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Corrosion inhibition effect of ethylamines on zinc in (HNO_3+H_3PO_4) binary acid mixture

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Abstract

The inhibition effect of ethylamines on zinc in (HNO_3+H_3PO_4) binary acid mixture has been studied by weight loss and polarization techniques. Corrosion rate increases with concentration of mix acid. The inhibition efficiency of ethylamines increases with the inhibitor concentration. The adsorption of inhibitor on zinc surface has been found to obey Langmuir adsorption isotherm. The values of activation energy (Ea), free energy of activation (ΔGa), Heat of adsorption (ΔQa), enthalpy of adsorption (ΔH) and entropy of adsorption (ΔS) were calculated. Corrosion rate increases and inhibition decreases with rise in temperature. Potentiostatic polarization results revealed that ethylamines act as mixed typed inhibitors.

Key Words: Corrosion, Zinc, Nitric and Phosphoric acid mixture, Ethylamines.

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 [1-9]. In this paper, the role of ethylamines in inhibiting the corrosion of zinc in (HNO_3 + H_3PO_4) binary acid mixture is reported.

RESULTS AND DISCUSSION

The results are given in Tables 1 to 3 and Figs. 1 to 4. To assess the effect of corrosion of zinc in (HNO_3 + H_3PO_4) binary acid mixture, ethylamines are added.

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

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 (p = corrosion rate, T = absolute temperature) (Fig.4) and also with the help of the Arrhenius equation [10].

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

Where P_1 and P_2 are the corrosion rate at temperature T_1 and T_2 respectively.

The values of heat of adsorption (Qa) were calculated by the following equation [10].

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

Where , θ_1 and θ_2 [$\theta = (Wu - Wi) / Wi$] 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 [11].

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

Where, $\log B = -1.74 - (\Delta G^0 a / 2.303 RT)$ and C is the inhibitor concentration.

The enthalpy of adsorption (ΔH^0_a) and entropy of adsorption (ΔS^0_a) are calculated using the following equation [12].

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

$$\Delta S^0_a = [\Delta H^0_a - \Delta G^0_a] / T \quad \text{-----(6)}$$

From Table-2 it is evident that the values of Q_a were found to be negative and lies in the range of –24.7 to –14.0 kJ/mol. Oguzje [13] explained that the degree of surface coverage decreased with rise in temperature. The higher negative values of heat of adsorption also show that the inhibition efficiency decreased with a rise in temperature [14].

From Table-2 the negative mean ΔGa values ranging from -29.63 to -27.19 kJ / mole indicate that the adsorption of the inhibitors are spontaneous. The most efficient inhibitor shows more negative $\Delta G^0 a$ value. This suggests that they are strongly adsorbed on the metal surface. The values of enthalpy changes (ΔH) were positive (in the range of 20.52 to 26.21 kJ/mole) indicating the endothermic nature of the reaction [15] suggesting that higher temperature favours the corrosion process. Adeyen [16] described that if the heat of adsorption. ΔH < 10 kJ / mole the adsorption is probably physisorption and if ΔH > 10 kJ/ mole values indicates that the ethylamines strongly adsorbed on zinc is chemisorption. The entropy (ΔS) are positive (in the range of 0.14 to 0.18 kJ / mole) confirming that the corrosion process is entropically favourable [17]

The mode of inhibition action appears to be the chemisorption because the plot of log (θ/1-θ) versus log C obtained straight line (Fig.1) suggest that the inhibitors cover both anodic and cathodic regions through general adsorption following Langmuir isotherm.

Polarization behavior

Anodic and cathodic galvenostatic polarization curves (Fig.2 and Fig. 3) show little anodic but significant cathodic polarization. as well as anodes. I.E. calculated from corrosion current obtained by extrapolation of the cathodic and anodic Tafel lines were given in Table- 3. The inhibition efficiency obtained from weight loss and polarization measurement showed fairly good agreement.

Mechanism

The mechanism of inhibition of corrosion is generally believed to be due to the formation and maintenance of a protective film on the metal surface. Zinc dissolves in (HNO_3 + H_3PO_4) acid mixture. In (HNO_3 + H_3PO_4) mix acid, generally at all inhibitor concentration the order of I.E. of these three amines are; Ethylamine > Diethylamine > Triethylamine. The following points explain the mechanism of inhibition.

(1) As the number of alkyl groups increase on the N-atom, it increases crowding around N-atom. This crowding result in strain which is less in ethylamine and maximum in triethylamine. Due to this, the stability of molecule is high in ethylamine than triethylamine and so basicity is also reduce. Because of this effect ethylamine gives higher inhibition than di and triethylamine in this acid mixture. The results are in agreement with the work of Vashi et al.[18] and Stupnisek et al.[19] .

(2) Triethylamine shows the lowest inhibition. This is due to the structure, as the degree of chain branching appears to have the opposite effect with respect to charge density. The number of the functional groups is assumed [20] to reduce the protective properties owing to steric hindrance but the protection could be improved by functional groups acting as adsorption centres.

MATERIAL AND METHODS

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 $\pm$ 1 K for 24 h. After the test, the specimens were cleaned by using 10 % CrO_3 solution having 0.2 % $BaCO_3$ [21] 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_3 + 0.05 N H_3PO_4) 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 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_3 + 0.05 N H_3PO_4) via salt bridge. The change in potential was measured by Potentiostst/Galvanostat (EG and G PARC model 273) against the reference electrode.

Table 1. Corrosion rate (CR) and Inhibition efficiency (IE) of zinc in various concentrations of mix acid containing ethylamines as inhibitors for an immersion period of 24 h at 301 $\pm$ 1 K

System	Inhibitor Conc. (%)	Acid Concentration					
		0.01 N		0.05 N		0.1 N	
		CR mg/dm^2	IE %	CR mg/dm^2	IE %	CR mg/dm^2	IE %
A	-	146.5	-	774.1	-	1417.0	-
B	0.1	50.8	65.3	233.7	69.8	357.1	74.8
	0.5	13.8	90.6	47.1	93.1	29.6	97.9
	1.0	07.9	94.6	32.4	95.8	13.0	99.1
C	0.1	51.2	65.0	232.5	69.9	343.5	75.8
	0.5	14.1	90.4	60.8	92.2	29.9	97.9
	1.0	10.1	93.2	39.2	94.9	14.0	99.0
D	0.1	58.8	60.1	285.1	63.2	410.8	71.0
	0.5	24.4	83.3	96.9	87.5	83.3	94.1
	1.0	14.6	90.1	60.8	92.2	25.9	98.2

A = (HNO_3 + H_3PO_4) *C = (HNO_3 + H_3PO_4) + diethylamine*
B = (HNO_3 + H_3PO_4) + ethylamine *D = (HNO_3 + H_3PO_4) + triethylamine*

Table- 2. Effect of temperature on Corrosion rate (CR), Inhibition efficiency (IE %) for zinc in (0.05 N HNO_3 + 0.05 N H_3PO_4) mix acid containing ethyalamines as an inhibitor

Effective area of specimen : 0.2935 dm^2 Immersion period : 3 h Inhibitor concentration : 1%

System	Temperature (K)								Mean E_a From eq. (2) kJ/mol	E_a from Arrhenius plot kJ/mol	Q_{ads} kJ/mol			Mean ΔG kJ/mol
	303		313		323		333				303-313	313-323	323-333	
	CR mg/ dm^2	IE %	CR mg/ dm^2	IE %	CR mg/ dm^2	IE %	CR mg/ dm^2	IE %						
A	436.1	-	494.0	-	552.3	-	593.3	-	8.5	9.5	-	-	-	-
B	15.1	96.5	21.7	95.6	31.4	94.3	41.0	93.1	27.9	27.9	-19.6	-22.9	-18.7	-24.5
C	17.4	96.0	26.1	94.7	34.2	93.8	47.5	92.0	28.1	27.9	-14.0	-24.7	-23.9	-24.1
D	24.7	94.7	33.1	93.3	46.5	91.6	63.3	89.3	26.4	25.5	-20.9	-23.3	-17.2	-23.3

A = (HNO_3 + H_3PO_4) *C = (HNO_3 + H_3PO_4) + diethyalamine*
B = (HNO_3 + H_3PO_4) + ethyalamine *D = (HNO_3 + H_3PO_4) + triethyalamine*

Table 3. Polarization data and Inhibition efficiency (IE%) of ethyalamines for zinc in (0.01 N HNO_3 + 0.01 H_3PO_4) at 301 $\pm$ 1 K with 1% inhibitor concentration

System	E_{corr} mV	I_{corr} μA/sq.cm	Tafel Slope (mV/decade)			IE(in %) from methods	
			Anodic β_a	Cathodic $-\beta_c$	B mV	By polarization	Weight Loss
A	-935	0.180	400	562	101.6	-	-
B	-210	0.016	757	1190	201.1	91.1	94.6
C	-225	0.018	657	1000	172.4	90.0	93.2
D	-260	0.018	600	800	149.1	90.0	90.1

A = (HNO_3 + H_3PO_4) *C = (HNO_3 + H_3PO_4) + diethylamine*
B = (HNO_3 + H_3PO_4) + ethylamine *D = (HNO_3 + H_3PO_4) + triethyalamine*

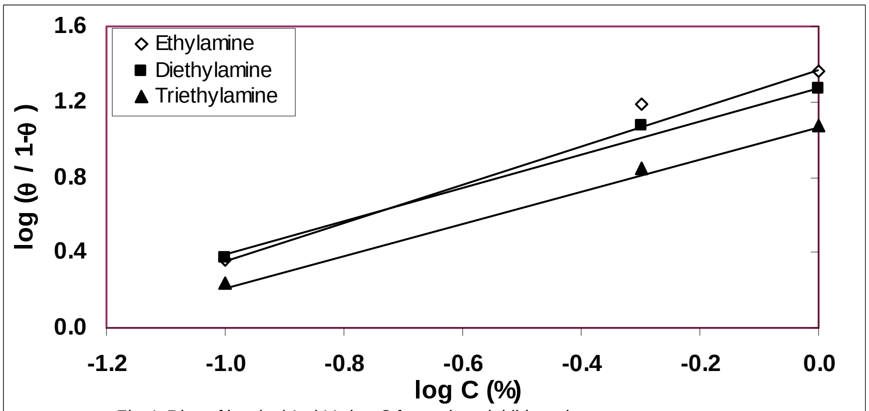

Fig :1: Plot of log (θ / 1-θ) Vs log C for verious inhibitors in (0.05 N HNO_3+0.05 N H_3PO_4) mix acid concentration.

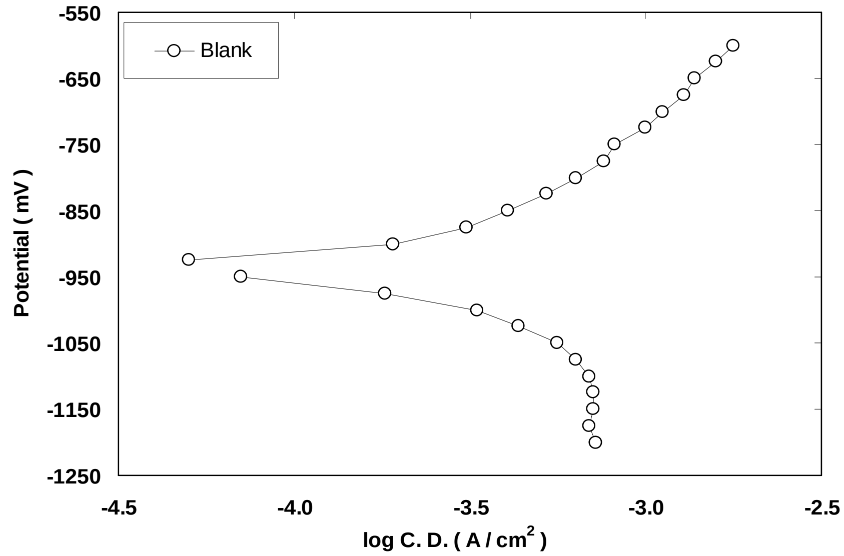

Fig : 2 : Polarisation curves for corrosion of zinc in (0.01 N HNO_3 +0.01 N H_3PO_4) mix acid

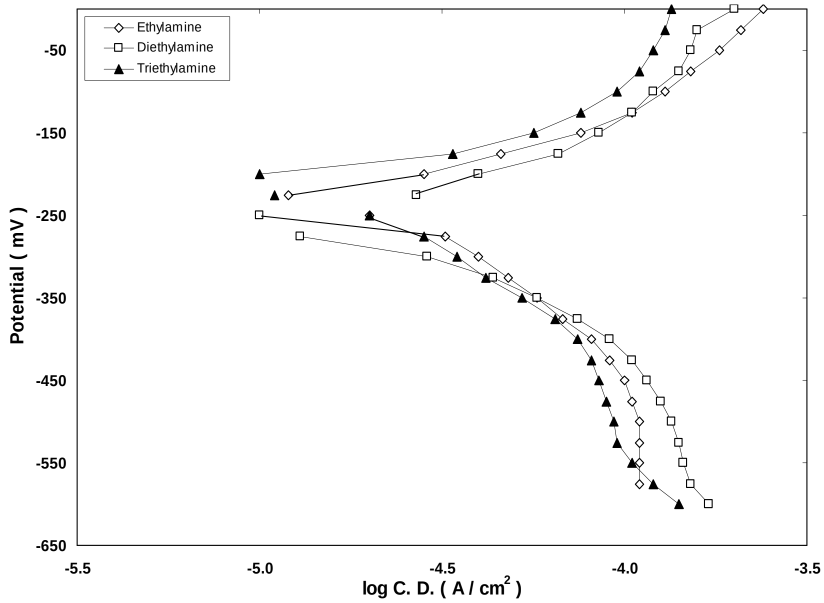

Fig : 3 : Polarisation curves for corrosion of zinc in (0.01 N HNO_3 +0.01 N H_3PO_4) mix acid containing 1.0 % inhibitor ethylamine, diethylamine and triethylamine.

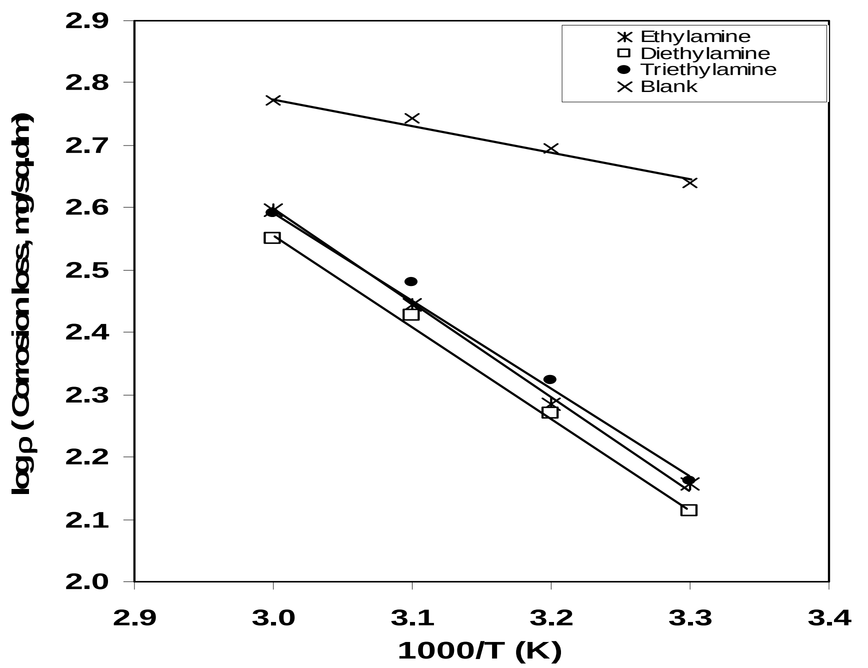

Fig : 4 : Arrhenius plots for corrosion of zinc in (0.05 N HNO_3 + 0.05 N H_3PO_4) mix acid in presence of 0.1 % inhibitor concentration.

CONCLUSION

As the concentration of acid mixture increases corrosion rate increases. Concentration of inhibitors increases I.E increases. As the temperature increases corrosion rate increases while I.E. decreases. Among ethyalamines, ethyalamine show better inhibition.

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