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Original Research Paper

Chemistry

CORROSION INHIBITION OF ZINC IN HYDROCHLORIC ACID BY A NEW CONDENSATION PRODUCT

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ABSTRACT

The corrosion of zinc in hydrochloric acid containing a new condensation product has been studied at different acid concentrations, inhibitor concentration and temperatures. The inhibition efficiency of condensation product increases with concentration of inhibitor and decreases with the increase in concentration of acid. As temperature increases, corrosion rate increases while percentage of inhibition efficiency decreases. The mass loss and electrochemical investigations suggest that the inhibitor cover both the anodic and cathodic regions through adsorption to form a protective film. The electrochemical studies of zinc specimens are performed in aqueous acid solution using galvenostatic polarization technique and electrochemical impedance spectroscopy. The inhibition efficiency increased with increase in inhibitor concentration and decreased with increase in temperature and concentration of acid medium.

KEYWORDS : Corrosion, condensation product, hydrochloric acid, zinc.

INTRODUCTION

Corrosion is a process that occurs when a material deteriorates due to its interaction with its surrounding environment in which the material gets consumed through oxidation. Zinc is an active metal with numerous industrial applications and its coatings is largely used for the protection of steels [1]. Zinc corrodes in solution having pH lower than 6.0 and higher than 12.5, while within this range the corrosion is slow [2]. Hydrochloric acid is highly corrosive, strong mineral acid since it is completely dissociated in water and has major industrial uses. To avoid the zinc corrosion generally a coating of passive layer is given to its surface. The chromate solutions have been applied successfully to protect zinc surface. Chromium element being toxic in nature, this has to be replaced with non-toxic solution, which exhibits the same protection as that of chromate solution [3].

The metal zinc is exposed to various solutions in which the corrosion of zinc is controlled by the addition of organic compounds. Sometimes many special chemicals like aromatic, aliphatic and heterocyclic amines have been extensively investigated as corrosion inhibitors to control the metal loss [4, 5]. It is established that the free electrons of pi orbitals and the protonation property of the compound used as an inhibitor to form a protective film on the surface of metal. Schiff's bases were used as corrosion inhibitors for various metals [6, 7]. Such organic compounds containing electron donating groups decreases the corrosion rate by increasing the hydrogen overvoltage on corroding metal. Few authors had studied the effect of aldehydes and amines as inhibitors for corrosion of many metals in different corrosive environments [7, 8]. In our earlier works we have synthesized new electroactive organic compounds and they were highly efficient in the protection of metals from corrosion in various corrosive media by surface modification of metals [9 – 11]. In the present work, the corrosion inhibition of zinc by a new condensation product in hydrochloric acid medium has been reported.

MATERIALS AND METHODS

Preparation of Condensation product:

3.72g of p-methylamine benzaldehyde is dissolved in 15mLof alcohol and heated nearly 30°C for about ½ an hour and then 2-3 drops of concentrated hydrochloric acid is added. In another beaker 3.8g anthranilic acid is dissolved in 15mL of alcohol and then added to the above solution drop wise. The orange red compound thus separated out is collected and is taken as a new condensation product.

Corrosion inhibition studies:

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) was selected and coupons of desired shapes (5cm × 1 cm × 0.4 cm and 5cm × 2cm × 0.4 cm) were prepared. These samples were polished with SiC papers of different grit size (200 to 1200). The electrodes were degreased with trichloroethylene vapor to remove oil and grease. The samples were rinsed with ethanol, followed by distilled water wash.

The so prepared samples were immersed in 0.1, 0.3 and 0.5 M Hydrochloric acid concentration with and without inhibitor containing 230 ml test solution at 301 K for 2 to 12 h immersion period, for weight loss measurements. After the test, specimens were cleaned by 10% chromic acid solution having 0.2 % $BaCO_3$ for a period of about 2 minutes [12]. After cleaning, test specimens were washed with distilled water followed by acetone and dried with air drier.

For polarization study, zinc specimens were immersed in 100 ml HCl solution without and with the condensation product. The test cell includes the metal specimen as a working electrode, corrosive solution in which the specimen was to be tested and saturated calomel electrode (SCE) as a reference electrode as well as Platinum electrode as an auxiliary electrode. The polarization study was made by using the above electrodes in a conventional three compartment cell and a DC power supply (Tektronix 36B). Polarization curves were plotted with potential against log current density (called Tafel plots). Cathodic and anodic polarization curves give cathodic and anodic Tafel lines correspondingly. The intersect point of cathodic and anodic Tafel lines gives the corrosion current (I_{corr}) and the corrosion potential (E_{corr}) [13].

The electrochemical impedance spectra of zinc in absence and presence of various concentrations of inhibitors at 30°C is presented as Nyquist plot. The experimental data and calculated inhibition efficiency are summarized. The %IE at different concentration of each inhibitor in 0.1 M HCl were calculated from the corresponding electrochemical impedance data according to equation. Where R_{ct} and R_{ct}^{I} are the charge transfer resistances in the presence and absence of inhibitors. It is evident from these plots that the impedance response of zinc has significantly altered after the addition of inhibitors to the corrosive solutions.

To study the effect of temperature on corrosion of zinc in 0.1 M HCl, the specimens were immersed in 100 ml of corrosive solution and corrosion loss was determined at solution temperature of 298, 308, 318, 328 and 333 K for an immersion period of 2 h with and without inhibitors.

Scanning electron microscopic studies:
The surface morphology of the zinc samples after immersion in 0.1M HCl in absence and presence inhibitors, was analyzed using scanning electron microscopy (JEOL, JSM 6400)

3. RESULTS AND DISCUSSION

3.1. Weight loss measurements

Table 1 gives the values of inhibition efficiencies of CP for the corrosion of zinc in 0.1M HCl. At a concentration of 0.3M exhibits maximum inhibition efficiency (92%). The inhibition efficiency was increased with increase in the concentration of the inhibitor. This behavior could be attributed due to strong interaction of compounds with the metal surface that results in the adsorption of inhibitor molecules [14]. The increase in adsorption is due to electron density at the reactive C=N, C=O groups and π electrons of aromatic ring [15]. The presence of higher electron density on aldehyde group in CP causes stronger interaction with metal surface and hence higher inhibition of the corrosion with increase in time [16]. Percent inhibition efficiency (%IE) was calculated using the following equation:

$$\%IE = \frac{W_o - W}{W_o} \times 100$$

Where W_o and W are the weight-losses in the absence and presence of inhibitors in HCl. It has been observed that the %IE at a given inhibitor concentration of inhibitor was decreased with increasing the concentration of the acid. This may be due to desorption of the organic molecule from the surface of metal at higher acid concentration [17].

Table 1: Corrosion parameters in the presence of CP in 0.1M HCl

Conc. of inhibitor	2hrs		4hrs		6hrs		8hrs		10hrs	
	Weight loss	% IE	Weight loss	% IE	Weight loss	% IE	Weight loss	% IE	Weight loss	% IE
Blank	0.01	-----	0.0115	-----	0.0157	-----	0.03	-----	0.037	-----
0.05	0.0051	49	0.0057	50	0.009	43	0.0204	32	0.0194	46
0.1	0.0043	57	0.0043	62	0.0085	46	0.0201	33	0.017	51
0.15	0.0029	71	0.003	74	0.0065	59	0.016	47	0.0151	59
0.2	0.0019	81	0.0026	77	0.0057	64	0.013	57	0.012	66
0.25	0.0013	88	0.0015	87	0.0054	66	0.0106	65	0.0115	68
0.3	0.0008	92	0.0016	91	0.003	81	0.008	73	0.009	74

3.2. Polarization measurements

The anodic and cathodic polarization behavior of zinc in the presence and absence of CP in 0.1M HCl is shown in Fig. 2 Various corrosion parameters such as corrosion current density (I_{corr}), corrosion potential (E_{corr}), Tafel slopes (b_a and b_c), surface coverage and inhibition efficiencies (%IE) are given in Table 2. The % IE was calculated from the relation,

$$\%IE = \frac{I^o_{corr} - I_{corr}}{I^o_{corr}} \times 100$$

Where I^o_{corr} and I_{corr} are the corrosion current densities in absence and presence of inhibitor respectively. The results showed that I_{corr} values decreased with increase in the concentrations of inhibitors and least I_{corr} was obtained at 0.3M of the inhibitors. The values of Tafel slopes show that the corrosion inhibition may be due to the control of hydrogen evolution reaction. The degree of surface coverage (θ) was determined using the expression [18, 19].

$$\theta = 1 - \frac{(I_{corr})_{inhibited}}{(I_{corr})_{uninhibited}}$$

The inhibition efficiency data showed that CP has better interaction with zinc and the higher activity and effectiveness is due to the presence of number of N, O atoms and aromatic rings.

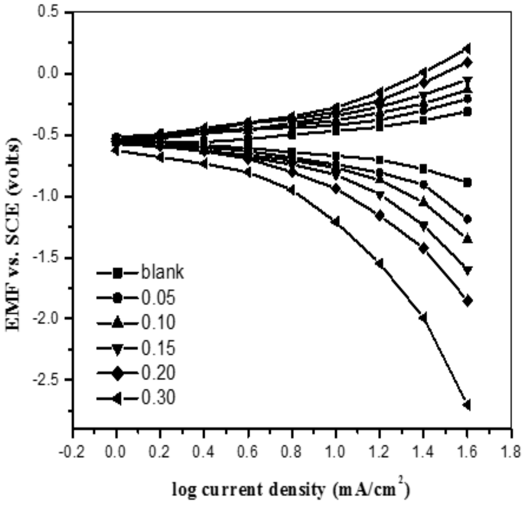

Fig. 2. Galvanostatic polarization curves in the presence of CP in 0.1M HCl.

Table 2: Corrosion parameters obtained from polarization measurements for zinc in 0.1M HCl containing various concentrations of inhibitors at 303K

Inhibitor conc.	$-E_{corr}$ (mV)	I_{corr} (μAcm^{-2})	θ	b_a (mV dec^{-1})	b_c (mV dec^{-1})	*IE* (%)
Blank	-0.50	680	------	0.40	0.58	-------
0.05	-0.51	350	0.49	0.37	0.42	48.6
0.1	-0.55	310	0.55	0.22	0.33	54.4
0.15	-0.58	200	0.70	0.2	0.28	70.0
0.2	-0.63	130	0.81	0.18	0.27	81.0
0.3	-0.67	80	0.90	0.13	0.22	91.0

3.3. Electrochemical impedance spectroscopy (EIS):

The impedance spectra for zinc in 0.1M HCl in the absence and presence of various concentrations of CP are similar in shape, as seen from Fig. 3. The semicircle radii depend on the additive concentration. The results show that Rp values increase with increasing CP concentration. This indicates the formation of a surface film with increasing concentration of CP [20].

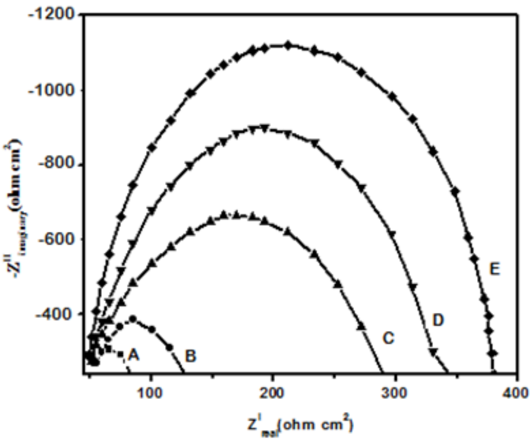

Fig . 3. Nyquist plots for zinc in 0.1M HCl containing different concentrations of inhibitor at 298 K

The polarization resistance R_p and double layer capacitance C_{dl}, were determined by analysis of complex plane impedance plots and their values are given in Table 3. The increase in R_p and decrease in C_{dl} with increase in CP concentration indicates higher surface coverage by the inhibitor. The values of protection efficiencies indicate that there is an interaction of the compound with the active sites of metal [21]. Decrease in the capacitance, which can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that the inhibitor molecule act by adsorption at the metal/solution interface. The %IE at different concentration of each inhibitor in 0.1M HCl were calculated from the corresponding electrochemical impedance data according to equation.

$$\%IE_{\square} = \frac{R_{Ct} - R^{I}_{Ct}}{R_{Ct}} \times 100$$

where R_{Ct} and R'_{ct} are the polarization resistances in the presence and absence of inhibitors, respectively. The highest inhibition efficiency was 87% for CP at a concentration of 0.3M. The parallel increase in the inhibition efficiencies for corrosion of zinc in HCl with increasing concentration can be explained on the basis of inhibitor adsorption.

Table 3: Corrosion parameters obtained from EIS measurements for zinc in 0.1M HCl containing various concentrations of inhibitors at 303K

Inhibitor conc.	*Rct* (Ωcm^2)	Capacitance (mFcm-2)	IE (%)
Blank	55	362.3	-------
0.05	112	195.6	49.3
0.1	215	270.1	74.4
0.15	290	280.7	81.1
0.2	345	101.3	84.5
0.3	398	353.8	87.0

3.4. Effect of acid concentration:

The influence of acid concentration on the dissolution of zinc was studied. When the concentration of acid increased beyond 0.5M the protection efficiency was decreased, as given in the Table 4. At higher acid concentration the hydrogen evolution dominates which results in the stripping of the adsorbed organic compound from the metal surface and exposes the bare metal to corrosive environment.

Table 4: Corrosion inhibition efficiencies in the presence of CP in 0.1, 0.3 and 0.5M Hcl.

Conc. of inhibitor	% Inhibition Efficiency with different acid concentrations								
	0.1M			0.3M			0.5M		
	2hr	6hr	10hr	2hr	6hr	10hr	2hr	6hr	10hr
Blank	-----	-----	-----	-----	-----	-----	-----	-----	-----
0.05	52	47	45	49	48	46	49	43	46
0.10	60	55	54	58	51	52	57	46	51
0.15	73	64	62	70	60	60	71	59	59
0.20	87	73	71	82	68	69	81	64	66
0.25	93	71	69	90	68	70	88	66	68
0.30	94	88	77	93	84	93	92	81	74

3.5. Temperature effect:

The effect of temperature on the inhibitive efficiency of CP was studied by gravimetric method at various temperatures. Weight losses were determined in 0.1 M HCl solutions without and with 0.3 M of the inhibitor studied in the temperature range (298-338 K), after one hour of immersion. The results given in Table 5 show that in inhibited as well as in uninhibited solutions the corrosion rate increases with a rise in temperature and as a result the inhibition efficiency decreases indicating that at higher temperatures the dissolution of Zinc predominates over inhibitor adsorption. This may be attributed to the desorption of the inhibitor molecules, thus exposing the metal surface to further attack. Further this may be due to the catalytic activity of the metal surface for the hydrogen evolution or for the metal dissolution [22].

Table 5. Corrosion parameters and inhibition efficiencies for zinc in 0.1 M HCl without and with the addition of 0.3 M CP at different temperatures.

T, K	W°_{corr}, mg/cm^2 h	W_{corr}, mg/cm^2 h	E_w, %
298	99.65	10.18	90.10
308	89.3	15.27	82.90
318	67.05	24.30	63.76
328	44.64	21.03	52.88
338	44.55	21.1	52.64

3.6. Scanning Electron Microscopic Studies:

Scanning electron microscopy (SEM) study was performed on the zinc surface, immersed in corrosive solution, in the absence (Fig. 4 (a)) and presence of CP (Fig. 4 (b)). It can be seen from Fig. 4 (a) shows that the zinc surface is damaged in the absence of the inhibitor, due to the attack of the aggressive medium. In Fig. 4 (b) it can be seen that the surface of zinc in the presence of CP shows some intergranular attack and rest of the surface is nearly intact as even the original polishing scratches are seen after the exposure. This indicated that the CP forms a protective layer on the metal surface, which in turn reduces the metal loss by dissolution or hydrogen evolution in acid medium, CP can inhibit the corrosion of zinc significantly [23].

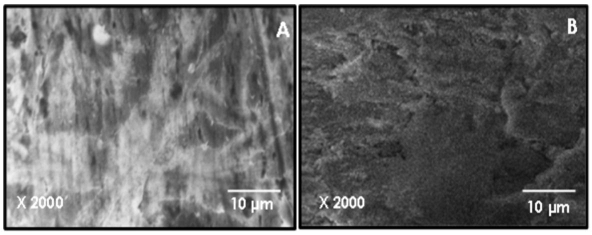

Fig. 4. SEM photomicrographs of the zinc surface taken after anodic polarization in 0.1M HCl in the absence (A) and presence (B) of CP.

4.0. CONCLUSIONS:

The prepared condensation product CP reduced the corrosion rate of zinc considerably in HCl medium. Both the weight loss and electrochemical studies showed that zinc surface treated with CP has a better corrosion resistance to acid medium. The IE% resulted from electrochemical and weight loss measurements were in good agreement. The observed protection against corrosion was particularly affected by the concentration of condensation product, concentration of aggressive medium, and temperature. The treatment induced a modification of the electrode behavior of zinc and decreasing the electron transfer rate during corrosion. The protection resulted from the formation of a stable organometallic film due to the interaction of hetero atoms of CP with the zinc surface, confirmed by the EIS and SEM studies. These results show that CP acts as good corrosion inhibitor for zinc in HCl medium.

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