H₂SO₄ medium. The IE% resulted from electrochemical and weight loss measurements were in good agreement. The rate of corrosion decreased with inhibitor concentration and increased with temperature. The data revealed that the inhibition action of tested compounds was through Langmuir adsorption. These results show that Veratraldehyde are good corrosion inhibitor for zinc in HCl and H₂SO₄ medium.

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