Available online at www.derpharmachemica.com

Scholars Research Library

Der Pharma Chemica, 2010, 2(4): 51-56
(http://derpharmachemica.com/archive.html)

ISSN 0975-413X

Ethanolamines as corrosion inhibitors for zinc in (HNO_3 + HCl) binary acid mixture

R. T. Vashi* and H. M. Bhajiwala

Department of Chemistry, Navyug Science College, Surat, Gujarat, India

---

Abstract

The inhibition effect of ethanolamines on zinc in (HNO_3 + HCl) binary acid mixture has been studied by weight loss method and polarization techniques. Corrosion rate increases with the concentration of acid mixture. The inhibition efficiency (I.E.) of ethanolamines increases with the concentration of inhibitors. Corrosion rate increases while I.E. decreases with increase in temperature. The values of activation energy (Ea), free energy of activation (ΔGa) , Heat of adsorption (Qa), enthalpy of adsorption (ΔH) and entropy of adsorption (ΔS) were calculated. Potentiostatic polarization results revealed that ethanolamines act as mixed typed inhibitors.

Key words: Corrosion, zinc, nitric and hydrochloric 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 [1-7]. In this paper, the role of ethanolamines in inhibiting the corrosion of zinc in (HNO_3 + HCl) binary acid mixture has been reported.

MATERIALS 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 % $BaCO_3$ [18] washed with water, acetone and dried in air.

To study the Effect of temperature on corrosion rate, zinc plates were immersed in 230 ml (0.05 N HNO_3 + 0.05 N HCl) mix acid at solution temperatures of 303, 313, 323, and 333 K for an immersion period of 3 h with and without inhibitors. 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 remains in contact with the corrosive solution (0.05 N HNO_3 + 0.05 N HCl) via salt bridge. The change in potential was measured by Potentiostst / Galvanostat (EG and G PARC model 273) against the reference electrode.

RESULTS AND DISCUSSION

The results are given in Tables 1 to 3 and figs. 1 to 2. To assess the effect of corrosion of zinc in (HNO_3 + HCl) binary acid mixture, ethanolamines were added. I.E. was calculated by the following formula.

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

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 (p = corrosion rate, T = absolute temperature) and also with the help of the Arrhenius equation [8].

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

Where p_1 and p_2 are the corrosion rate at temperature T_1 and T_2 respectively.

The values of heat of adsorption (Qads) were calculated by the following equation [8].

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

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 [9].

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

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

The enthalpy of adsorption (ΔH^0_{ads}) and entropy of adsorption (ΔS^0_{ads}) are calculated using the following equation [10].

$$\Delta H^0_{ads} = E_a - RT \qquad \text{-----(5)}$$

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

Table 1. Corrosion rate (CR) and Inhibition efficiency (IE) of zinc in (0.01 N HNO_3 + 0.01 N HCl), (0.05 N HNO_3 + 0.05 N HCl) and (0.1 N HNO_3 + 0.1 N HCl) 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^2	IE %	CR mg/dm^2	IE %	CR mg/dm^2	IE %
A	-	176.5	-	1011.8	-	2112.8	-
B	0.1	61.2	65.1	509.9	69.9	547.2	74.1
	0.5	10.3	94.2	43.0	95.7	26.0	98.8
	1.0	04.4	97.5	16.1	98.4	06.1	99.7
C	0.1	72.1	59.2	397.9	60.7	563.3	73.3
	0.5	31.5	82.2	103.5	89.7	170.9	91.9
	1.0	16.3	90.7	69.4	93.1	60.8	97.1
D	0.1	86.1	51.2	372.9	63.1	576.6	72.7
	0.5	46.1	73.8	200.8	80.2	234.1	88.9
	1.0	33.2	81.2	169.7	83.2	128.0	93.9

A=(HNO_3+HCl), B=(HNO_3+HCl)+ethanolamine, C=(HNO_3+HCl)+diethanolamine, D=(HNO_3+HCl)+ triethanolamine

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

Effective area of specimen: 0.2935 dm^{2,} Immersion period: 3h, 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	703.1	-	774.4	-	836.8	-	931.4	-	7.9	7.7	-	-	-	-
B	9.2	98.7	14.3	98.2	20.3	97.6	31.0	96.7	33.9	34.5	-27.7	-23.4	-29.0	-26.8
C	24.2	96.6	37.1	95.2	52.8	93.7	80.4	91.4	33.6	33.5	-27.0	-24.5	-30.4	-24.2
D	38.7	94.5	61.3	92.1	97.5	88.4	128.4	86.2	33.3	33.5	-30.7	-35.9	-17.2	-22.7

A=(HNO_3+HCl), B=(HNO_3+HCl)+ethanolamine, C=(HNO_3+HCl)+diethanolamine, D=(HNO_3+HCl)+ triethanolamine

Table 3. Polarization data and Inhibition efficiency (IE %) of ethanolamines for zinc in (0.01 N HNO_3 + 0.01 N HCl) 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	-882	0.210	545	1600	176.8	-	-
B	-705	0.012	1086	1466	271.2	94.3	97.5
C	-700	0.015	666	1619	205.2	92.9	90.7
D	-737	0.030	800	1180	207.3	85.7	81.2

A=(HNO_3+HCl), B=(HNO_3+HCl)+ethanolamine, C=(HNO_3+HCl)+diethanolamine, D=(HNO_3+HCl)+ triethanolamine

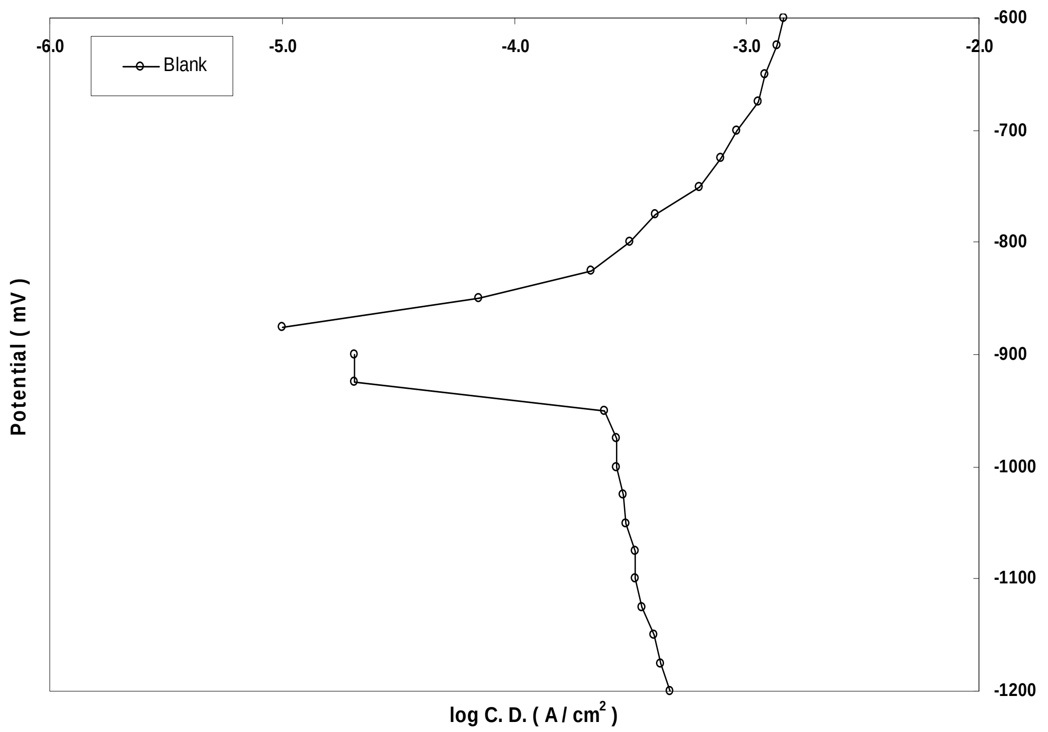

Fig : 1 : Polarisation curves for corrosion of zinc in (0.01 N HNO_3 +0.01 N HCl) mix acid

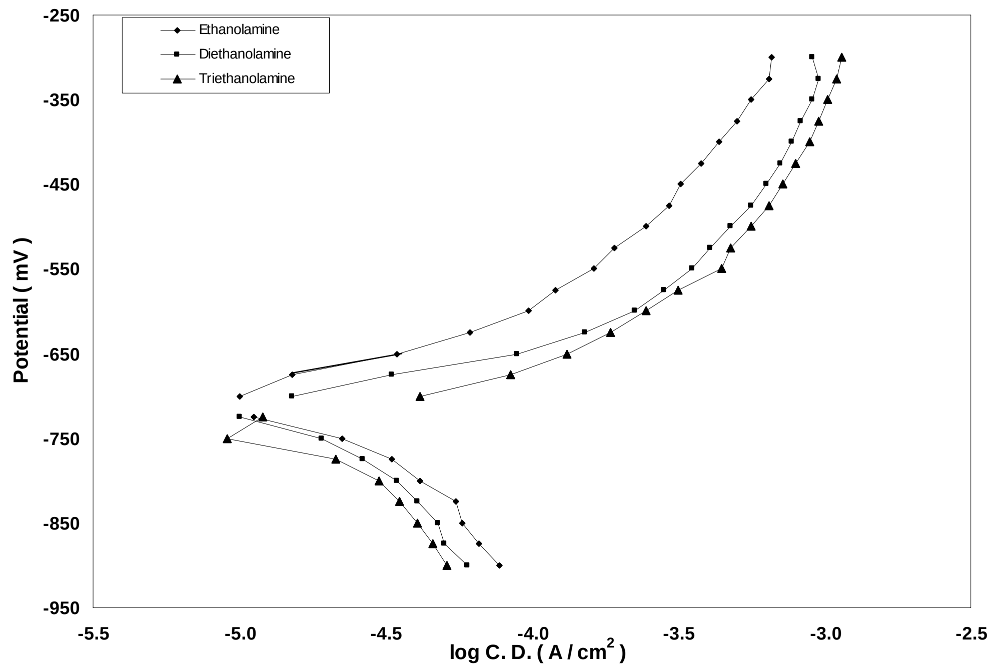

Fig : 2 : Polarisation curves for corrosion of zinc in (0.01 N HNO_3 +0.01 N HCl) mix acid containing 1.0 % inhibitor ethanolamine, diethanolamine and triethanolamine

From Table-2 it is evident that the values of Q_{ads} were found to be negative and lies in the range of –35.9 to –17.2 kJ/mol. Oguzje [11] 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.

From Table-2 the negative mean ΔGa values ranging from -26.8 to -22.7 kJ / mole indicate that the adsorption of the inhibitors are spontaneous. The most efficient inhibitor shows more negative ΔG^0a value. This suggests that they are strongly adsorbed on the metal surface. The values of enthalpy changes (ΔH) were positive (in the range of 31.10 to 33.76 kJ/mole) indicating the endothermic nature of the reaction [12] suggesting that higher temperature favors the corrosion process. Adeyen [13] described that if the heat of adsorption. H < 10 kJ / mole the adsorption is probably physisorption and if H > 10 kJ/ mole values indicates that the ethanolamines strongly adsorbed on zinc is chemisorptions. The entropy (ΔS) are positive (in the range of 0.18 to 019 kJ / mole) confirming that the corrosion process is entropic ally favorable [14].

Polarization behaviour: Anodic and cathodic galvenostatic polarization curve without inhibitor shown in fig -1 and with inhibitors shown in fig - 2 indicates polarization of both anodes and cathodes. I.E. calculated from corrosion current obtained by extrapolation of the cathodic and anodic Tafel lines are given in Table 3. The I.E. obtained from weight loss and polarization measurement were in 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 +

HCl) acid mixture. In (HNO_3 + HCl) mix acid, generally at all inhibitor concentration the order of I.E. of these three amines are; Ethanolamine > Diethanolamine > Triethanolamine.

As the number of ethanol group's 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 reducing. 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. [15] and Stupnisek et al. [16].

Triethanolamine 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 [17] to reduce the protective properties owing to steric hindrance but the protection could be improved by functional groups acting as adsorption centers.

CONCLUSION

1. Corrosion rate increases with the concentration of binary acid mixture.
2. Corrosion rate increases while I.E. decreases with rise in temperature.
3. Among ethanolamines, ethanolamine was found to be better inhibitor.

Acknowledgement

The authors are thankful to Department of Chemistry, Navyug Science College, and Surat for providing laboratory facilities.

REFERENCES

[1] V. Chandrasekaran , K. Kannan and M. Natesan , *Asian J. Chem.*,**2005**, 17, 1921- 1934.
[2] V.K.V. Unni and J.C. Ramachar , *J. Electrochem. Soc.*, Japan, **1965**, 33, 557.
[3] M. N. Desai and J. S. Joshi , *J Indian Chem Soc.*, **1975**, 9, 878.
[4] J. D. Talati and J. M. Pandya , *Corros. Sci.*, **1976**, 16(9)**,** 609.
[5] R. T. Vashi , S. A. Desai and P. S. Desai, *Asian J Chem.*, **2008**, 20 (6), 4553-4560.
[6] R. T. Vashi , S. A. Desai and P. S. Desai , *Asian J Chem.*, **2008**, 3 (1), 97-104.
[7] R. T. Vashi , H. M. Bhajiwala and S. A. Desai , *Oriental J Chem.*,**2009**, 25(3), 555-560.
[8] N. Subramanian and K. Ramakrishnaiah , *Ind. J Tech.*, **1970**, 8 ,369.
[9] A. M. S. Abdel and A. E. L. Saied , *Trans SAEST,* **1981**, 16, 197.
[10] V. Chandrasekaran , K. Kannan and M. Natesan ., *J. Metallur. Mater. Sci.* , **20 (6) ,** 4 6 , 253.
[11] E. E. Oguzie, *Mater. Chem. Phys.*, **2004**, 87, 212.
[12] A. K. Agrawal, D. Singhal, S. Chadha and A. Gulati , *Tran. SAEST*, **2003**, 38, 111.
[13] O. O. Adeyen , *Bull.Electrochem.*, **2005**, 21, 363.
[14] R. M. Issa, A. Z. El-Sonbati , A. A. El-Bindary and H. M. Kera , *Eu. Poly J.*, **2002**, 38, 561.
[15] R. T. Vashi and S. A. Desai, *Bull Electrochem.*, **2004**, 20, 187-192.
[16] E. L. Stupnisek, D. Kopper and A. D. Mance, *Bull Electrochem.*, **1998**, 14(1)**,** 10-15.
[17] A. Popova , E. Sorolova and V. V. Raicheva., *Khimia I Industria.*, **1987,** 2 **,** 72.
[18] E.J. Stroud , J *Appl.Chem.* , **1951**,1,93.