

Ethylamines as Corrosion Inhibitors for Zinc in Nitric Acid

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The corrosion of zinc in nitric acid containing ethylamines has been studied. In plain nitric acid, the corrosion rate increases with the acid concentration and temperature. At constant acid concentration, the inhibition efficiency of ethylamines increase with the inhibitor concentration. Similarly, at constant inhibitor concentration, the inhibition efficiency increases with the increase in concentration of acid. At 40 mM inhibitor concentration in 0.01 M HNO₃ at 301 ± 1 K for 24 h immersion period, the inhibition efficiency of inhibitors decreases in the order: ethylamine (92 %) > diethylamine (91 %) > triethylamine (82 %). As temperature increases, the value of ΔG_a increase while percentage of inhibition decrease. Plot of log (θ/1-θ) vs. log C results in a straight line suggest that the inhibitors cover both anodic and cathodic regions through general adsorption following Langmuir isotherm. Anodic and cathodic galvanostatic polarization curves show little anodic but significant cathodic polarization.

Key Words: Corrosion, Zinc, Nitric acid, Ethylamines.

INTRODUCTION

The problem of corrosion is of considerable importance, due to increasingly use of metals and alloys in the modern life day-by-day. Zinc is one of the most important non-ferrous metals which find extensive use in metallic coating. Zinc, like aluminium, is amphoteric in its behaviour towards acidic and alkalies¹. Aromatic, aliphatic and heterocyclic amines have been extensively investigated as corrosion inhibitors²⁻⁴. According to Hackerman *et al.*^{5,6} 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.

In the present work, the corrosion of zinc by nitric acid containing ethylamine [C₂H₅NH₂], diethylamine [(C₂H₅)₂NH] and triethylamine [(C₂H₅)₃N] has been reported.

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EXPERIMENTAL

The chemical composition of test specimen was found to be Zn = 98.50 %, Pb = 0.02 %, Cd = 0.02 % and Fe = 0.01 %. Rectangular specimens (5.0 cm × 2.0 cm × 0.1 cm) of zinc with small hole of 0.75 cm diameter near the one end having an area of 0.2116 dm² were used for determination of corrosion rate. All the specimens were cleaned by buffing and wrapped in plastic bag to avoid atmospheric corrosion before used.

To study the corrosion of zinc in nitric acid, weight loss method, temperature effect, potential as well as polarization measurements have been used.

The specimens having an area of 0.2116 dm² were immersed in 0.01, 0.02 and 0.03 M acid concentration with and without inhibitor containing 230 mL test solution at 301 ± 1 K for 24 h. After the test, specimens were cleaned by 10 % chromic acid solution having 0.2 % BaCO₃ for a period of about 2 min⁷. 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 values of weight loss were reported in form of corrosion rate as shown in Table-1. All chemicals used were of AR grade. The test solutions were prepared in double distilled water.

To study the effect of temperature on corrosion of zinc in 0.03 M HNO₃, the specimens were immersed in 230 mL of corrosive solution and corrosion rate was determined at solution temperature of 303, 313, 323 and 333 K for an immersion period of 2 h with and without inhibitors. From these data inhibition efficiency (I.E.), energy of activation (E_a), heat of adsorption (Q_{ads}), free energy of adsorption (ΔG^o_a), change of enthalpy (ΔH^o_a) and entropy of adsorption (ΔS^o_a) were calculated in Table-2.

A zinc specimen having an area of 0.0675 dm² was immersed in 0.01 M HNO₃ with and without 40 mM inhibitors concentration in 100 mL test solutions and potential (mV) were measured against saturated calomel electrode as a reference electrode for every 5 min till the constant value of potential was attained.

For polarization study, metal specimens having an area of 0.0247 dm² were exposed in 500 mL corrosive solution with and without 40 mM inhibitor concentration in 0.01 M HNO₃. 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) was used as a reference electrode. Two counter electrodes were used to supply the current flowing at the working electrode during the test. The polarization study was made using galvanostate/potentiostate meter [EG and GPARC model 273]. Graphs were plotted between potential and log current density (called Tafel plots). Cathodic and anodic polarization curves give cathodic and

anodic Tafel lines correspondingly. The intersect point of cathodic and anodic Tafel lines gives the corrosion current (I_{corr}) and the potential⁸.

Inhibition efficiency (I.E.) has been calculated as follows:

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

where, W_u = weight loss of metal in uninhibited acid and W_i = weight loss of metal in inhibited acid.

Energy of activation (E_a) has been calculated from the slope of $\log p$ vs. $1/T$ (p = corrosion rate, T = absolute temperature) and also with the help of the Arrhenius equation⁹.

$$\log p_2/p_1 = E_a/2.303 R[(1/T_1) - (1/T_2)] \quad (2)$$

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

The value of heat of adsorption (Q_{ads}) was calculated by the following equation⁹.

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

where, θ_1 and θ_2 [$\theta = (W_u - W_i)/W_i$] 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 (ΔG_a°) were calculated with the help of the following equation¹⁰.

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

where, $\log B = -1.74 - (\Delta G_a^\circ/2.303 RT)$ and C is the inhibitor concentration.

The enthalpy of adsorption ($\Delta H_{\text{ads}}^\circ$) and entropy of adsorption ($\Delta S_{\text{ads}}^\circ$) are calculated using the following eqns. 5 and 6.

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

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

RESULTS AND DISCUSSION

The results are given in Tables 1-3. To assess the effect of corrosion of zinc in nitric acid, ethylamines are added as inhibitors.

Corrosion by plain acid: The rate of corrosion increases with the increase in acid concentration. The corrosion rate was 250.7, 515.1 and 699.5 mg/dm² in 0.01, 0.02 and 0.03 M HNO₃ concentrations, respectively for a period of 24 h at 301 ± 1 K as shown in Table-1.

Effect of specific conductivity: It was found that specific conductivity was 2.9×10^{-3} , 5.8×10^{-3} and 9.5×10^{-3} ms/cm for 0.01, 0.02 and 0.03 M acid concentration, respectively. This suggests that specific conductivity increases with increase of acid concentration. The addition of inhibitors decrease the specific conductivity for ethylamine, diethylamine and triethylamine are 1.14×10^{-3} , 0.88×10^{-3} and 1.01×10^{-3} ms/cm, respectively at 40 mM inhibitor concentration in 0.01 M acid concentration.

TABLE-1
CORROSION RATE (CR) AND INHIBITION EFFICIENCY (I.E.) OF
ZINC IN 0.01, 0.02 AND 0.03 M HNO₃ CONTAINING INHIBITORS
Immersion period: 2 h

System	Inhibitor conc. (mM)	Acid concentration					
		0.01 M		0.02 M		0.03 M	
		System	I.E. (%)	CR (mg/dm ²)	I.E. (%)	CR (mg/dm ²)	I.E. (%)
A	-	250.7	-	515.1	-	699.5	-
B	10	147.2	41	255.8	50	287.7	59
	20	115.3	54	201.5	61	207.9	70
	30	72.9	71	125.3	76	79.4	89
	40	19.1	92	24.3	95	22.5	97
C	10	161.5	36	283.3	45	354.3	49
	20	127.3	49	245.5	52	262.6	63
	30	86.5	66	171.9	67	216.5	69
	40	23.9	91	36.5	93	37.8	95
D	10	171.3	32	311.9	40	403.1	42
	20	136.4	46	257.7	50	277.1	60
	30	96.6	62	181.4	65	207.9	70
	40	45.8	82	60.0	88	63.8	91

A = HNO₃; B = HNO₃ + ethylamine, C = HNO₃ + diethylamine, D = HNO₃ + triethylamine.

Effect of inhibitor concentration: At constant acid concentration, the I.E. of the ethylamines increases with the inhibitor concentration, *e.g.* in the case of ethylamine for 0.03 M HNO₃ the I.E. was found to be 58.9, 70.3, 88.7 and 96.8 % with respect to 10, 20, 30 and 40 mM inhibitor concentration respectively (Table-1).

Effect of acid concentration: At constant inhibitor concentration, the I.E. increases with the increase in acid concentration. At 40 mM inhibitor concentration, the I.E. of ethylamine is 92, 95 and 96 % with respect to 0.01, 0.02 and 0.03 M acid concentration, respectively (Table-1). At 40 mM inhibitor concentration in 0.03 M acid, the efficiency of inhibitors decreases in order: ethylamine (97 %) > diethylamine (95 %) > triethylamine (91 %). It is observed that ethylamine acts as efficient inhibitor.

Effect of temperature: To determine the effect of temperature on corrosion, corrosion rate was measured in 0.03 M HNO₃ containing 10, 20, 30 and 40 mM inhibitor concentration at solution temperature of 303, 313, 323 and 333 K for an immersion period of 2 h. As the temperature increases, corrosion rate increases (Table-2). shows that corrosion rate increases. This may be due to the desorption of the adsorbed molecules-inhibitor and/or aggressive at higher temperature and thus exposing the

TABLE-2
EFFECT OF TEMPERATURE ON CORROSION RATE (CR), INHIBITION EFFICIENCY (I.E.) FOR
ZINC IN 0.03 M HNO₃ CONTAINING 40 mM ETHYLAMINES AS INHIBITORS

Effective area of specimen: 0.2116 dm²; Acid concentration: 0.03 M; Immersion period: 2 h; Inhibitor concentration: 40 mM

System	Temperature (K)						Mean E _a from eqn. 2 (kJ/mol)	E _a from Arrhenius plot (kJ/mol)	Q _{ads} (kJ/mol)		Mean (kJ/mol)					
	303		323		333				301- 313	313- 323	323- 333	ΔG _a	ΔH _a	ΔS _a		
	CR (mg/dm ²)	I.E. (%)	CR (mg/dm ²)	I.E. (%)	CR (mg/dm ²)	I.E. (%)			CR (mg/dm ²)	I.E. (%)	ΔG _a	ΔH _a	ΔS _a			
A	270.5	-	327.8	-	377.2	-	483.8	-	16.4	17.0	-	-	-	-	-	-
B	26.0	90	38.7	88	60.2	84	87.3	82	33.9	34.5	-18.1	-29.3	-13.3	-12.8	28.8	0.136
C	37.4	86	56.3	83	80.8	79	128.9	75	34.9	35.1	-20.5	-23.0	-16.1	-12.6	29.8	0.139
D	45.2	83	67.4	80	94.7	75	148.6	69	3.3	32.8	-20.3	-21.8	-24.9	-12.5	28.9	0.136

A = HNO₃, B = HNO₃ + ethylamine, C = HNO₃ + diethylamine, D = HNO₃ + triethylamine.

TABLE-3
POLARIZATION DATA AND INHIBITION EFFICIENCY OF ETHYLAMINES FOR ZINC IN 0.01 M HNO₃
Inhibitor concentration: 40 mM; Effective area of specimen: 0.247 dm²

System	E _{corr} (mV)	I _{corr} (μA/sq cm)	Tafel slope (mV/decade)			I.E. (%) from methods	
			Anodic β _a	Cathodic -β _c	B (mV)	Weight loss methods	Polarization methods
A	-939	0.250	83.3	138.4	22.6	-	-
B	-712	0.017	101.8	198.4	29.3	90	95
C	-825	0.022	100.7	185.2	28.4	91	93
D	-819	0.039	90.0	150.0	24.5	84	86

A = HNO₃, B = HNO₃ + ethylamine, C = HNO₃ + diethylamine, D = HNO₃ + triethylamine

fresh metal surface to further attack¹¹ which results in intensification of the kinetics of electrochemical reaction¹² and thus explains the higher corrosion rate at elevated temperature. The addition of ethylamines in corrosive media indicates that as the temperature increases I.E. decreases, *e.g.* in 0.03 M HNO₃ at 40 mM inhibitor concentration, the I.E. for ethylamine was 90, 88, 84 and 81 % at 303, 313, 323 and 333 K, respectively.

Mean 'E_a' value calculated (eqn. 2) for zinc in 0.03 M HNO₃ is 16.4 kJ/mol. In acid containing inhibitors, the mean E_a values are found to be 2 times higher than that of uninhibited system. Mean E_a values are 33.9, 34.9 and 33.5 kJ/mol for ethylamine, diethylamine and triethylamine, respectively (Table-2). The higher values of mean E_a indicates physical adsorption of the inhibitors on metal surface¹³. The values of E_a calculated from the slope of Arrhenius plot and using eqn. 2 are almost similar. From Table-2, it is evident that in all cases, the Q_{ads} values are negative and range from -13.3 to -29.3 kJ/mol. As the temperature increases values of 'Q_{ads}' decreases (becomes more negative). The negative Q_{ads} values shows that the adsorption and hence the I.E. decreases with rise in temperature¹⁴.

The values of mean ΔG_a^o are given in Table-2. In all cases, mean ΔG_a^o values are negative and lie in the range of -12.5 (triethylamine) to -12.8 kJ/mol (ethylamine). The most efficient inhibitor shows more negative ΔG_a^o value. This suggests that they are strongly adsorbed on the metal surface.

The enthalpy changes (ΔH_a^o) are positive indicating the endothermic nature of the reaction¹⁵ suggesting that higher temperature favours the corrosion process. The entropy (ΔS_a^o) values are positive confirming that the corrosion process is entropically favourable¹⁶.

Polarization behaviour: Anodic and cathodic galvanostatic polarization curves for zinc in 0.01 M HNO₃ acid, alone and containing 40 mM concentration of ethylamines. The 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. In almost all the cases, the efficiencies from Tafel plots agree well (within ± 5 %) with the values obtained from weight loss data.

Mechanism

Zinc dissolves in HNO₃ by the following reaction.



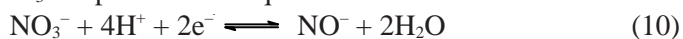
Various cathodic reactions can also occur simultaneously on a metal surface as shown below.



HNO₃ is a strong acid and therefore ionize completely and undergoes dissolution with the formation of H⁺ ions as only positive ions¹⁷.



In dilute HNO_3 the partial ionic equation is as follows¹⁸.



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 $\log [(\theta/1-\theta)]$ is plotted against $\log C$ straight lines are obtained in the all the three inhibitors studied. This suggests that the inhibitors cover both the anodic as well as cathodic regions through general adsorption following Langmuir isotherm. In HNO_3 , generally at all concentrations, the order of I.E. in the decreasing order as follows: ethylamine > diethylamine > triethylamine.

Following points are important for mechanism of these compounds: The I.E. of these compounds does not depends on pK_a value. +I inductive 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 so the corrosion increases. Number of ethyl group increases while lone pair of electron remain same in all these three inhibitors. Triethylamine shows the lowest inhibition. This is due to structure, the degree of chain branching appears to the opposite effect with respect to charge density¹⁹.

Conclusion

(a) As the acid concentration increase the corrosion increases. (b) At constant inhibitor concentration, the inhibition energy (I.E.) of all inhibitors increases as the concentration of acid increases. (c) At all concentration of acid, as the inhibitor concentration increases I.E. increases and corrosion rate decreases. (d) At 40 mM inhibitor concentration and 0.01 M acid concentration ethylamine shows better I.E. while triethylamine shows less effective. (e) Addition of inhibitors in corrosive media indicates that as the temperature increases corrosion rate increases while I.E. decreases. (f) In all cases, the values of heat of adsorption (Q_{ads}) and the values of free energy of adsorption ($\Delta G_{\text{a}}^{\circ}$) are negative. (g) Value of change of enthalpy ($\Delta H_{\text{a}}^{\circ}$) and entropy of adsorption ($\Delta S_{\text{a}}^{\circ}$) are positive shows higher the positive value higher the inhibition. (h) Mean value of ' E_{a} ' in inhibited acid are higher then the value of ' E_{a} ' in acid only, which shows that chemisorption's of the inhibitor molecule. (i) $\log [(\theta/1-\theta)]$ vs. $\log C$ (inhibitor concentration) shows straight line, which indicate that the inhibition action appears to be the chemisorption's and inhibitors cover both anodic and cathodic region through general adsorption following Langmuir isotherm.

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