

## Prevention of zinc metal in ( $\text{HNO}_3 + \text{H}_2\text{SO}_4$ ) binary acid mixture by ethylamines

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### ABSTRACT

The inhibition effect of ethylamines on corrosion of zinc in ( $\text{HNO}_3 + \text{H}_2\text{SO}_4$ ) binary acid mixture has been studied. In mix acid, corrosion rate increases with the concentration of mix acid and with the temperature. At constant mix acid concentration, the inhibition efficiency (I.E.) of ethylamines increases with the inhibitor concentration. Similarly, at constant inhibitor concentration, the I.E. increases with the increase in concentration of mix acid. At all inhibitor concentration in binary acid mixture at 301 K for 24 h immersion period, the I.E. of inhibitors decreases in the order : Ethylamine > Diethylamine > Triethylamine. As temperature increases, percentage of inhibition decreases. The value of activation energy and free energy of adsorption have also been calculated. Anodic and cathodic galvanostatic polarization show little anodic but significant cathodic polarization.

**Key words:** Corrosion, Zinc, Nitric and Sulphuric acid mixture, Ethylamines.

### INTRODUCTION

Zinc is one of the most vital non-ferrous metal, having extensive use in metallic coating. Concentrated mineral acid mixture widely used in pickling, chemical cleaning, descaling and oil well acidising of metallic materials, causes damage of corrosion.<sup>1-3</sup> Sulphuric acid ( $\text{H}_2\text{SO}_4$ ) and nitric acid ( $\text{HNO}_3$ ) mixture is widely used in nitration, sulfonation reactions. Aliphatic, heterocyclic and aromatic amines have been extensively investigated as corrosion inhibitors.<sup>4-8</sup> The corrosion behavior of stainless steel in mixed anhydrous  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  acid solution at the temperature from 50°C to 100°C was investigated in.<sup>9</sup> In this paper, the role of ethylamines in inhibiting the corrosion of zinc in ( $\text{HNO}_3 + \text{H}_2\text{SO}_4$ ) binary acid mixture is reported.

### EXPERIMENTAL

Rectangular specimens (5 x 2 x 0.1 cm) having an area of 0.2935 sq.dm of zinc were used for the determination of the corrosion rate. All the specimens were cleaned by buffing and wrapped in plastic till use. A specimen, suspended by a glass hook and was immersed in 230 ml in three different concentration test solution at 301 + 1 K for 24 h. After the test, the specimens were cleaned by using 10 %  $\text{CrO}_3$  solution having 0.2 %  $\text{BaCO}_3$ .<sup>10</sup> After cleaning, the specimens were washed with distilled water followed by acetone and dried with air dryer. Triplicate experiment were performed in each case and mean value of the corrosion loss was reported. To study the effect of temperature on corrosion loss of zinc the specimens were immersed in 230 ml

(0.05 N HNO<sub>3</sub> + 0.05 N H<sub>2</sub>SO<sub>4</sub>) mix acid at solution temperature of 303, 313, 323, and 333 K for an immersion period of 3 h with and without inhibitors and corrosion loss was reported.

For polarization study, metal specimen of circular design, having an area of 4.7 sq.dm. were exposed corrosive media. The volume of corrosive media was kept 500 ml. Auxiliary platinum electrode was placed in a corrosive media through which external current was supplied from a regulated power supply and Ag/AgCl reference electrode placed in saturated KCl solution remain s in contact with the corrosive solution (0.05 N HNO<sub>3</sub> + 0.05 N H<sub>2</sub>SO<sub>4</sub>) via salt bridge. The change in potential was measured by Potentiostat/Galvanostat (EG and G PARC model 273) against the reference electrode. I.E. has been calculated as follows :

$$\text{I.E. (\%)} = [(W_u - W_i) / W_u] \times 100 \quad \dots(1)$$

Where, W<sub>u</sub> is the weight loss of metal in uninhibited acid and

W<sub>i</sub> is the weight loss of metal in inhibited acid.

Energy of activation (E<sub>a</sub>) has been calculated from the slope of log ρ versus 1/T (ρ = corrosion rate, T = absolute temperature) and also with the help of the Arrhenius equation.<sup>11</sup>

$$\log (\rho_2 / \rho_1) = E_a / 2.303 R [(1/T_1) - (1/T_2)] \quad \dots(2)$$

Where P<sub>1</sub> and P<sub>2</sub> are the corrosion rate at temperature T<sub>1</sub> and T<sub>2</sub> respectively.

The values of heat of adsorption (Q<sub>ads</sub>) were calculated by the following equation<sup>11</sup>.

$$Q_{ads} = 2.303 R [\log (\theta_2 / 1 - \theta_2) - \log (\theta_1 / 1 - \theta_1)] \times [T_1 \cdot T_2 / T_2 - T_1] \quad \dots(3)$$

Where, θ<sub>1</sub> and θ<sub>2</sub> [θ = (W<sub>u</sub> - W<sub>i</sub>) / W<sub>i</sub>] are the fractions of the metal surface covered by the inhibitors at temperature T<sub>1</sub> and T<sub>2</sub> respectively. The values of the free energy of adsorption (ΔG<sub>a</sub>) were calculated with the help of the following equation.<sup>12</sup>

$$\log C = \log (\theta / 1 - \theta) - \log B \quad \dots(4)$$

Where, log B = -1.74 - (ΔG<sup>0</sup><sub>a</sub> / 2.303 RT) and C is the inhibitor concentration.

The enthalpy of adsorption (ΔH<sup>0</sup><sub>ads</sub>) and entropy of adsorption (ΔS<sup>0</sup><sub>ads</sub>) are calculated using the following equation (5) and (6).

$$\Delta H_{ads}^0 = E_a - RT \quad \dots(5)$$

$$\Delta S_{ads}^0 = [\Delta H_{ads}^0 - \Delta G_{ads}^0] / T \quad \dots(6)$$

## RESULTS AND DISCUSSION

The results are given in Tables 1 to 3. To assess the effect of corrosion of zinc in (HNO<sub>3</sub> + H<sub>2</sub>SO<sub>4</sub>) binary acid mixture, ethylamines are added.

### Corrosion in acid mixture

The rate of corrosion increases with the increase in mix acid concentration. The corrosion rate was 213.7, 975.2, and 1924.4 mg/dm<sup>2</sup> in mix acid concentration of (0.01 N HNO<sub>3</sub> + 0.01 N H<sub>2</sub>SO<sub>4</sub>), (0.05 N HNO<sub>3</sub> + 0.05 N H<sub>2</sub>SO<sub>4</sub>) and (0.1 N HNO<sub>3</sub> + 0.1 N H<sub>2</sub>SO<sub>4</sub>) in mix acid concentration respectively for a period of 24 h at 301 ± 1 K as shown in Table 1.

**Corrosion in presence of inhibitors:** To assess their protective value, ethylamines are added having 0.1, 0.5 and 1.0 % concentration in (0.01 N HNO<sub>3</sub> + 0.01 N H<sub>2</sub>SO<sub>4</sub>), (0.05 N HNO<sub>3</sub> + 0.05 N H<sub>2</sub>SO<sub>4</sub>) and (0.1 N HNO<sub>3</sub> + 0.1 N H<sub>2</sub>SO<sub>4</sub>) concentration (Table 1).

### Effect of inhibitor concentration

At constant acid concentration, the I.E. of the ethylamines increases with the inhibitor concentration, e.g. in case of ethanolamine in (0.01 N HNO<sub>3</sub> + 0.01 N H<sub>2</sub>SO<sub>4</sub>) the I.E. was found to be 65.1, 90.7 and 95.1 % with respect to 0.1, 0.5 and 1.0 % inhibitor concentration respectively (Table 1).

### Effect of acid concentration

At constant inhibitor concentration, the I.E. increases with the increase in acid concentration. At 1% inhibitor concentration, the I.E. of ethylamine is 95.1, 97.5 and 99.9 % with respect to 0.01, 0.05,

and 0.1 N (  $\text{HNO}_3 + \text{H}_2\text{SO}_4$  ) mix acid concentration respectively (Table 1). It is observed that ethylamine acts as a better inhibitor.

### Effect of temperature

To determine the effect of temperature on corrosion, corrosion rate was measured in ( 0.05 N  $\text{HNO}_3 + 0.05$  N  $\text{H}_2\text{SO}_4$  ) mix acid containing 0.1, 0.5 and 1.0 % inhibitor concentration at solution temperature of 303, 313, 323 and 333 K for an

immersion period of 3h. The result in Table -2 shows that as the temperature increases corrosion decreases while I.E. decreases. In acid containing inhibitors, the mean Ea values were found to be higher than that for uninhibited system (6.8 kJ/mol). Mean Ea values were 45.8, 43.0 and 39.8 kJ/mol for ethylamine, diethylamine and triethylamine respectively (Table 2). The higher value of mean Ea indicates physical adsorption of the inhibitors on metal surface.<sup>13</sup> The values of Ea calculated from

**Table 1: Corrosion rate (CR) and Inhibition efficiency (IE) of zinc in ( 0.01 N  $\text{HNO}_3 + 0.01$  N  $\text{H}_2\text{SO}_4$  ), ( 0.05 N  $\text{HNO}_3 + 0.05$  N  $\text{H}_2\text{SO}_4$  ) and ( 0.1 N  $\text{HNO}_3 + 0.1$  N  $\text{H}_2\text{SO}_4$  ) mix acid containing ethylamines as inhibitors for an immersion period of 24 h at  $301 \pm 1$  K**

System	Inhibitor Conc (in %)	Acid Concentration					
		0.01 N		0.05 N		0.1 N	
		CR mg/sq.dm	IE %	CR mg/sq.dm	IE %	CR mg/sq.dm	IE %
A	-	213.7	-	975.2	-	1921.4	-
B	0.1	74.5	65.1	239.1	75.5	110.5	94.3
	0.5	19.9	90.7	53.2	94.5	13.8	99.3
	1.0	10.4	95.1	24.9	97.5	1.5	99.9
C	0.1	91.4	57.7	291.4	70.1	202.7	89.5
	0.5	38.3	82.1	112.2	88.5	24.0	98.8
	1.0	25.1	88.1	62.2	93.6	8.2	99.6
D	0.1	123.9	42.1	334.2	65.7	360.3	81.3
	0.5	63.5	70.3	161.9	83.4	101.8	94.7
	1.0	42.9	80.2	101.8	89.6	38.4	98.0

A = ( $\text{HNO}_3 + \text{H}_2\text{SO}_4$ )

B = ( $\text{HNO}_3 + \text{H}_2\text{SO}_4$ ) + ethylamine

C = ( $\text{HNO}_3 + \text{H}_2\text{SO}_4$ ) + diethylamine

D = ( $\text{HNO}_3 + \text{H}_2\text{SO}_4$ ) + triethylamine

**Table 3: Polarization data and Inhibition efficiency (IE%) of ethylamines for zinc in ( 0.01 N  $\text{HNO}_3 + 0.01$  N  $\text{H}_2\text{SO}_4$  ) at  $301 \pm 1$  K with 1% inhibitor concentration**

System	$E_{\text{corr}}$ mV	$I_{\text{corr}}$ mA/sq.cm	Tafel Slope (mV/decade)			IE% from Methods	
			Anodic $\beta_a$	Cathodic $-\beta_c$	B mV	By polari- zation	Weight Loss
B	-665	0.0125	1643.0	1555.0	347.0	95.8	95.1
C	-647	0.0400	312.0	625.0	90.6	86.7	88.1
D	-683	0.0760	384.0	615.0	102.9	74.7	80.2

A = ( $\text{HNO}_3 + \text{H}_2\text{SO}_4$ )

C = ( $\text{HNO}_3 + \text{H}_2\text{SO}_4$ ) + diethylamine

B = ( $\text{HNO}_3 + \text{H}_2\text{SO}_4$ ) + ethylamine

D = ( $\text{HNO}_3 + \text{H}_2\text{SO}_4$ ) + triethylamine

the slope of Arrhenius plot and using eq.2 are almost similar.

From Table 2 it is evident that the values of  $Q_{ads}$  were found to be negative and lies in the range of  $-29.5$  to  $-43.6$  kJ/mol. The negative values show that the adsorption, and hence the inhibition efficiency, decreases with a rise in temperature<sup>14</sup>.

In all cases, mean  $\Delta G^{\circ}$  values are negative and lies in the range of  $-29.3$  to  $-26.4$  kJ/mol. This suggests that they are strongly adsorbed on the metal surface. The values enthalpy changes ( $\Delta H$ ) are positive (in the range of  $36.6$  to  $41.1$  kJ/mole) indicating the endothermic nature of the reaction<sup>15</sup> suggesting that higher temperature favours the corrosion process. The entropy ( $\Delta S$ ) are positive (in the range of  $0.21$  to  $0.24$  kJ/mole) confirming that the corrosion process is entropically favourable<sup>16</sup>.

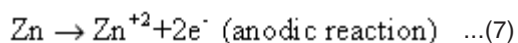
#### Polarization behaviour

Anodic and cathodic galvanostatic polarization curves for zinc in (0.01 N  $HNO_3$  + 0.01 N  $H_2SO_4$ ) mix acid alone and containing 1 % concentration of ethylamines shows both, the cathodes as well as anodes. I.E. calculated from corrosion current obtained by extrapolation of the cathodic and anodic Tafel lines are given in Table 3. In these cases, the efficiencies from Tafel plots agree well (within + 5 %) with the values obtained from weight loss data.

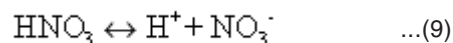
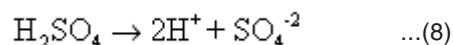
#### Mechanism of inhibition

Generally, zinc dissolves in ( $HNO_3$  +  $H_2SO_4$ ) acid mixture due to somewhat hydrogen type of attack.

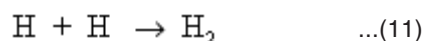
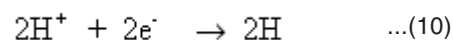
Zinc dissolves in ( $HNO_3$  +  $H_2SO_4$ ) mix acid by the following reaction.



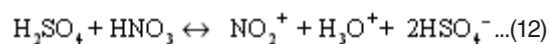
Both acids are strong acid and are therefore, completely or almost completely ionized and are undergoes dissolution with the formation of hydrogen ions are only positive ions<sup>17</sup>.



Reduction reaction is indicated by decrease in valence as shown by the following equation .



Sulphuric acid and nitric acid ionizes, the equation<sup>18</sup>,



+I effect is lowest in ethylamine and highest in triethylamine. As the +I effect increases the I.E. decreases because due to +I effect electron releasing power increases and so the corrosion increases. Number of ethyl group increases while I.p. of electron remain same in all these three inhibitors.

Triethylamine shows lowest inhibition. This is due to the fact of structural factor, the degree of chain branching appears to have opposite effect with respect to charge density.<sup>19</sup> The steric effect of branching chains on the adsorption of free amines increased with increasing degree of branching alkyl group, which result in a lowering of the anodic I.E.<sup>20</sup> Better inhibiting characteristics of diethylamine than triethylamine can be explained by steric hindrance in tertiary amine which may have influence on the electron density and on the base strength.<sup>21</sup>

As the number of alkyl group increases, the I.p. of electron will becomes more available due to +I effect of alkyl group and the basicity of the amine will increase on alkylation. When proton is added to N-atom, its increases crowding around N-atom. This crowding results in strain which becomes maximum in tertiary amines. Due to this, the stability of molecule is reduced, i.e., its basicity is reduced. This is borne out by the fact that as the

**Table 2 : Effect of temperature on Corrosion rate (CR), Inhibition efficiency (IE%) for zinc in ( 0.05 N HNO<sub>3</sub> + 0.05 N H<sub>2</sub>SO<sub>4</sub> ) mix acid containing ethylamines as an inhibitor**

System	Temperature (K)						Mean E <sub>a</sub> From kJ/mol eq. (2)	E <sub>a</sub> Arrhenius plot kJ/mol	Q <sub>ads</sub>	ΔG kJ/mol
	303		313		323					
	CR mg/dm <sup>2</sup>	IE %	CR mg/dm <sup>2</sup>	IE %	CR mg/dm <sup>2</sup>	IE %	CR mg/dm <sup>2</sup>	IE %		
A	700.5	-	783.2	-	832.0	-	895.2	-	-	-
B	2.3	99.7	4.03	99.5	7.2	99.1	11.9	98.7	45.8	47.4
C	3.1	99.5	5.1	99.3	8.5	98.9	14.2	98.4	43.0	42.4
D	9.5	98.6	15.6	98.0	25.1	96.9	39.4	95.6	39.8	39.1
									6.8	7.7
									-33.7	-43.6
									-38.2	-40.2
									-30.5	-35.9
									301-313	313-323
									313	323
									301-313	323-333

A = (HNO<sub>3</sub> + H<sub>2</sub>SO<sub>4</sub>) B = (HNO<sub>3</sub> + H<sub>2</sub>SO<sub>4</sub>) + ethylamine

C = (HNO<sub>3</sub> + H<sub>2</sub>SO<sub>4</sub>) + diethylamine

D = (HNO<sub>3</sub> + H<sub>2</sub>SO<sub>4</sub>) + triethylamine

Effective area of specimen : 0.2935 dm<sup>2</sup>

Immersion period : 3 h

Inhibitor concentration : 1%

size of the alkyl group increases, there by, increasing the steric repulsion<sup>22</sup>. The results are in agreement with the results obtained by J.D.Talati *et al.*<sup>23</sup> and V. Chandrasekaran *et al.*<sup>6</sup>

### CONCLUSIONS

The corrosion rate increases with the increases in mix acid concentration.

At constant acid concentration, the I.E. of the ethanolamines increases with the inhibitor concentration.

At constant inhibitor concentration, the I.E. increases with the increase of mix acid

concentrations.

Corrosion rate increases as the temperature increases and I.E. of inhibitors decreases with rise in the temperature.

The I.E. of inhibitors decreases in the order : ethylamine > diethylamine > triethylamine.

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