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Hexamine as corrosion inhibitor for zinc in (HNO_3 + H_2SO_4) binary acid mixture

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ABSTRACT

The corrosion of zinc in (HNO_3+ H_2SO_4) acid mixture containing hexamine as inhibitor has been studied at different mix acid concentration, inhibitor concentration and temperatures. Corrosion increases with the concentration of acid and with the temperature. The inhibition efficiency (I.E.) of hexamine increases with the concentration of inhibitor. The I.E. decreases with the increase in concentration of acid. As temperature increases, percentage of inhibition 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 anodic polarization.

Key words: Corrosion, zinc, (HNO_3+ H_2SO_4) acid mixture, hexamine

INTRODUCTION

The problem of corrosion is of considerable importance, nowadays due to increase in uses of metals and alloys. Zinc is one of the most important non-ferrous metals, which finds extensive use in metallic coating. Sulphuric acid and nitric acid are a major chemical product, which has uses many important especially in the production of fertilizers.

Aromatic, aliphatic and heterocyclic amines have been extensively investigated as corrosion inhibitors **[1-3].** According to Hackerman et al**. [4]** 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. Hexamine was reported as effective corrosion inhibitor for various metals in acid **[5-8].** In the present work, the corrosion of zinc by (HNO_3+ H_2SO_4) mix acid containing isomer of hexamine has been reported.

MATERIALS AND METHODS

To study the corrosion of zinc in phosphoric acid, weight loss method, temperature effect, potential as well as polarization measurements have been used. Rectangular specimens (5.0 x 2.0 x 0.1 cm) of zinc having an area of 0.2935 dm^2 were cleaned by buffing and immersed in 0.01, 0.05 and 0.10 N acid concentration with and without inhibitor containing 230 ml test solution at 301 ± 1 K for 24 h duration period. After the test, specimens were cleaned by 10% chromic acid solution having 0.2 % $BaCO_3$ for a period of about 2 minutes **[9].** After cleaning, test specimens were washed with distilled water followed by acetone and dried with air drier. Triplicate experiments were performed in each case and the mean value of weight loss was reported in form of corrosion rate. All chemicals used were of AR grade. The test solution was prepared in double distilled water.

For polarization study, metal specimens having an area of 0.047 dm^2 were immersed in 230 ml corrosive solution without and with 1.0% inhibitor concentration in binary acid mixture (0.01 N HNO_3 + 0.01 N H_2SO_4). 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 Potentio-Galvano-Scan (Weaving PGS 81) meter. Polarization curves were plotted with potential against log current density (called Tafel plots). Tafel lines correspondingly. The intersect point of cathodic and anodic Tafel lines gives the corrosion current (Icorr) and the corrosion potential (E_{corr}) **[10].**

RESULTS AND DISCUSSION

The results are presented in Tables 1 to 3 and Figs. 1 to 3. To assess the effect of corrosion of zinc in phosphoric acid, hexamine is added as an 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 **[11].**

$$\log \frac{\rho_2}{\rho_1} = \frac{Ea}{2.303\,R}\ [\ (1/T_1)\ -\ (1/T_2)\ ] \qquad -\,-\,-\,-\,-\,(2)$$

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

The value of heat of adsorption (Q_{ads}) were calculated by the following equation **[11].**

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

where, θ_1 and θ_2 [θ = (Wu – Wi)/Wi] are the fractions of the metal surface covered by the inhibitors 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 **[12].**

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

Where, log B = –1.74 – (ΔGa / 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.

$$\Delta H^{\circ}_a = E_a - RT \qquad \text{---------(5)}$$
$$\Delta S^{\circ}_a = \Delta H - \Delta G / T \qquad \text{---------(6)}$$

Corrosion in acid: The rate of corrosion increases with the increase in acid concentration. The corrosion rate was 213.7, 975.2 and 1921.4 mg/dm^2 in 0.01, 0.05 and 0.1 N (HNO_3+ H_2SO_4) mixed acid concentrations respectively for a period of 24 h at 301 ± 1 K as shown in Table-1.

Effect of inhibitor concentration: The I.E. of the hexamine increases with the inhibitor concentration, e.g. in case of hexamine in 0.10 N HNO_3 + 0.10 N H_2SO_4 acid mixture the I.E. was found to be 32.1, 50.5 and 59.8 % with respect to 0.1, 0.5 and 1.0 % inhibitor concentration respectively [Table- 1].

Effect of acid concentration: The I.E. decreases with the increase in acid concentration. At 1.0 % inhibitor concentration, the I.E. of hexamine was 33.2, 49.9 and 59.8% with respect to 0.01, 0.05 and 0.10 N (HNO_3+ H_2SO_4) mixed acid concentration respectively [Table -1].

Table 1: Corrosion rate (CR) and inhibition efficiency (I.E.) of zinc in 0.01, 0.05 and 0.10 N (HNO_3 + H_2SO_4) acid containing hexamine as inhibitor for an immersion period of 24 h at 301 ± 1 K.

Syatem	Conc. of inhibitor	Acid concentration					
		0.01 N		0.05 N		0.10 N	
		CR	I.E.	CR	I.E.	CR	I.E.
	(%)	mg/dm^2	%	mg/dm^2	%	mg/dm^2	%
A	-	213.7	-	975.2	-	1921.4	-
B	0.1	171.0	20.0	684.9	29.8	1292.9	32.1
	0.5	154.7	27.6	551.7	43.4	951.3	50.5
	1.0	142.7	33.3	488.2	49.9	771.5	59.8

A = (HNO_3 + H_2SO_4) *B = Hexamine + (HNO_3 + H_2SO_4)*

Effect of temperature: The effect of temperature on the corrosion of zinc is shown in Table- 2. In (0.05 N HNO_3 + 0.05 N H_2SO_4) mixed acid, corrosion rate increases as temperature increases i.e. corrosion rate was 700.5, 783.2, 832.0 and 895.2 mg/dm^2 for 3 h immersion period. Inhibition efficiency was decrease with temperature. The I.E. for hexamine at 1.0% concentration was 80.9, 75.0, 68.8 and 61.4% at 303, 313, 323 and 333 K respectively for 3 h immersion period. .

Value of 'Ea' calculated from eq.2 was found to be higher (26.4 kJ mol^{-1}) than that of uninhibited system (6.8 kJ mol^{-1}). This suggests that the presence of reactive centres on the inhibitor can block the active sites for corrosion, resulting in an increase in 'Ea'**[13].** The values of Ea calculated from the slope of Arrhenius plot and using eq.2 are almost similar. It was evident that in all cases, the Q_{ads} values were negative and ranging from –25.9 to –29.1 kJ mol^{-1}. Oguzie **[14]** explained that the negative values of Q_{ads} also signify that the degree of surface coverage decreased with rise in temperature.

Table 2: Effect of temperature on corrosion rate (CR), inhibitive efficiency (IE%), energy of activation (Ea) and heat of adsorption (Qads) for zinc in 0.05 N (HNO_3 + H_2SO_4) binary acid mixture containing inhibitor.

Inhibitor concentration = 1.0 % **Immersion period = 3 h**

System	Temperature, K								Mean Ea from eq.2	Ea from Arrhenious Plot	Q_{abs} (kJ mol^{-1})			ΔG_a	ΔH_a	ΔS_a
	303		313		323		333									
	CR	I.E.	CR	I.E.	CR	I.E.	CR	I.E.								
	mg/dm^2	%	mg/dm^2	%	mg/dm^2	%	mg/dm^2	%	kJ mol^{-1}	kJ mol^{-1}	303-313	313-323	323-333	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}
A	700.5	-	783.2	-	832.0	-	895.2	-	6.8	7.65	-	-	-	-	-	-
B	134.0	80.9	196.1	75.0	260.0	69.8	345.6	61.4	26.4	27.4	-27.2	-25.9	-29.1	-19.2	27.5	0.155

A = (HNO_3 + H_2SO_4) *B = Hexamine + (HNO_3 + H_2SO_4)*

The mean ΔG_a values was (-19.2 kJ mol^{-1}). This suggests that they are strongly adsorbed on the metal surface. This statement was supported by the work of Talati and Darji **[15].** The enthalpy changes (ΔH_a) was positive (27.5 kJ mol^{-1}) indicating the endothermic nature of the reaction **[16]** suggesting that higher temperature favours the corrosion process. Adeyen **[17]** described that if the $\Delta H < 10$ kJ mol^{-1} the adsorption is probably physisorption and if the $\Delta H > 10$ kJ mol^{-1} values indicate that the hexamine strongly adsorbed on zinc is chemisorption. The entropy (ΔS°_a) values was positive (0.155 kJ mol^{-1}) confirming that the corrosion process is entropically favourable **[18].**

Polarization behaviour: Anodic and cathodic galvenostatic polarization curves for Zinc in 0.01 N HNO_3 + 0.01 N H_2SO_4 acid mixture, alone and containing 1.0 % concentration of hexamine is shown in Fig. 3. The curves show anodic polarization . I.E. calculated from corrosion current obtained by extrapolation of the cathodic and anodic Tafel lines are given in Table-3. The I.E. calculated from Tafel plots agree well (within ± 3%) with the values obtained from weight loss data.

Table 3: Polarisation data and inhibition efficiency (I.E.) of hexamine for zinc in (0.01 N HNO_3 + 0.01 N H_2SO_4) binary acid mixture at 301 ± 1 K.

Inhibitor concentration: 1.0% **Effective area of specimen = 0.047 dm^2**

System	E_{corr}	CD	Tafel slope (mV/decade)		B	I.E. (%) from methods	
	(mV)	Icorr (mA/cm^2)	Anodic β_a	Cathodic $-\beta_c$	(mV)	Weight loss	By polarization
A	-1140	0.300	466	200	60.9	-	-
B	-1075	0.210	365	238	62.7	33.2	30.0

A = (HNO_3 + H_2SO_4) *B = Hexamine + (HNO_3 + H_2SO_4)*
β_a = Anodic Tafel constant, *β_C = Cathodic Tafel constant.* *$\beta = (\beta_a \times \beta_c)/[2.3 (B_a + \beta_c)]$*
CD = Corrosion current density from intersection of anodic and cathodic lines.

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

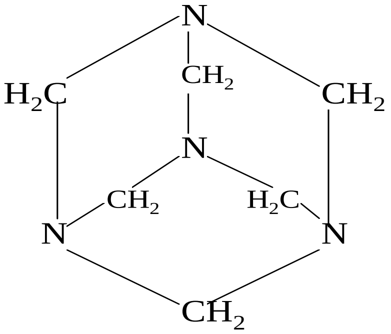
Zn -------> Zn^{+2} + $2e^-$ (anodic reaction) --------(7)

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

$2H^+$ + $2e^-$ -------> $2H_{(ads.)}$ (cathodic reaction) --------(8)

or $H + H_3O^+ + e^-$ -------> $H_2 \uparrow + H_2O$ --------(9)

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 were 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 adsorption isotherm.



Structure of Hexamine

Macro molecular size and higher number of N-atoms of hexamine **[19]** 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 centre **[20]** and the hexamine molecules might have been chemisorbed to form a thin monolayer on the zinc surface.

Hexamine (hexamethylenetetramine) consists of four nitrogen atoms and six CH_2 groups. Because of the presence of three nitrogen atoms electrons are disposed easily in the ring and therefore it is expected to be an effective inhibitor. The inhibitor action can be accounted by the interaction of lone pair of electrons in the nitrogen atom on the positively charged metal surface. 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. [**21**].

In case of hexamine cathodic polarization was greater than anodic polarization. Therefore, it is reveled that hexamine is a cathodic inhibitor and controls cathodic corrosion process. The protective effect of the inhibitor is probably due to formation of an insoluble film **[22]** Hence, the mechanism of the inhibitive action is possibly due to the blocking of cathodic sites by adsorption, which enables the formation of a protective insoluble film.

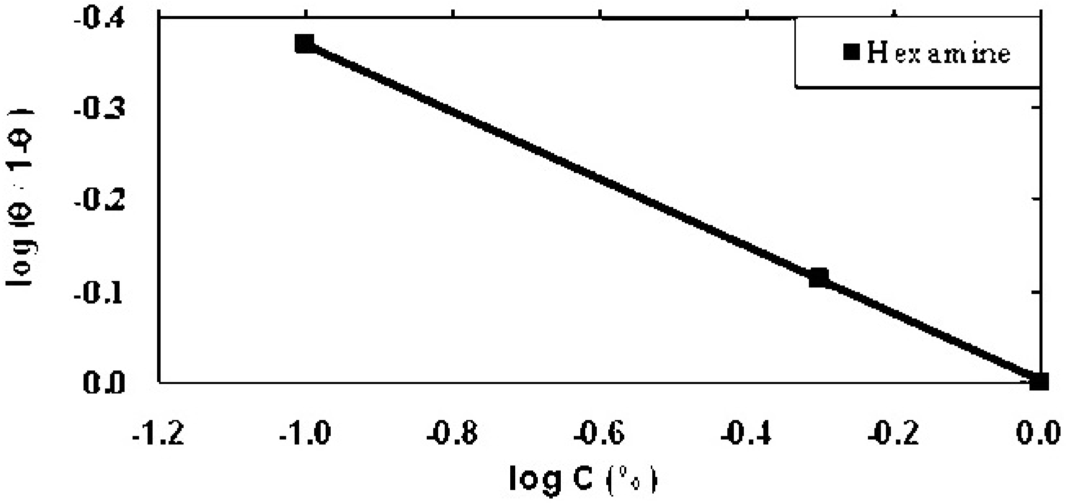


Fig.1 : Plot of (θ / 1- θ) versus C for hexamine in (0.05 N HNO_3+ 0.05 N H_2SO_4) mix acid concentration.

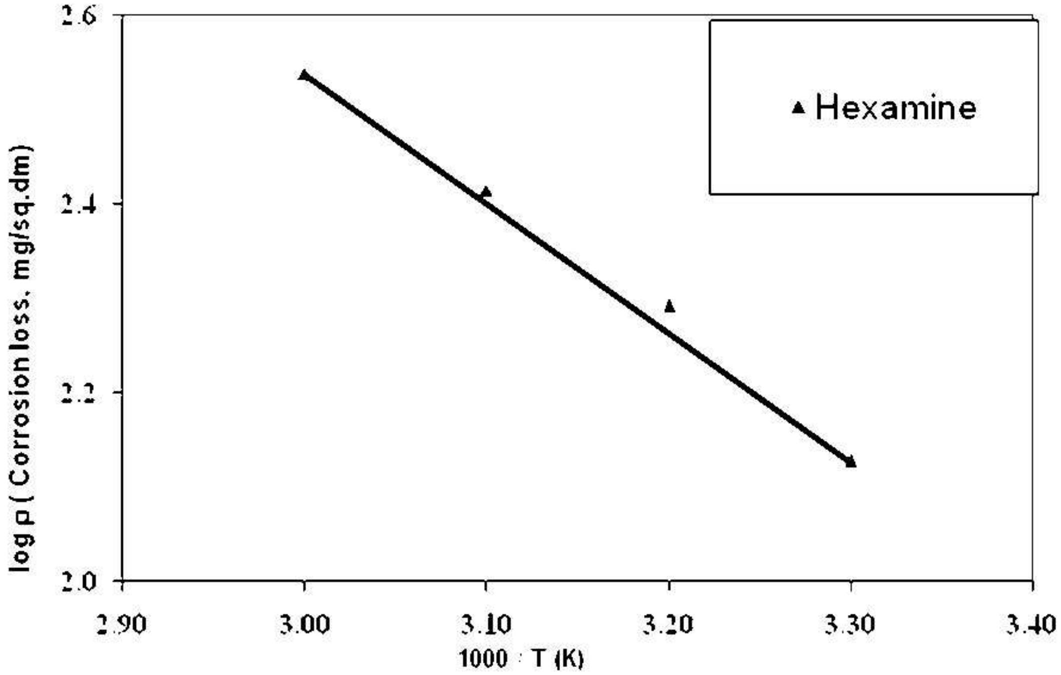


Fig. 2 : Arrhenius plots for corrosion of Zinc in (0.05 N HNO_3 + 0.05 N H_2SO_4) mix acid in presence of 1.0 % inhibitor concentration.

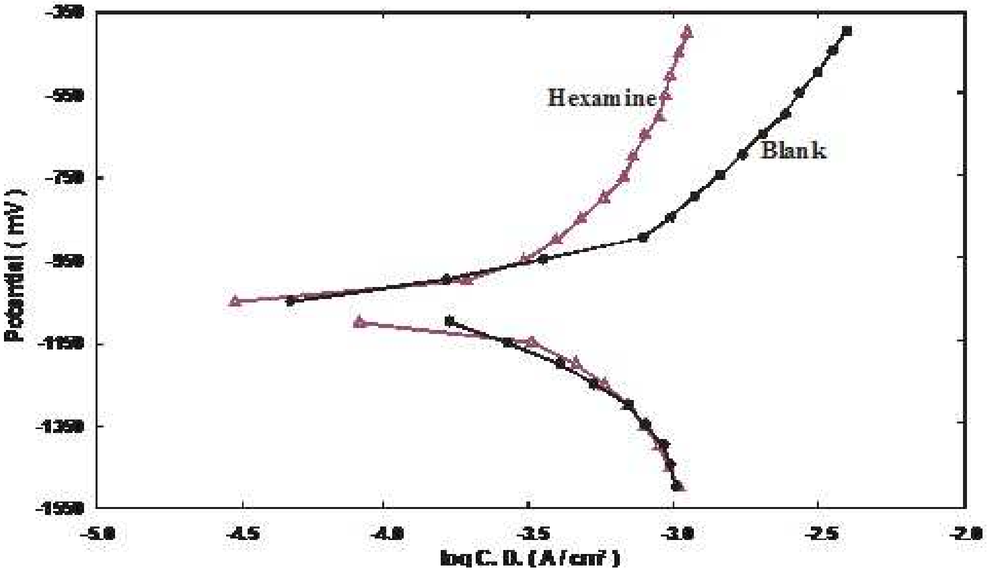


Fig. 3 : Polarisation curves for corrosion of zinc in (0.01 N HNO_3 + 0.01 N H_2SO_4)mix acid containing 1.0 % inhibitor concentration.

CONCLUSION

* As the acid concentration increase the corrosion rate increases and I.E. of inhibitor decreases.
* At all concentration of acid, as the inhibitor concentration increases I.E. increases and corrosion rate decreases.
* Mean value of 'Ea' in inhibited acid are higher than the value of 'Ea' in acid only, which shows that chemisorptions of the inhibitor molecule.
* As the temperature increases corrosion rate increases while I. E. decreases.

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