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Corrosion inhibitory effect of ethylamine on zinc in HCl solution

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Abstract

Corrosion inhibitory action of ethylamine on zinc in HCl acid solution was studied by mass loss, temperature effect and polarization methods. With increase in acid concentrations corrosion rate increases while inhibition efficiency (I.E.) of inhibitor decreases. With increase in temperature corrosion rate increases while I.E. decreases. Inhibition efficiency of ethylamine increases with increase in inhibitor concentrations. Maximum I.E. was found 98.35 % at 20 mM ethylamine in 0.01M HCl. The inhibition effect is discussed in view of ethylamine molecules adsorbed on the metal surface. Polarization study shows that ethylamine behaves as cathodic type inhibitor.

Keywords: Corrosion, zinc, HCl, ethylamine, adsorption, mass loss, polarization.

Introduction

Corrosion of metal is a major problem in industry. The major use of zinc for corrosion controls is in the form of coating for steel. Several types of amines were investigated as corrosion inhibitors[1-3]. Industrial acid cleaning, acid descaling and acid pickling are some of the important fields of HCl applications. Many researchers[4-14] studied corrosion of zinc in hydrochloric acid and its inhibition by various organic and green inhibitors. Various investigators[15-23] have studied ethylamine as corrosion inhibitor in different acid media. Present investigation was carried out to study the effect of ethylamine as corrosion inhibitor for zinc in HCl solution.

Materials and methods

Sample and solution preparation: In the present study, zinc specimens with a chemical composition of 99.96% Zn, 0.01% Fe, 0.01% Pb, and 0.01% Cd were used. The metal specimens of size 4.65 x 2.15 x 0.16cm were used. The specimens were degreased by acetone, washed with doubled distilled water and finally dried. Hydrochloric acid was used as corrosive solution having concentration of 0.01, 0.05, 0.10 and 0.15M prepared by diluting HCl with double distilled water.

Mass loss measurements: For mass-loss study, cleaned specimens were immersed in HCl solutions in absence and presence of 5, 10, 15 and 20mM concentrations of ethylamine as an inhibitor at 301± 1K for 24h.

Temperature effect: To study the influence of temperature on corrosion rate, zinc specimens were immersed in in 0.05M HCl at 313, 323 and 333K temperature for an immersion period of 2h without and with ethylamine. From the corrosion rate data, I.E. and energy of activation (E_a) were calculated.

Electrochemical measurement: The polarization studies were made using potentiostat / galvanostat meter (Gamry, USA). Galvanostatic polarization has been taken with and without inhibitor in 0.01M HCl. In electrochemical cell, zinc metal ($1cm^2$) was used as a working electrode, Ag/AgCl electrode as a reference electrode and platinum electrode as an auxiliary electrode. The corrosion current density (icorr) values were determined by extrapolation of Tafel lines to the corresponding corrosion potentials (Ecorr)[24]. Cathodic Tafel slope (βc) and anodic Tafel slope (βa) were calculated from the software installed in the instrument.

Results and discussion

Mass-loss experiments: The corrosion rate of zinc 0.01, 0.05, 0.10 and 0.15M HCl solution in absence and presence of 5, 10, 15 and 25mM concentration of ethylamine for an immersion period of 24h at room temperature was calculated from mass loss data using the following equation:

$$C.R.\ (mg/dm^2d) = \text{Weight loss (gm.)} \times 1000 / \text{Area in } dm^2 \times day \quad (1)$$

From mass loss (C.R.) data, I.E. were calculated by using the equation:

$$I.E.(\%) = \frac{W_{uninh} - W_{inh}}{W_{uninh}} \times 100 \quad (2)$$

Where, W_{uninh} is the mass loss of metal in uninhibited acid and Winh is the mass loss of metal in inhibited acid. The degree of surface coverage 'θ' for various concentration of ethylamine in HCl solutions were calculated from mass loss data using the equation:

$$\theta = \frac{W_{uninh} - W_{inh}}{W_{uninh}} \quad (3)$$

Effect of acid concentration: As concentrations of acid increase rate of corrosion increases. Corrosion rate was increases from 81.98 to 5221.85mg/dm^{2}d as acid concentrations increases from 0.01 to 0.15M (Table-1).

Effect of inhibitor concentration: With increase in inhibitor concentration rate of corrosion decreases while I.E. increases. I.E. was found to be 93.38, 95.06, 96.71 and 98.35% corresponding to 5, 10, 15 and 20m Methylamine respectivelyin 0.01M HCl (Table-1, Figure-1). As acid concentration increases I.E. of ethylamine decreases (Table-1).

Temperature effect: Mass loss experiments were performed at 313, 323 and 333K in 0.05M HCl to investigate the influence of temperature on rate of corrosion in absence and presence of 5, 10, 15, 20mM inhibitor concentrationsfor an immersion period of 2h. With increase in temperature corrosion rate increases while percentage of I.E. of ethylamine decreases. Corrosion rate was increase as 11389.4, 19137.3 and 26220.6mg/dm^{2}d corresponding to 313, 323 and 333 K respectively (Table-2). I.E. for ethylamine was 99.19, 97.83 and 95.90% at 313, 323 and 333K respectively at 20mM inhibitor concentration.

Energy of activation (Ea): The value of 'Ea' was calculated from the slop of log ρ versus 1/T (ρ= corrosion rate, T= absolute temperature) and also by using Arrhenius equation[14]. Results given in Table-2, shows that mean 'Ea' values were higher in inhibited acid (ranging from 70.66 to 74.92kJmol^{-1}) than the 'Ea' value for uninhibited system (29.29kJmol^{-1}) (Table-2).

Table-1: Effect of acid concentration on Corrosion rate (CR) and Inhibition Efficiency (I.E.) of zinc in HCl acid containing ethylamine at 301±1K for an immersion period of 24h.

Inhibitor concentration (mM)	Concentration of HCl							
	0.01 M		0.05 M		0.10 M		0.15 M	
	C.R. (mg /dm^{2}d)	I.E. (%)	C.R. (mg/dm^{2}d)	I.E. (%)	C.R. (mg/dm^{2}d)	I.E. (%)	C.R. (mg/dm^{2}d)	I.E. (%)
Blank	81.98	-	1136.48	-	3151.05	-	5221.85	-
5	5.43	93.38	104.45	90.81	1138.22	63.88	3528.59	32.43
10	4.05	95.06	85.55	92.47	952.27	69.78	2876.63	44.91
15	2.70	96.71	56.73	95.01	843.76	73.22	1765.87	66.18
20	1.35	98.35	25.21	97.78	346.24	89.01	657.36	87.41

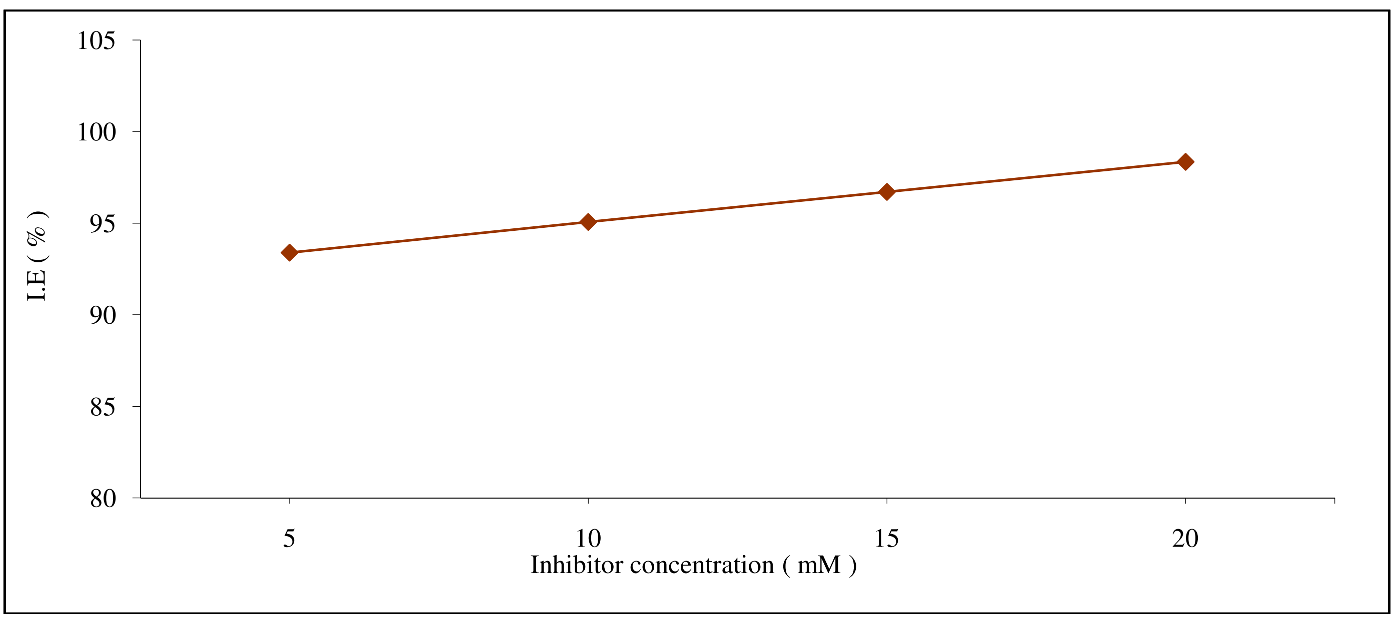

Figure-1: Effect of inhibitor concentration on inhibition efficiency (I.E.) of ethylamine for zinc in 0.01M HCl.

Heat of adsorption (Qads): The value of Q_{ads} were calculated by using the equation[25].

$$Q_{ads} = 2.303\,R\left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)\right] \times \left[\frac{T_1 \times T_2}{T_2 - T_1}\right] \quad (4)$$

Where, θ_1 and θ_2 are the fractions of the metal surface covered by the ethylamine at temperatureT_1 and T_2 respectively. From Table-2, it is evident that Q_{ads} values were negative and ranging from -33.00 to -84.92kJmol^{-1}. I.E. decreases with rise in temperature supporting the physisorption mechanism[26].

Adsorption isotherm: Basic information on the interaction between inhibitor and a metal surface can be provided using the adsorption isotherm[27]. A plot of log [θ / (1 - θ)] *vs.* log C for ethylamine in 0.05M HCl was shown in Figure-3, which gives straight line with slope values equal to unity indicates that the system follows Langmuir adsorption isotherm[28].

Free energy of adsorption (ΔG°a): The mean ΔG_a^o value is ranging from -30.82 to -37.13kJmol^{-1} indicates that the adsorption mechanism of ethylamine on zinc in HCl acid at the studied temperatures is physisorption with adsorptive layer having electrostatic character[29]. This is concluded on the fact that the values of ΔG^o_a -20kJmol^{-1} are consistant with physisorption, while those around –40kJmol^{-1} or higher are associated with chemisorption[30]. This is also supported by the fact that the I.E. of the investigated inhibitor decreases at higher temperature.

Table-2: Effect of temperature on Corrosion rate (CR), Inhibition Efficiency (I.E.) and thermodynamic parameters (Ea and Qa) for zinc in 0.05 M HCl acid at various concentrations of ethylamine for an immersion period of 2h.

Inhibitor concen tration (mM)	Temperature (K)						Mean (E_a) from Equation (4) (kJ mol^{-1})	Qads (kJ mol^{-1})	
	313		323		333				
	C.R. (mg/dm^{2}d)	I. E. (%)	C.R. (mg/dm^{2}d)	I. E. (%)	C.R. (mg/dm^{2}d)	I. E. (%)		313-323 K	323-333 K
Blank	11389.4	-	19137.3	-	26220.6	-	29.29	-	-
5	394.44	96.54	1172.40	93.87	3787.44	85.56	74.92	-50.44	-84.92
10	340.44	97.01	913.08	95.23	2447.52	90.67	71.76	-40.82	-64.39
15	270.12	97.63	664.56	96.53	1788.36	93.18	72.95	-33.00	-63.59
20	91.80	99.19	416.04	97.83	1075.20	95.90	70.66	-84.00	-58.69

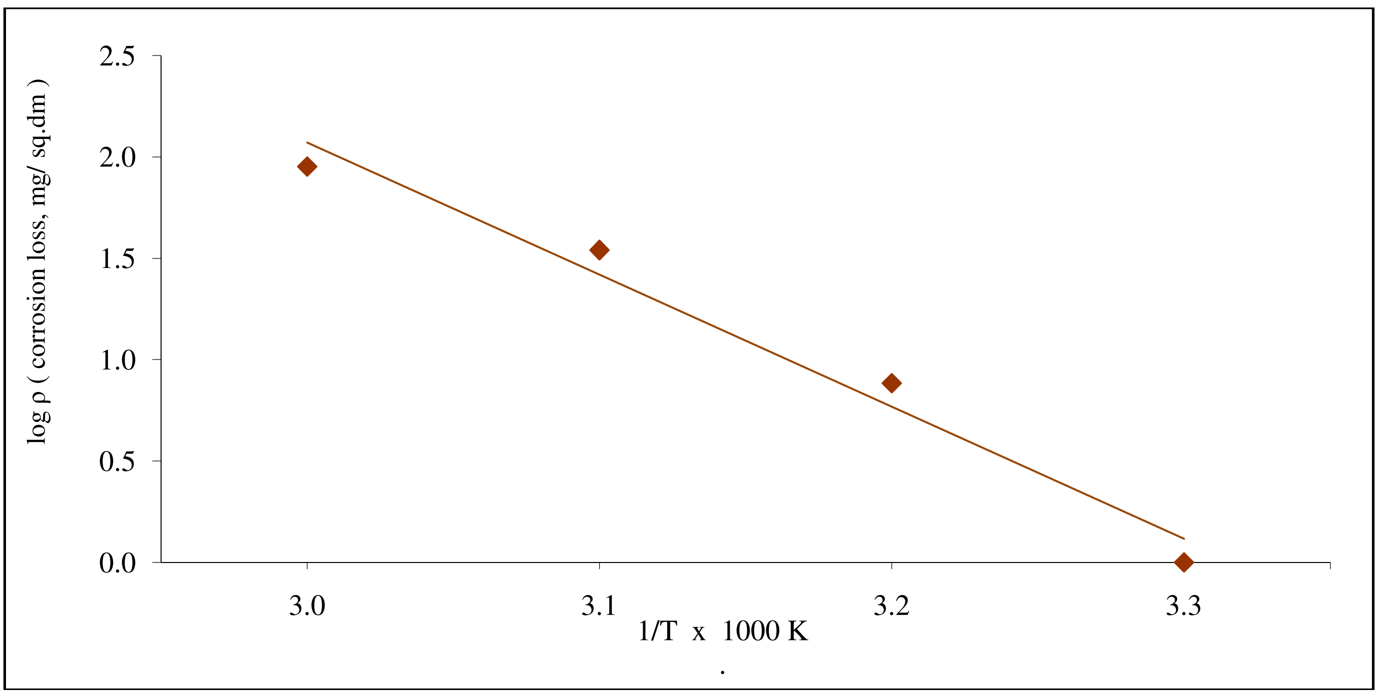

Figure-2: Arrhenius plot for zinc in 0.05M HCl acid containing 20mM Ethylamine.

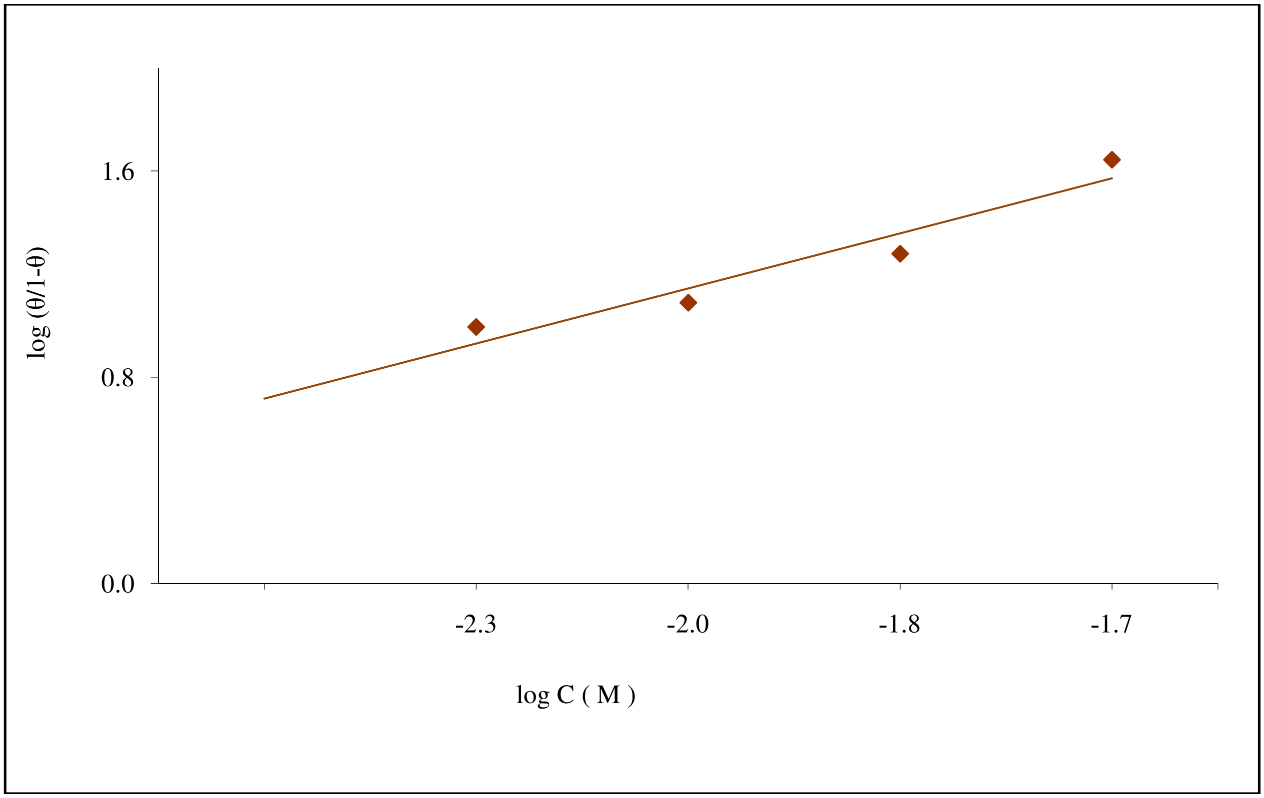

Figure-3: Plot of log (θ/1-θ) versus log C for corrosion of zinc in 0.05M HCl containing ethylamine.

Enthalpy of adsorption (ΔH°a): The 'ΔH^o_a' were calculated using the equation,

$$\Delta H^o_a = E_a - RT \quad (5)$$

Results showed that values of ΔH°_a were positive and lie in a range from 73.08 to 124.45kJmol^{-1}.

Entropy of adsorption (ΔS°a): ΔS^o_a was calculated [31] using the equations,

$$\Delta S^o_a = \Delta H^o_a - \Delta G^o_a / T \quad (6)$$

Value of ΔS°_a were found positive and lie between 0.33 to 0.50kJ mol^{-1} K^{-1} indicates the corrosion process is entropically favorable[32].

Rate constant (k) and Half-life ($t_{1/2}$) values: The rate constant 'k' was calculated using the equation[33],

$$k = 1/t \quad \ln (W_i / W_f) \quad (7)$$

Where, 'W_i' is the initial weight of the plate, 'W_f' is the final weight of the plate, 't' is the immersion time (in hours). The values of half-life ($t_{1/2}$) were calculated by using the following equation[34],

$$t_{1/2} = 0.693 / k \quad (8)$$

where, 't' is time (in h) and 'k' is rate constant (k×10^{-3}h^{-1}). As concentration of inhibitor increases rate constant 'k' decreases whereas the half-life values were increases[35]. Corrosion rate constant 'k' increases with increase in acid concentration (Table-3).

Electrochemical measurements: Electrochemical parameters such as corrosion potential (Ecorr), corrosion current density (icorr) and percentage of I.E. were given in Table-4. Polarization curves for zinc in 0.01M HCl in absence and presence of 20mM ethylamine were shown in Figure-4 and Figure-5. Calculated I.E. from Tafel plots were in good agreement with the I.E. obtained from weight loss data (within ± 1%).

In general, an inhibitor is anodic or a cathodic if the variation of E_{corr} against the blank is higher or above than 85mV[36]. In this study, the displacement of the E_{corr} was about 150mV (Table - 4), which suggest that ethylamine function as cathodictype of inhibitor.

I.E. calculated from (i_{corr}) by using following equation:

$$\text{I.E. } (\%) = \frac{i_{corr(uninh)} - i_{corr(inh)}}{i_{corr(uninh)}} \times 100 \quad (9)$$

Where $i_{corr\ (uninh)}$ indicates corrosion current density in uninhibited acid whereas $i_{corr\ (inh)}$ indicates corrosion current density in inhibited acid.

Table-3: Calculated values of rate constant 'k' and Half-life '$t_{1/2}$' for the corrosion of zinc in various concentrations of HCl solutions containing ethylamine.

Inhibitor	Inhibitor concen-tration (mM)	Concentration of HCl							
		0.01 M		0.05 M		0.10 M		0.15 M	
		Rate const. ($k\times10^{-3}$) (h^{-1})	Half Life ($t_{1/2}$) (h)	Rate const. ($k\times10^{-3}$) (h^{-1})	Half life ($t_{1/2}$) (h)	Rate const. ($k\times10^{-3}$) (h^{-1})	Half life ($t_{1/2}$) (h)	Rate const. ($k\times10^{-3}$) (h^{-1})	Half life ($t_{1/2}$) (h)
Blank	---	1.61	430.43	21.77	31.83	63.12	10.98	109.64	6.32
Ethylamine	5	0.10	6930.00	2.03	341.38	22.30	31.08	70.61	9.81
	10	0.08	8662.50	1.67	414.97	18.72	37.02	56.03	12.36
	15	0.05	13860.00	1.10	630.00	16.47	42.08	33.99	20.38
	20	0.03	23100.00	0.49	1414.28	6.77	102.36	12.78	54.22

Table-4: Polarization data for zinc in 0.01 M HCl containing 20mM ethylamine.

System	E_{corr} (mV)	I_{corr} ($\mu A/cm^2$)	Tafel slope (mV/decade)		B (mV)	I.E. (%)	
			βa	- βc		By Weight Loss method	By polarization method
Blank	-1040	0.119	36.36	277.77	13.96	-	-
Ethylamine	-1190	0.0035	179.80	120.15	31.31	98.49	97.06

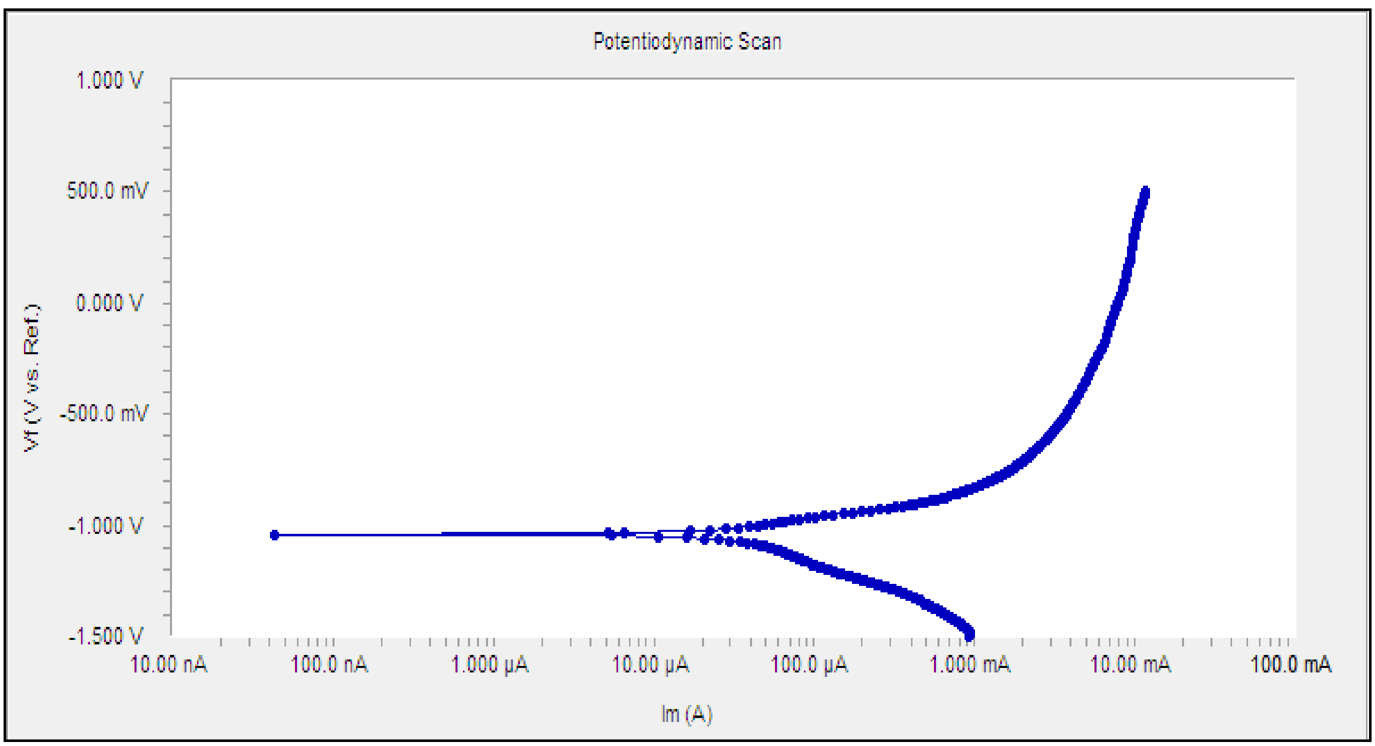

Figure-4: Polariaztion curve for zinc in 0.01M HCl acid in absence of ethylamine.

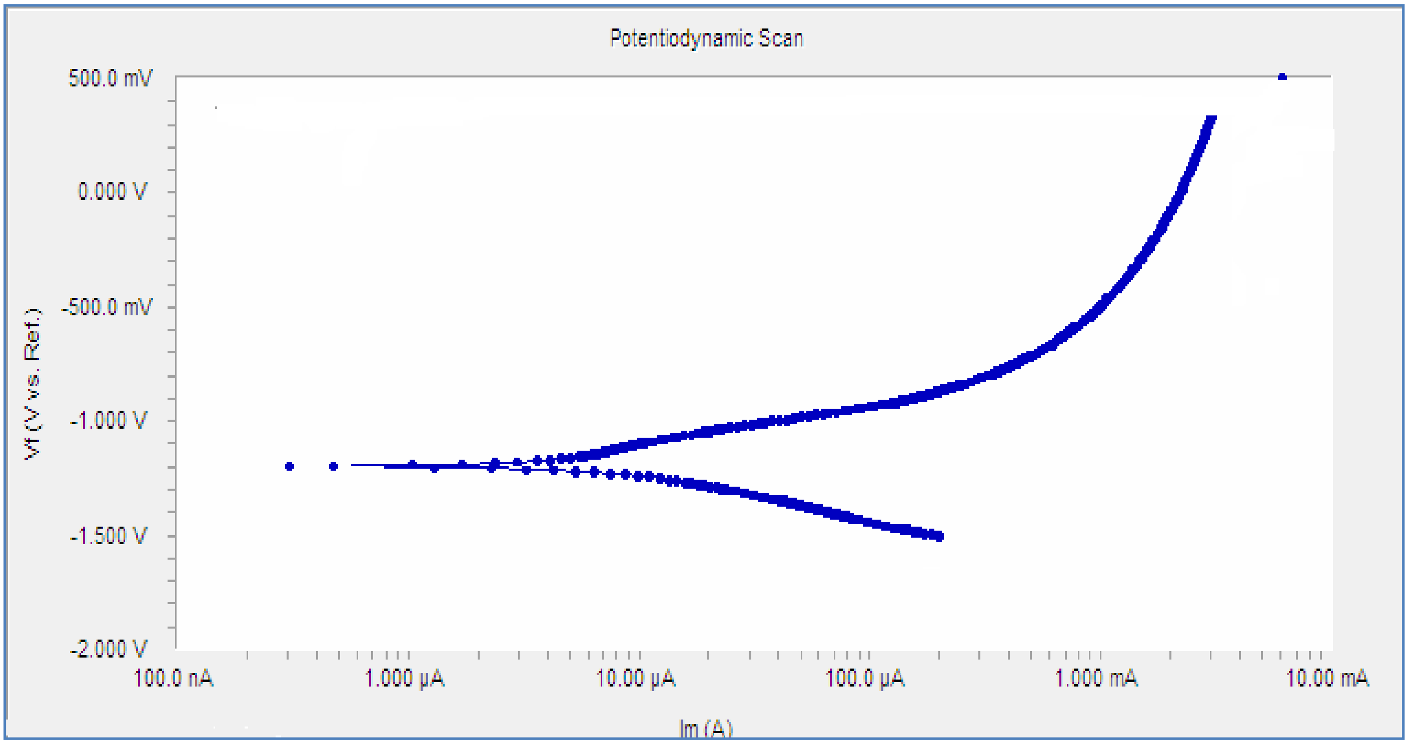

Figure-5: Polarization curve for zinc in 0.01M HCl containing 20mM ofethylamine.

Mechanism of inhibition by ethylamine: The mechanism of inhibition of corrosion is believed to be due to the formation of a protective film on the metal surface. The inhibitive action of ethylamine has been attributed to the strong adsorption on the metal surface using the lone pair of electrons available on the heteroatoms.

Conclusion

Corrosion rate of zinc increases with the increase of acid concentration. The I.E. increases with increase in ethylamine concentration. With increase in temperature, corrosion rate increases while I.E. of ethylamine decreases. Ethylamine shows maximum I.E. of 98.35%. Ethylamine adsorbed on zinc surface follows Langmuir adsorption isotherm. Tafel plot indicates that ethylamine act as a cathodic type inhibitor. Results obtained from polarization and mass loss data were in good agreement with each other.

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