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Hexamine as corrosion inhibitor for zinc in hydrochloric acid

R. T. Vashi* and Krunal Desai

**Department of Chemistry, Navyug Science College, Rander Road, Surat, Gujarat, INDIA*

ABSTRACT

The corrosion of zinc in hydrochloric acid containing hexamine has been studied at different acid concentrations, inhibitor concentration and temperatures. Corrosion increases with the increase of acid concentration . Inhibition efficiency (I.E.) of hexamine increases with the concentration of inhibitor and decreases with the increase in concentration of acid. As temperature increases, corrosion rate increases while percentage of I.E. decreases. The plot of log (θ/1-θ) versus log C results in a straight line suggest that the inhibitor cover both the anodic and cathodic regions through general adsorption following Langmuir isotherm. Galvenostatic polarization curves show polarization of both anode as well as cathode.

Key words: Corrosion, zinc, hydrochloric acid, Hexamine.

INTRODUCTION

Corrosion is a process that occurs when a material deteriorates due to its interaction with the surrounding environment in which an electrochemical reaction consumes the material through oxidation **[1]**. Zinc is one of the most important non-ferrous metals, which finds extensive use in metallic coating. Zinc corrodes in solution having pH lower than 6.0 and higher than 12.5, while within this range the corrosion is very slow **[2]**. Hydrochloric acid is highly corrosive, strong mineral acid since it is completely dissociated in water and has major industrial uses.

Aromatic, aliphatic and heterocyclic amines have been extensively investigated as corrosion inhibitors **[3-5]**. According to Hackerman et al. **[6-7]** the inhibitive properties of a series of secondary aliphatic and cyclic amines in acid media are controlled by the percentage of π - orbital of free electron on the nitrogen atom of these compounds. R.T.Vashi et al. **[8-9]** studied the corrosion inhibition of zinc in (HNO_3+HCl) by ethanolamines and by ethylamines. R.T.Vashi et al. [**10**] studied Hexamine as corrosion inhibitor of zinc in phosphoric acid. In the present work, the corrosion of zinc by hydrochloric acid containing hexamine has been reported.

MATERIALS AND METHODS

To study the corrosion of zinc in hydrochloric acid, weight loss method, temperature effect, potential as well as polarization measurements have been used. Rectangular specimens (4.65 x 2.15 x 0.16 cm) of zinc having an area of 0.2221 dm^2 were taken and cleaned by buffing and immersed in 0.01, 0.05, 0.10 and 0.15 M Hydrochloric acid concentration with and without inhibitor containing 230 ml test solution at 301 K for 24 h immersion period. After the test, specimens were cleaned by 10% chromic acid solution having 0.2 % $BaCO_3$ for a period of about 2 minutes **[11]**. After cleaning, test specimens were washed with distilled water followed by acetone and dried with air drier.

The mean value of weight loss was reported as mg/dm^2 shown in Table- 1. All chemicals used were of AR grade. The corrosive solution was prepared in double distilled water.

To assess the protective value, hexamine was added in 5, 10, 15 and 20 mM concentration in 0.01, 0.05, 0.10 and 0.15 M HCl concentration for 24 h duration period (Table-1).

To study the effect of temperature on corrosion of zinc in 0.05 M HCl, the specimens were immersed in 230 ml of corrosive solution and corrosion loss was determined at solution temperature of 303, 313, 323 and 333 K for an immersion period of 2 h with and without inhibitors. From the data I.E., energy of activation (Ea), heat of adsorption (Q_{ads}), free energy of adsorption (ΔG_{ap}), change of enthalpy (ΔH) and entropy of adsorption (ΔS) were calculated and shown in Table -2.

For polarization study, metal specimens having an area of 0.2221 dm^2 were immersed in 230 ml corrosive solution without and with 20 mM inhibitor concentration in 0.01 M HCl. 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 potentiostat / galvanostat make Gamry, USA with inbuilt corrosion software. 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 (Icorr) and the corrosion potential (Ecorr) **[12].**

RESULTS AND DISCUSSION

The results are presented in Tables 1 to 3 and fig. 1 to 4. To assess the effect of corrosion of zinc in hydrochloric acid, hexamine is added as inhibitor.

I.E. has been calculated as follows:

$$\text{I.E. (\%)} = \{(Wu - Wi) / Wu\} \times 100 \qquad \text{------------- (1)}$$

Where, W_u is the weight loss of metal in uninhibited acid and

W_i is the weight loss of metal in inhibited acid.

Energy of activation (Ea) has been calculated from the slope of log ρ versus 1/T (ρ = corrosion rate, T = absolute temperature) (Fig. 2) and also with the help of the Arrhenius equation **[13].**

$$\log (p_2/ p_1)= Ea/ 2.303\, R\, [(1/T_1) - (1/T_2)] \qquad \text{--------------(2)}$$

Where, ρ_1 and ρ_2 are the corrosion rate at temperature T_1 and T_2 respectively.

The value of heat of adsorption (Qads) was calculated by the following equation **[14]**.

$$Q_{ads} = 2.303\, R\, [\log (\theta_2 / 1 - \theta_2) - \log (\theta_1 / 1 - \theta_1)] \text{ x } [T_1 . T_2 / T_2 - T_1] \qquad \text{--------------(3)}$$

where, θ_1 and θ_2 [$\theta = (Wu - Wi)/Wi$] are the fractions of the metal surface covered by the inhibitor at temperature T_1 and T_2 respectively.

The values of the free energy of adsorption (ΔGa) were calculated with the help of the following equation **[14]**.

$$\log C = \log (\theta / 1 - \theta) - \log B \qquad \text{------------- (4)}$$

Where, $\log B = -1.74 - (\Delta Ga / 2.303\, RT)$ and C is the inhibitor concentration.

The enthalpy of adsorption (ΔH°_{a}) and entropy of adsorption (ΔS°_{a}) are calculated using the equation.

$\Delta H^{o}{}_{a} = E_a - RT$ ------------- (5)

$\Delta S^{o}{}_{a} = \Delta H - \Delta G / T$ ------------- (6)

Corrosion in acid: The corrosion rate increases with the increase in concentration of acid. The corrosion rate was 81.98, 1136.48, 3151.05 and 5221.85 mg/dm^2 in 0.01, 0.05, 0.10 and 0.15 M HCl concentrations respectively for a period of 24 h at 301 ± 1 K as shown in Table-1.

Effect of inhibitor concentration: At constant acid concentration, the I.E. of the hexamine increases with the inhibitor concentration, e.g. in case of Hexamine in 0.01 M HCl the I.E. was found to be 93.96, 96.16, 97.79 and 97.80 % with respect to 5, 10, 15 and 20 mM inhibitor concentration respectively [Table- 1].

Effect of acid concentration: At constant inhibitor concentration, the I.E. decreases with the increase in acid concentration. At 20 mM inhibitor concentration, the I.E. of Hexamine is 97.80, 97.38, 92.18 and 82.74 % with respect to 0.01, 0.05, 0.10 and 0.15 M acid concentration respectively [Table-1].

Effect of temperature: As the temperature increases, corrosion rate increases while percentage of I.E. decreases [Table-2]. Mean 'Ea' values were calculated by using eq.2 for zinc in 0.05 M HCl is 29.29 kJmol^{-1} while in acid containing inhibitor, the mean Ea value is 93.45 (Table -2). The higher values of mean Ea indicate physical adsorption of the inhibitor on metal surface **[15]**. The values of Ea calculated from the slope of Arrhenius plot (Fig. 2) and using eq.2 are almost similar. From Table-2, it is evident that in all cases, the Qads values are negative and ranging from –63.12 to – 68.23 kJmol^{-1}. The enthalpy change ($\Delta H^o a$) is positive (90.85 kJmol^{-1}) indicating the endothermic nature of the reaction **[16]** suggesting that higher temperature favours the corrosion process. The entropy ($\Delta S^o a$) values are positive (0.39 kJmol^{-1}) confirming that the corrosion process is entropically favourable **[17]**.

Polarization behaviour: Anodic and cathodic galvenostatic polarization curves for zinc in 0.01 M HCl acid, alone and containing 20 mM concentration of Hexamine is shown in Fig. 3 and Fig.4. The curves show polarization of both, the cathodes as well as anodes. I.E. calculated from corrosion current obtained by the extrapolation of the cathodic and anodic Tafel lines are given in Table- 3. In almost all the cases, the I.E. from Tafel plots agree well (within ± 4 %) with the values obtained from weight loss data.

Mechanism of corrosion inhibition: Generally, zinc dissolve in hydrochloric acid solution due to somewhat hydrogen type of attack, the reaction taking place at the microelectrodes of the corrosion cell being represented as,

$Zn \text{ -------> } Zn^{+2} + 2e^{-}$ (anodic reaction) --------------(7)

Reduction reaction is indicated by decrease in valence or the consumption of electrodes, as shown by the following equation.

$2H^{+} + 2e^{-} \text{ -------> } 2H_{(ads.)}$ (cathodic reaction) --------------(8)
or $H + H_3O^{+} + e^{-} \text{ -------> } H_2\uparrow + H_2O$

The mechanism of inhibitor of corrosion is believed to be due to the formation and maintenance of a protective film on the metal surface. Further, when log (θ /1-θ) is plotted against log C straight lines are obtained in the case of hexamine studied (Fig. 1). This suggests that the inhibitor cover both the anodic as well as cathodic regions through general adsorption following Langmuir isotherm.

Hexamine is reported as effective acid corrosion inhibitor for various metals **[18-22]**. Macro molecular size and higher number of N-atoms of hexamine **[22]** might have covered almost all active source of zinc. Four nitrogen atom of the hexamine having high electron density must have functioned as the reaction center **[23]** and the hexamine molecules might have been chemisorbed to form a thin monolayer on the zinc surface. At lower concentration, it might have been chemisorbed in the flat position and at higher concentration in the vertical position **[24]**. The inhibitor action can be accounted by the interaction of loan pairs of electrons in the nitrogen atom on the positively charged metal surface. I. E. The presence of six methylene groups also helps to lead to an enhancement of electron density at the nitrogen atom, which enhances its adsorption on the metal surface. This in turn leads to an increase in the value of I.E **[25]**.

Table – 1 Corrosion rate (CR) and inhibition efficiency (I.E.) of zinc in 0.01, 0.05, 0.10 and 0.15 M HCl containing Hexamine as inhibitors for an immersion period of 24 h at 301 ± 1 K. K.

System	Inhibition Concentration	0.01 M		0.05 M		0.10 M		0.15 M	
		Acid concentration							
	mM	CR mg/dm^2	I.E. %	CR mg/dm^2	I.E. %	CR mg/dm^2	I.E. %	CR mg/dm^2	I.E. %
A	--	81.98	-	1136.48	-	3151.05	-	5221.85	-
B	5	4.95	93.96	185.95	83.64	1418.28	54.99	2833.86	45.73
	10	3.15	96.16	89.6	92.12	676.72	78.52	1987.84	61.93
	15	1.81	97.79	51.33	95.48	327.78	89.6	1022.51	80.42
	20	1.8	97.8	29.72	97.38	246.28	92.18	901.39	82.74

A = HCl *B = HCl + Hexamine*

Table - 2 Effect of temperature on corrosion rate (CR), inhibitive efficiency (I.E %.), energy of activation (E_a), heat of adsorption (Q_{ads}) and free energy of adsorption ($\Delta G°_a$) for zinc in 0.05 M HCl acid containing hexamine.
Inhibitor concentration = 20 mM Immersion period = 2 h Effective area of specimen = 0.2221 dm^2

	Temperature (K)								Mean from Ea Eq(1)	Ea from Arrhenius Plot	Q_{abs}					
	303		313		323		333									
System	CR mg/dm^2	I.E. %	CR mg/dm^2	I.E. %	CR mg/dm^2	I.E. %	CR mg/dm^2	I.E. %	kJ mol^{-1}	kJ mol^{-1}	303-313	313-323	323-333	$\Delta \Gamma_\alpha$	ΔH_α	$\Delta\Sigma_\alpha$
											kJ mol-1			(Kj mol-1)		
A	773.9	-	949.1	-	1594.8	-	2181.1	-	29.2	34.2	-	-	-	-	-	-
B	4.9	99.3	13.9	98.5	51.8	96.7	139.1	93.6	93.4	95.7	- 66.2	- 68.2	- 63.1	- 30.9	90.8	0.39

A = HCl *B = HCl + Hexamine*

Table-3 Polarisation data and inhibition efficiency (I.E.) of hexamine for zinc in 0.01 M HCl at 301 ± 1 K
Inhibitor concentration: 20 mM Effective area of specimen = 0.2221 dm^2

System	E_{corr} mV	CD I_{corr} mA/cm^2	Tafel slope (mV/decade) Anodic β_a	Tafel slope (mV/decade) Cathodic $-\beta_c$	B (mV)	I.E. (%) By Weightlossmethod	I.E. (%) By polarization method
A	-1040	0.1190	36.36	277.77	13.96	-	-
B	-1170	0.0059	111.11	12.30	4.81	98.02	94.05

A = HCl *B = HCl + Hexamine*
β_a = Anodic Tafel constant, β_C = Cathodic Tafel constant.
CD = Corrosion current density from interception of anodic and cathodic lines.

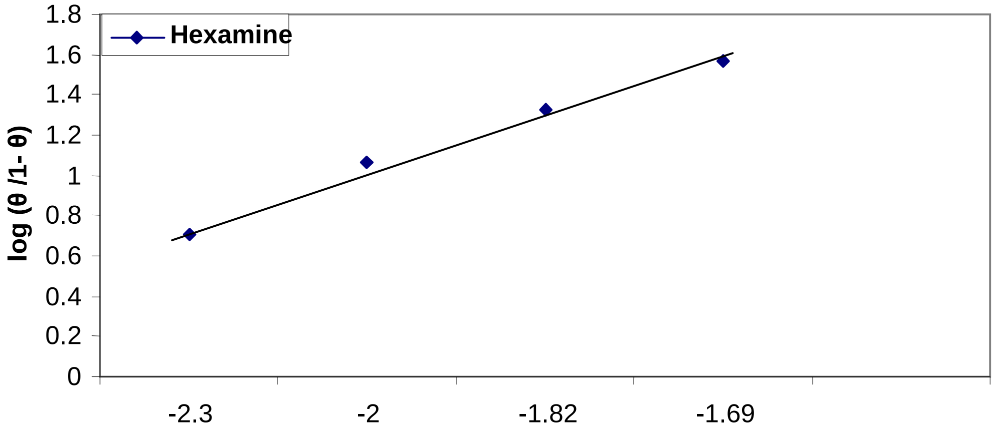

Fig. 1 : Plot of log (θ /1- θ) versus log C for hexamine in 0.05 M hydrochloric acid concentration

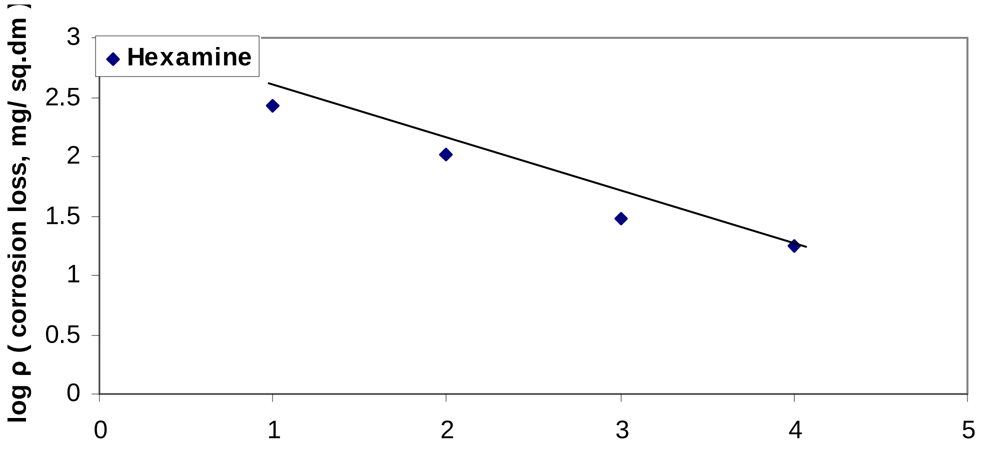

Fig. 2 : Arrhenius plots for corrosion of zinc in 0.05M hydrochloric acid in presence of 10 mM inhibitor concentration

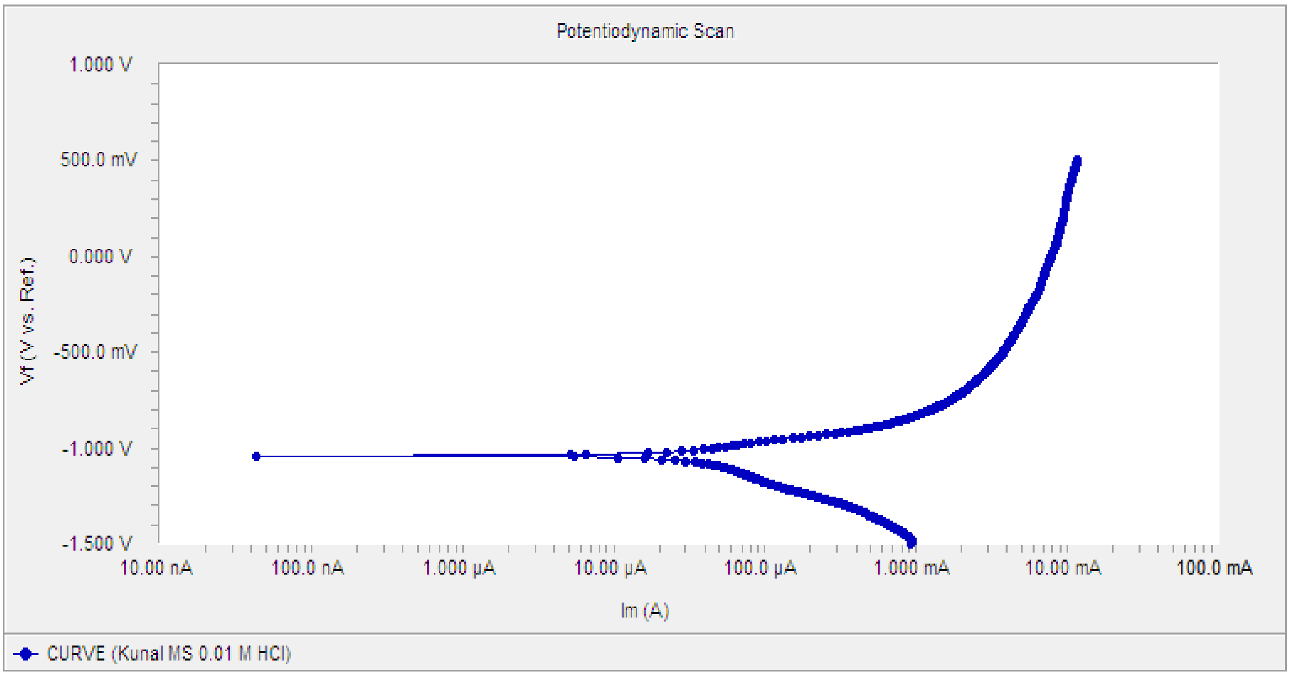

Fig.3: Polarisation curve for corrosion of zinc in 0.01 M HCl.

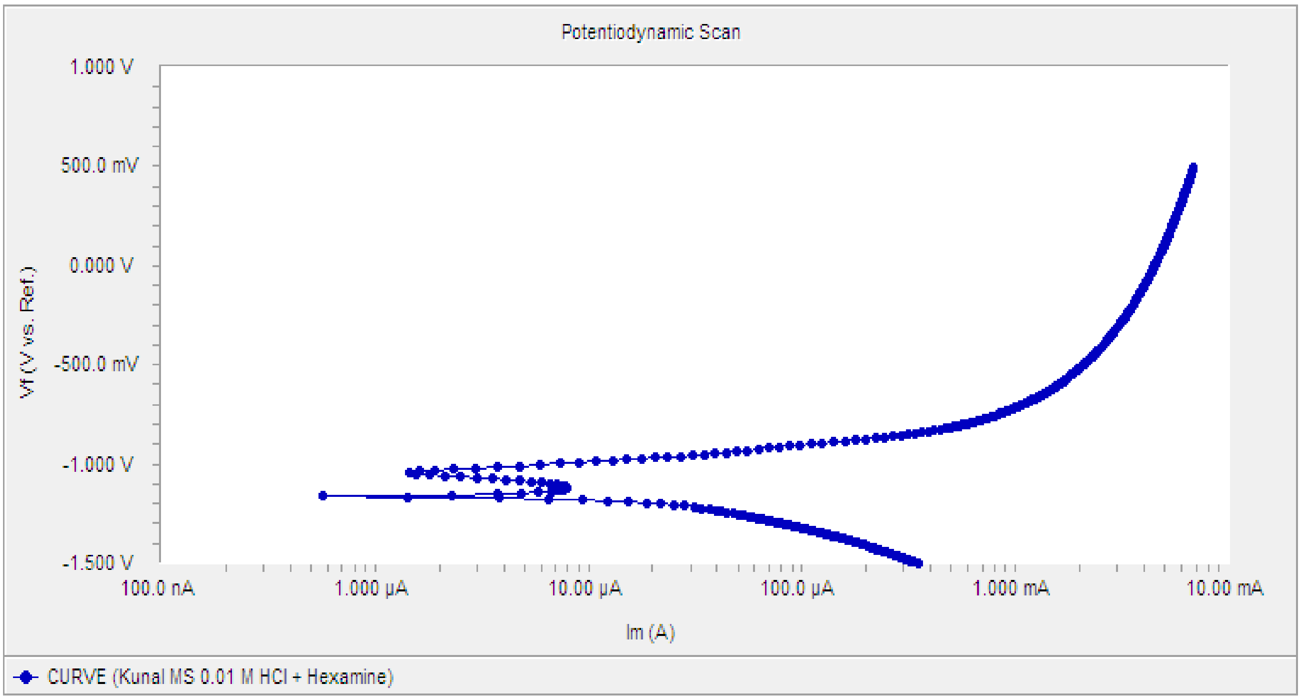

Fig.4: Polarisation curve for corrosion of zinc in 0.01 M HCl containing 20 mM hexamine inhibitor.

CONCLUSION

- As the acid concentration increase the corrosion rate increases and I.E. of inhibitor decreases.
- As the inhibitor concentration increases I.E. increases and corrosion rate decreases.
- Addition of inhibitor in corrosive media indicates that as the temperature increases corrosion rate increases while I.E. decreases.
- Galvenostatic polarization curves show polarization of both anode as well as cathode.

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