



## Ethanolamines as Corrosion Inhibitors for Zinc in (HNO<sub>3</sub> + H<sub>2</sub>SO<sub>4</sub>) Binary Acid Mixture

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**Abstract:** This work deals with the study of corrosion behaviour for zinc in (HNO<sub>3</sub> + H<sub>2</sub>SO<sub>4</sub>) binary acid mixture containing ethanolamines. Corrosion rate increases with concentration of acid and temperature. At constant acid concentration, the inhibition efficiency of ethanolamines increases with the inhibitor concentration. Value of  $\Delta G_a$  increases and inhibition decreases with temperature. The mode of inhibition action appears to be chemisorption.

**Keywords:** Corrosion, Zinc, Nitric and Sulphuric acid mixture, Ethanolamines.

### Introduction

Zinc is one of the most vital non-ferrous metal, having extensive use in metallic coating. Aliphatic amines, heterocyclic amines and aromatic amines have been extensively investigated as corrosion inhibitors<sup>1-10</sup>. In this paper, the role of ethanolamines in inhibiting the corrosion of zinc in (HNO<sub>3</sub> + H<sub>2</sub>SO<sub>4</sub>) binary acid mixture is reported.

### Experimental

Rectangular specimens (5 x 2 x 0.1 cm) of zinc were used for the determination of corrosion rate. All the specimens were cleaned by buffing and wrapped in plastic bag to avoid atmospheric corrosion. A specimen, suspended by a glass hook, was immersed in 230 mL of three different concentration test solution at 301 ± 1 K for 24 h. After the test, the specimens were cleaned by using 10% CrO<sub>3</sub> solution having<sup>11</sup> 0.2% BaCO<sub>3</sub>, washed with water, acetone and dried in air.

Effect of temperature on corrosion loss of zinc was studied by immersing in 230 mL (0.05 N HNO<sub>3</sub> + 0.05 N H<sub>2</sub>SO<sub>4</sub>) acid at solution temperatures 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 0.047 sq.dm. was used. The volume of corrosive media was kept 100 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 Potentiostt/Galvanostat (EG and G PARC model 273) against the reference electrode.

## 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, ethanolamines are added.

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

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.

**Table 1.** Corrosion rate (CR) and Inhibition efficiency (IE) of zinc 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>) mix acid containing ethanolamines as inhibitors for an immersion period of 24 h at 301 ± 1 K.

System	Inhibitor Conc., %	Acid Concentration					
		0.01 N		0.05 N		0.1 N	
		CR mg/dm <sup>2</sup>	IE %	CR mg/dm <sup>2</sup>	IE %	CR mg/dm <sup>2</sup>	IE %
A	-	213.7	-	975.2	-	1921.4	-
B	0.1	85.4	60.1	327.3	66.4	54.9	71.1
	0.5	16.8	92.2	33.3	96.6	14.4	99.3
	1.0	06.8	96.8	16.4	98.3	02.1	99.9
C	0.1	97.6	54.3	386.7	60.4	31.5	72.3
	0.5	37.7	82.4	131.1	86.6	11.6	94.2
	1.0	23.4	89.0	74.1	92.4	58.0	97.0
D	0.1	106.2	50.3	444.9	54.4	62.0	60.3
	0.5	45.8	78.6	177.6	81.8	01.5	84.3
	1.0	31.6	85.2	95.5	90.3	50.8	92.2

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>) + ethanolamine, C = (HNO<sub>3</sub> + H<sub>2</sub>SO<sub>4</sub>) + diethanolamine, D = (HNO<sub>3</sub> + H<sub>2</sub>SO<sub>4</sub>) + triethanolamine.

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>12</sup>.

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

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>12</sup>.

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

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>13</sup>.

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

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).

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

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

From Table 2 it is evident that the values of  $Q_{ads}$  were found to be negative and lies in the range of  $-19.2$  to  $-97.4$  kJ/mol. The negative values show that the adsorption, and hence the inhibition efficiency, decreases with a rise in temperature<sup>14</sup>.

**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 ethanolamines as an inhibitor.

System	Temperature, K								Mean $E_a$ From eq. (2) kJ/mol	$E_a$ from Arrhenius plot kJ/mol	$Q_{ads}$ kJ/mol			Mean $\Delta G$ kJ/mol
	303		313		323		333				301-313	313-323	323-333	
	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	-	6.8	7.7	-	-	-	-
B	1.3	99.8	5.1	99.4	9.9	98.8	18.4	98.0	55.7	56.7	-97.4	-51.3	-49.5	-29.6
C	3.4	99.5	5.7	99.3	10.2	98.8	17.2	98.1	45.3	46.4	-31.6	-44.3	-40.5	-28.9
D	9.3	98.7	13.2	98.3	20.1	97.6	30.9	96.5	33.9	41.0	-19.2	-30.8	-33.0	-26.8

Effective area of specimen: 0.2935 dm<sup>2</sup>, Immersion period: 3 h Inhibitor concentration: 1% 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>)+ethanolamine, C=(HNO<sub>3</sub>+H<sub>2</sub>SO<sub>4</sub>)+diethanolamine, D=(HNO<sub>3</sub> +H<sub>2</sub>SO<sub>4</sub>) + triethanolamine.

The values of mean  $\Delta G_a$  are given in Table 2. In all cases, mean  $\Delta G^0_a$  values are negative. The most efficient inhibitor shows more negative  $\Delta G^0_a$  value. This suggests that they are strongly adsorbed on the metal surface. Similar results also reported by the work of Talati *et al.*<sup>15</sup>. The values enthalpy changes ( $\Delta H$ ) are positive (in the range of 25.3 to 53.3 kJ/mole) indicating the endothermic nature of the reaction<sup>16</sup> suggesting that higher temperature favours the corrosion process. The entropy ( $\Delta S$ ) are positive (in the range of 0.17 to 0.28 kJ / mole) confirming that the corrosion process is entropically favourable<sup>17</sup>.

**Polarization behaviour**

Anodic and cathodic galvanostatic polarization curves show polarization of 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. Inhibition efficiencies from Tafel plots agree well (within  $\pm 5\%$ ) with the values obtained from weight loss data.

**Table 3.** Polarization data and Inhibition efficiency (IE%) of ethanolamines for zinc in (0.01 N HNO<sub>3</sub> + 0.01 N H<sub>2</sub>SO<sub>4</sub>) at  $301 \pm 1$  K with 1% inhibitor concentration.

System	$E_{corr}$ mV	$I_{corr}$ $\mu$ A/sq.cm	Tafel Slope (mV/decade)			IE, in % from methods	
			Anodic, $\beta_a$	Cathodic- $\beta_c$	B mV	By polari-zation	Weight Loss
A	-1140	0.300	466	200	60.9	-	-
B	-590	0.009	1639	10666	617.7	96.9	96.8
C	-610	0.030	1222	4761	422.9	90.1	89.0
D	-490	0.044	285	3846	155.6	85.3	85.2

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>) + ethanolamine, C = (HNO<sub>3</sub>+H<sub>2</sub>SO<sub>4</sub>) + iethanolamine, D = (HNO<sub>3</sub> + H<sub>2</sub>SO<sub>4</sub>) + triethanolamine.

*Mechanism*

Zinc dissolves in (HNO<sub>3</sub> + H<sub>2</sub>SO<sub>4</sub>) acid mixture. In (HNO<sub>3</sub> + H<sub>2</sub>SO<sub>4</sub>) mix acid, generally at all inhibitor concentration the order of I.E. of these three amines are; Ethanolamine > Diethanolamine > Triethanolamine.

Following points are important for mechanism of these compounds:

- (a) pka value decreases; (9.50) ethanolamine > (8.88) Diethanolamine > (7.77) Triethanolamine .I.E. increases with basicity.
- (b) All amines have a lone pairs (l.p.) of electrons. However, the readiness with which the l.p. of electrons is available for co-ordination with a proton determines the basic strength of amines. Lone pair are increases for ethanol amines are as follows; 3 (Ethanolamine) > 5 (Diethanolamine) > 7 (Triethanolamine), indicates that as l.p. increases I.E. decreases.
- (c) As the number of ethanol groups increase on the N-atom, it increases crowding around N-atom. This crowding result in strain which is less in ethanolamine and maximum in triethanolamine. Due to this, the stability of molecule is high in ethanolamine than triethanolamine and so basicity is also reduce. Because of this effect ethanolamine gives higher inhibition than di and triethanolamine in this acid mixture. The results are in agreement with the work of Vashi *et al.*<sup>18</sup> and Stupnisek *et al.*<sup>19</sup>.
- (d) The better inhibiting characteristic of secondary amine than tertiary amine can be explained by steric hindrance in tertiary amines which may have influence as the electron density and on the base strength. The electron withdrawing ability of hydroxyl group in alkenol compounds and their overcrowding on the N-atom found to influence the extent of adsorption in the case of *di* and triethanolamine on the mercury surface<sup>20</sup>.

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