Inhibition Studies of a Few Organic Compounds and Their Condensation Products on the Corrosion of Zinc in Hydrochloric Acid Medium

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The corrosive behavior of zinc in HCl solution containing various concentrations of glutaraldehyde GTD, glycine GLN, methionine MTN, and their condensation products formed between GTD + GLN (CP1) and GTD + MTN (CP2) was investigated. The corrosion-inhibitive action of these compounds on zinc metal was studied using chemical and electrochemical methods. The results showed that the compound CP2 is the best inhibitor and that its inhibition efficiency reaches 92.56% at 10^{-2} M in 0.05 M acid concentration. As an inhibitor, CP2 was found to have a predominant cathodic effect and its adsorption was confirmed with the Temkin isotherm. The effect of temperature on the corrosion of zinc was investigated by the weight-loss method. The morphology of the corroded surface was studied by SEM technique to obtain information about the adsorption of inhibitor molecules on the zinc surface.

Introduction

Zinc is a metal with numerous industrial applications and is mainly used for the corrosion protection of steel[1]. Zinc is an industrially important metal and is corroded by many agents, of which aqueous acids are the most dangerous[2]. Looking at its increasing use the study, of corrosion inhibition is of paramount importance. The dissolution behavior of zinc in acidic and nearly neutral media is known to be inhibited by nitrogen and sulfur-containing organic compounds. Such compounds contain electron-donating groups that decrease the corrosion rate by increasing the hydrogen over voltage on the corroding metal[3]. Studies of the effect of organic additives on the corrosion rate of zinc have been the subject of many investigators[4−9]. The efficiency of aldehydes and amino acids as inhibitors of corrosion for different metals in different corrosive environments has been studied by several workers[10−12], and their inhibition efficiency is due to the formation of a protective layer or film on the metallic surface. The role of this film is to isolate the corroding metal from the corrosive medium.

The present study deals with the effect of GTD, GLN, MTN and their condensation products such as CP1 and CP2 on the corrosion behavior of zinc in HCl solution.

Experimental

Zinc samples of pure grade (Cu 0.17%, Ti 0.075%, Al < 0.05%, Pb - Cd < 0.003%, Fe 0.002%, Sn 0.001% and Mg 0.0005%) material were used for the measurement of the corrosion rate. Electrodes were prepared from a rectangular zinc plate and isolated with a Teflon band so that only a 1 cm^{-2} area was exposed. Prior to every experiment the electrode was degreased with vapors of trichloroethylene followed by mechanical polishing with 600 grit silicon carbide emery paper and washing with distilled water. The samples with an exposed total area of 6.0 cm^2 were used for weight loss measurements. These samples were immersed in 250 ml of test solution maintained at 298 K.

AR grade chemicals and double distilled water were used for the preparation of these solutions. The inhibitors were prepared by the reaction between GTD + GLN and GTD + MTN. Duplicate experiments were performed in each case, and the mean values of the losses in weight were recorded.

Electrochemical experiments were performed in aqueous 0.05 and 0.1M hydrochloric acid solution by means of a galvanostatic technique. A conventional three-electrode cell consisting of zinc specimen as working electrode, saturated calomel and platinum were used as reference and auxiliary electrodes respectively. The anodic and cathodic polarization values were measured under galvanostatic conditions using an Equiptronics digital potentiometer (model EQ 600). The potential of the working electrodes varied from the open circuit potential at the rate of 20 mV/min and steady values of current were noted using an ELICO Potentiostat/Galvanostate (model CL-95). The surface morphology of samples after the electrochemical test in the presence and absence of the inhibitors was investigated by scanning electron microscopy using SEM JSM-850 (Jeol).

Results

Weight-loss method

The corrosion of zinc in 0.05 M HCl solution containing various inhibitors was studied by weight-loss measurements.

The corrosion rate of zinc is determined by using the relation

$$W = \frac{\Delta m}{St} \tag{1}$$

where Δm is the mass loss, S is the area and t is the immersion period.

The percentage inhibition efficiency (IE %) is calculated using the relationship

$$IE\% = 1 - \frac{w^1}{w} \times 100 \tag{2}$$

where w and w^1 are the corrosion rate of zinc in the absence and presence of inhibitors.

Table 1 shows the percentage inhibition efficiency of GTD, GLN, MTN, CP1 and CP2 at various concentrations in 0.05 M HCl solution in an immersion period of 2 h, at 298 K. The results showed that inhibition efficiency increased as the concentration of inhibitor rose from 10^{-4} to 10^{-2} M. Further increases of inhibitor concentration provide a lower degree of protection. The concentration 10^{-2} M was found to be the optimum concentration for the inhibitors. The maximum inhibition efficiency was observed in CP2 85.33%. Further detailed study of zinc corrosion was undertaken with CP1 and CP2.

Table 1. Corrosion rate (mg/cm/h), Percentage inhibition efficiency at various concentrations in 0.05 M HCl at 298K.

Inh. Conc.	GTD		GLY		MTN		CP1		CP2	
M	W_{corr}	IE	W_{corr}	IE	W_{corr}	IE	W_{corr}	IE	W_{corr}	IE
Blank	0.266	——	0.266	——	0.266	——	0.266	——	0.266	——
1×10^{-4}	0.243	08.64	0.223	13.16	0.199	16.18	0.211	20.67	0.203	23.68
1×10^{-3}	0.226	15.03	0.203	23.68	0.182	31.57	0.164	38.34	0.127	52.25
5×10^{-3}	0.211	20.67	0.186	30.07	0.161	39.47	0.134	49.62	0.070	73.68
1×10^{-2}	0.196	25.56	0.173	34.96	0.144	45.86	0.081	69.54	0.041	84.58
5×10^{-2}	0.192	26.69	0.172	35.33	0.143	46.24	0.078	70.67	0.039	85.33

Polarization method

Anodic and cathodic polarized potentials were measured in the absence and presence of inhibitors in a current density range of 0.1 to 25 mA cm^{-2}. Figure 1 shows the anodic and cathodic polarization curves for CP1 and CP2 as a representative curve in 0.05 M HCl in the presence and absence of inhibitors at optimized concentration.
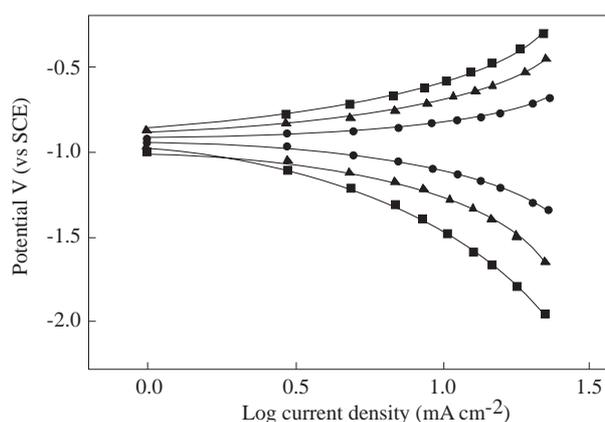
Figure 1. Anodic and cathodic polarization curves of zinc for CP1 and CP2 in 0.05M HCl. [•] Blank, [▲] CP1, [■] CP2.

It is evident from Figure 1 that cathodic curves are much more polarized than anodic curves. Thus the cathodic sites are blocked to greater extent than the anodic sites by the inhibitor molecules. It is clearly indicated that the derivatives of glutraldehyde compounds are more cathodic-type inhibitors. The I_{corr} was determined from Tafel extrapolation and linear polarization resistance measurements. The values of R_p were obtained from the slopes of the polarization curves at low polarized potentials of 20-mV.

The corrosion rates were determined from the polarization resistance R_p using the Stern-Geary equations

$$I_{corr} = \frac{b_a b_c}{2.303 R_p [b_a + b_c]} \tag{3}$$

The polarization resistance R_p is defined as the tangent of the polarization curve at E_{corr}

$$R_p = \left(\frac{dE}{dI} \right) \tag{4}$$

The inhibition efficiency was calculated using the relation

$$IE\% = 1 - \frac{I_{corr}^{1}}{I_{corr}} \times 100 \qquad (5)$$

where I_{corr} and I_{corr}^{1} are corrosion current densities in the presence and absence of inhibitors.

Table 2 gives the E_{corr}, I_{corr} and percentage inhibition efficiency obtained from the polarization technique in 0.05 M HCl at room temperature. The increase in the cathodic Tafel slopes indicates an increase in percentage inhibition efficiency. The results obtained from the polarization technique were in good agreement with those obtained from the weight-loss method with a small variation of $\pm$ 5%.

Table 2. Corrosion parameters of zinc in presence of 1 x 10^{-2} M concentration of inhibitors in 0.05 M HCl solution.

Inhi-bitors	E_{corr} (-V)	β_a (V/dec)	β_c (V/dec)	Tafel extrapolation I_{corr} (mA cm^{-2})	IE (%)	Linear polarization I_{corr} (mA cm^{-2})	IE (%)
Blank	0.938	0.06	0.14	3.2	——-	2.8	——-
GTD	0.934	0.063	0.166	2.4	25.00	2.2	21.42
GLN	0.927	0.065	0.202	2.1	34.37	1.9	32.14
MTN	0.926	0.068	0.218	1.8	43.75	1.6	42.85
CP1	0.922	0.072	0.22	1.0	68.75	0.95	66.07
CP2	0.918	0.076	0.224	0.5	84.38	0.52	81.42

The polarization curves for zinc in a higher acid concentration of 0.1 M HCl in the presence and absence of CP1 and CP2 is shown in Figure 2. Table 3 gives the corrosion parameters for zinc in 0.1 M HCl solution at the optimum concentration of inhibitors. The inhibition efficiency decreases with increases in the concentration of the acid.
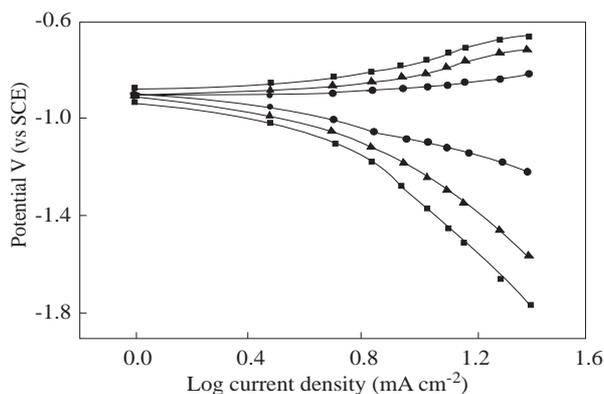

Figure 2. Anodic and cathodic polarization curves of zinc for CP1 and CP2 in 0.1M HCl. [•] Blank, [▲] CP1, [■] CP2.

Table 3. Corrosion parameters of zinc in the presence of 10^{-2} M concentration of inhibitors in 0.1 M HCl solution.

Inhi-bitors	E_{corr} (-V)	β_a (V/dec)	β_c (V/dec)	Tafel extrapolation I_{corr}	IE (%)	Linear polarization I_{corr}	IE (%)
Blank	0.924	0.038	0.12	6.5	——	5.4	——
CP1	0.93	0.052	0.18	2.7	58.46	2.5	53.70
CP2	0.944	0.64	0.194	1.9	70.76	1.5	68.51

Weight-loss measurement was carried out at various temperatures (298 – 328 K) in the absence and presence of an optimized concentration of inhibitors in 0.05 M HCl at immersion period of 2 h. The percentage inhibition efficiency with respect to different temperature is given in Table 4. The corrosion rate increased with the rise in temperature and was due to the increase in the transportation action of the acid proton (H^+) to the zinc surface, so that the reduction reaction at the cathode is enhanced in the absence of the inhibitors. However, in the presence of inhibitors the percentage inhibition efficiency increased with rises in temperature and activation energy obtained from the slopes of plots of the logarithmic corrosion rate against 1/T.

Table 4. Effect of temperature on the corrosion of zinc in the presence and absence of inhibitors (optimized concentration) in 0.05 M HCl.

Name of inhibitor	308		318		328	
	W_{corr}	IE(%)	W_{corr}	IE(%)	W_{corr}	IE(%)
Blank	0.492	——	0.892	——	1.232	——
CP1	0.135	72.56	0.202	77.35	0.243	93.26
CP2	0.052	89.43	0.057	93.60	0.061	95.04

Adsorption isotherm

The adsorption behavior of CP1 and CP2, assuming no change in the mechanism of both the hydrogen evolution reaction and zinc dissolution, and the degree of coverage θ_{inh} can be obtained using the equation

$$\theta_{inh} = 1 - (I_{inh}/I_{uninh})$$

The adsorption isotherm obtained from the above equation is shown in Figure 3. This isotherm follows that of Temkin, which characterizes the chemisorption of unchanged substances on a heterogeneous surface[13]. For such isotherm θ_{inh} is a linear function of logC according to the equation
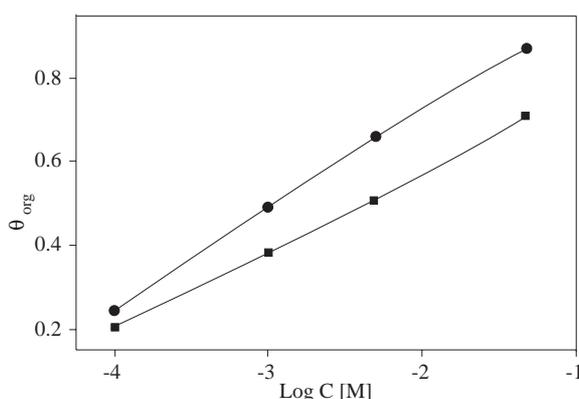
$$\theta = 1/f \ln B^* C$$

Figure 3. Adsorption isotherm of CP1 and CP 2 on zinc in 0.05M HCl. [■] CP1 and [●] CP2.

where B^* is the adsorption equilibrium constant, f is the heterogeneous factor of the metal surface and C is the bulk concentration of the adsorbate[13]. The parameter 'f' is a heterogeneous factor that gives the variation of adsorption energy with coverage. The values of B^*, f, and E_a are given in Table 5. The value of

'f' for CP2 is lower than that of CP1 and the inhibition efficiency of CP2 is higher than CP1. In both CP1 and CP2, the values of 'f' are greater than zero, indicating a Temkin adsorption isotherm.

Table 5. Values of 'f', B^* and activation energy (E_a) KJ Mole^{-1}.

Inhibitor	f	B^*	E_a (KJ Mol^{-1})
Blank	—-	—-	102.09
CP1	6.23	1.64 x 10^3	76.9
CP2	4.76	1.15 x 10^3	67.44

SEM analysis

The surface morphology of the zinc surface was studied by scanning electron microscopy (SEM). Figure 4a shows the SEM photograph of the zinc surface taken after anodic polarization (15 min) in the current density range of 5 mA cm^{-2} in 0.05 M HCl solution. Needle-like deposits appeared in the dissolution region of the zinc surface[14]. The SEM taken after anodic polarization in 0.05 M HCl containing CP1 and CP2 is shown in Figures 4b and 4c respectively. In the case of CP1 the surface of zinc covered with needle-like deposits is less comparatively blank, but in CP2 the surface of zinc is free from needle-like deposits, due to the adsorption of inhibitors. This indicated that the inhibitors become adsorbed onto the zinc surface and isolated the surface from the corrosive medium.
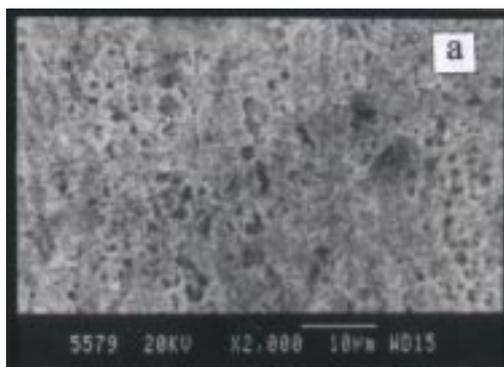

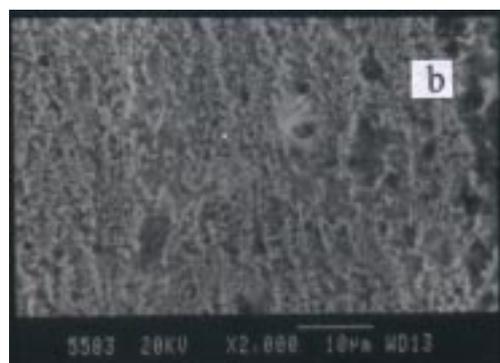**Figure 4a.** SEM micrograph of zinc surface taken after anodic polarization in 0.05 M HCl.

Figure 4b. SEM micrograph of zinc surface taken after anodic polarization in 0.05M HCl containing CP1.
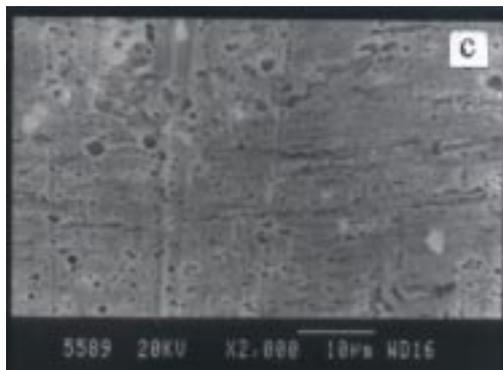
Figure 4c. SEM micrograph of zinc surface taken after anodic polarization in 0.05 M HCl containing CP2.

Mechanism of corrosion inhibition

The polarization data show that hydrogen reduction is the principle cathodic reaction during the corrosion of zinc in HCl solution. In acid solution the used inhibitors exist as protonated species, which can adsorb on the cathode sites of zinc and decrease the evolution of hydrogen[15]. The rate of cathodic reaction is thus reduced in the presence of inhibitors, and hence the potential values of cathodic polarization are shifted towards a more negative side as shown in Figure 1.

Discussion

Most organic inhibitors contain at least one polar group with an atom of nitrogen, sulfur or oxygen, and each of them is considered a chemisorption center. The protective properties of such compounds depend on the electron densities around the chemisorption center. The higher the electron density at the center, the more effective the inhibitor[16].

The corrosion rate values in the presence of various inhibitors indicated that CP2 has a greater effect on the dissolution of zinc in HCl medium. The mechanism of action of MTN as a corrosion inhibitor had already been established for different metals and alloys[12]. The reduction in the dissolution of zinc in the presence of these two inhibitors may be attributed to the sulfur and nitrogen atoms present in the functional group. These groups are electroactive and interact with the metal's surface to a greater extent. The S and -NH$_2$ group of MTN interacts with the zinc surface. In the condensation product the -NH$_2$ group is absent as it reacts with the CHO of the GTD to give imine, a condensation product. The corrosion rate is lower in this imine because it covers more of the metal surface. The other imine of CP1 shows less inhibition. The imine of CP2 is a more efficient corrosion inhibitor than the other compounds tested because of its sulfur atom, which confirms the earlier study[10].

The temperature effect was significant in CP1 and CP2. Inhibiting efficiency increases with temperature and with a simultaneous decrease in E$_a$ and thus indicates the chemisorption of these inhibitors. This result may be related to the modification of the metal dissolution mechanism interpreted by many authors[17] for the following reason. Temperature is a predominant factor in the formation of a protective layer at the metallic surface formed by metal inhibitor interaction. Based on this reason, the present inhibitors form a protective layer, and interaction between metal and inhibitor increases with temperature. This causes more surface coverage by the inhibitor and thus decreases the dissolution of zinc.

Conclusion

The developed inhibitors produced good corrosion inhibition for zinc in aqueous HCl medium. The inhibition efficiency of the tested inhibitors follows the order GTD < GLN < MTN < CP1 < CP2. The activation energy decreased in the presence of condensation products, indicating strong interaction between the metal surface and inhibitors. The increase in cathodic Tafel slopes reveals that the inhibitors control the cathodic reaction.

The compounds can be synthesized easily, are readily soluble in water and non-toxic, and can be used as effective corrosion inhibitors for zinc in acid medium.

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