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Ethanolamines as corrosion inhibitors for zinc in sulphuric acid

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ABSTRACT

The corrosion of zinc in sulphuric acid containing ethanolamines has been studied at different acid concentrations, inhibitor concentrations and temperatures. Corrosion rate increases with increase in acid concentrations. At constant acid concentration, the inhibition efficiency (I.E.) of ethanolamines increases with inhibitor concentration. Similarly at constant inhibitor concentration, the I.E. increases with the increase in acid concentration. At 60 mM inhibitor concentration in 0.1 M sulphuric acid at 301 K for 24 h immersion period, the I.E. decreases in the order: Ethanolamine (91%) > Diethanolamine (89 %) > Triethanolamine (86 %). As the temperature increases, corrosion rate increases while I.E. decreases. The mode of inhibition action appears to be chemisorptions since the plot of log (θ/1-θ) versus log C gives a straight line suggest that the inhibitors cover both the anodic and cathodic regions through general adsorption following Langmuir isotherm. Galvanostatic polarization curves showed significant anodic polarization.

Keywords: Corrosion, Zinc, Sulphuric acid, Ethanolamines.

INTRODUCTION

The problem of corrosion is of considerable importance due to increase in uses of metals and alloys. Zinc is one of the most important non-ferrous metals, which finds extensive use in metallic coating. Aromatic, aliphatic and heterocyclic amines have been extensively investigated as corrosion inhibitors [1-3]. According to Hackerman et al. [4] 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. Corry et al. [5] and Manning et al. [6] studied on the relative corrosion rate of alloys tested depends on HCl content on the mixture and reported that addition of HNO_3 to HCl again resulted in decrease in corrosion rate.

Sulphuric acid (H_2SO_4) is a strong acid and is used as a cleaner for rust, algae and scale from condensers and cooling tower [7]. Vashi et al. [8-10] studied ethanolamines as corrosion inhibitors for zinc in binary acid mixture (HNO_3 + H_3PO_4) and (HNO_3 + H_2SO_4). A.S. Fouda et al. [11] studied thiophine derivatives as corrosion inhibitors for CS in 0.5 M H_2SO_4. Inhibition study of *Caesalpinia Crista* on corrosion of mild steel in H_2SO_4 [12]. The present study was undertaken to evaluate various ethanolamines as corrosion inhibitors for zinc in sulphuric acid.

MATERIALS AND METHODS

Materials: Rectangular specimens (5.5 x 2.5 x 0.2 cm) of zinc having an area of 0.3013 dm^2 were used for the determination of the corrosion rate. The chemical composition of test specimen contain 99.39% Zn, 0.49% Mn and 0.12% Co. All specimens were cleaned by buffing to obtain a mirror like finish. All chemicals used were of AR grade. The corrosive solution was prepared in double distilled water.

Weight loss measurements: For weight-loss measurement, the zinc coupons were each suspended and completely immersed in 230 mL of various concentrations like 0.1, 0.3 and 0.5 M H_2SO_4 solution without and with different concentrations of ethanolamines at 301± 1 K for 24 h immersion period. After the test, the specimen was cleaned by using 10% CrO_3 acid solution having 0.2% $BaCO_3$ [13]. After cleaning, test specimens were washed with distilled water followed by acetone and dried with air drier and reweight. The mean value of corrosion rate was reported in mg dm^{-2} d^{-1} as shown in
table 1.

Temperature effect: To study the effect of temperature on corrosion of zinc in 0.1 M sulphuric acid, the specimens were immersed in 230 ml of the corrosive solution and weight loss was determined at solution temperature of 313, 323 and 333 K for an immersion period of 3 h in absence and presence of three ethanolamines at 60 mM concentration. Attention is paid to compensate the evaporation loss of corrosive media. Wesley [14] and ASTM [15] pointed out that thermostatic control to within ± 1 °C usually be considered satisfactory. From the data, % I.E., energy of activation (Ea), heat of adsorption (Q_{ads}), Free energy of adsorption (ΔG_a^0), Enthalpy of adsorption (ΔH_a) and Entropy of adsorption (ΔS_a) were calculated.

Polarization measurements: For polarization study, metal specimens having as area of 1 cm^2 were immersed to 230 mL 0.1 M H_2SO_4 in absence and presence of ethanolamines in the test cell (using CH instruments, Inc., USA) includes the metal specimens as a working electrode, Ag/AgCl electrode as a reference electrode as well as platinum electrode as an auxiliary electrode and allowed to establish a steady-state open circuit potential (OCP) for approximately 70 min. Polarization curves were plotted with potential against 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 corrosion potential (E_{corr}) [16].

Electrochemical impedance spectroscopy (EIS) measurements: EIS measurements were made (using CH instruments, Inc., USA) at corrosion potentials over a frequency range of 1 KHz to 100 KHz by a sine wave with potential perturbation amplitude of 5 mV. The real Z' and imaginary -Z'' parts were measured at various frequencies. From the plot of Z' Vs. -Z'', the charge transfer resistance (R_{ct}), and double layer capacitance (C_{dl}) were calculated. Impedance measurements were carried out both in the absence and presence of inhibitor.

Scanning electron microscope (SEM) study: The zinc specimen immersed in 0.1 M H_2SO_4 (blank) and containing 60 mM of *o*-toluidine, aniline, ethylamine, ethanolamine as inhibitors for a period of one day at 298 K. After exposure, specimen was removed, rinsed with double distilled water, dried and observed in scanning electron microscope to examine the surface morphology. The SEM image of polished zinc specimen was also taken. The surface morphology measurements of zinc specimens were examined using JEOL-5610 LV (made in Japan) computer controlled SEM.

RESULTS AND DISCUSSION

The results were presented in tables 1 to 4 and in figures 1 to 10. To assess the inhibition effect of corrosion of zinc in sulphuric acid, ethanolamines were added as inhibitors. I.E. has been calculated as follows:

$$\text{I. E. (\%)} = \frac{\text{Wu} - \text{Wi}}{\text{Wu}} \times 100 \quad \ldots\ldots\ldots (1)$$

Where, W_u is the weight loss of metal in uninhibited acid and W_i is the weight loss of metal in inhibited acid.

Table 1: Effect of H_2SO_4 concentration on corrosion rate (CR) and inhibitor efficiency (I.E.) on zinc metal having different concentration of different amines

Inhibitor	Inhibitor concentration (mM)	Acid concentration					
		0.1 M		0.3 M		0.5 M	
		CR mg $dm^{-2}d^{-1}$	I. E. %	CR mg $dm^{-2}d^{-1}$	I. E. %	CR mg $dm^{-2}d^{-1}$	I. E. %
Blank	-	1035.5	-	2880.84	-	6179.88	-
Ethanolamine	30	355.59	65.66	893.63	67.98	1896.01	69.31
	40	105.93	89.77	277.42	90.37	449.72	92.73
	50	102.92	90.06	180.34	93.79	316.40	94.88
	60	93.09	91.01	170.54	94.08	285.51	95.36
Diethanolamine	30	377.43	63.55	967.67	66.41	2036.27	67.05
	40	150.97	85.42	395.53	86.27	635.29	89.72
	50	121.46	88.27	229.84	92.02	419.61	93.21
	60	112.66	89.12	202.23	92.98	369.55	94.02
Triethanolamine	30	406.32	61.05	1063.31	63.09	2322.39	62.42
	40	159.25	84.62	432.70	84.98	807.09	86.94
	50	152.11	85.31	252.93	91.22	465.34	92.47
	60	141.13	86.37	244.29	91.52	391.18	93.67

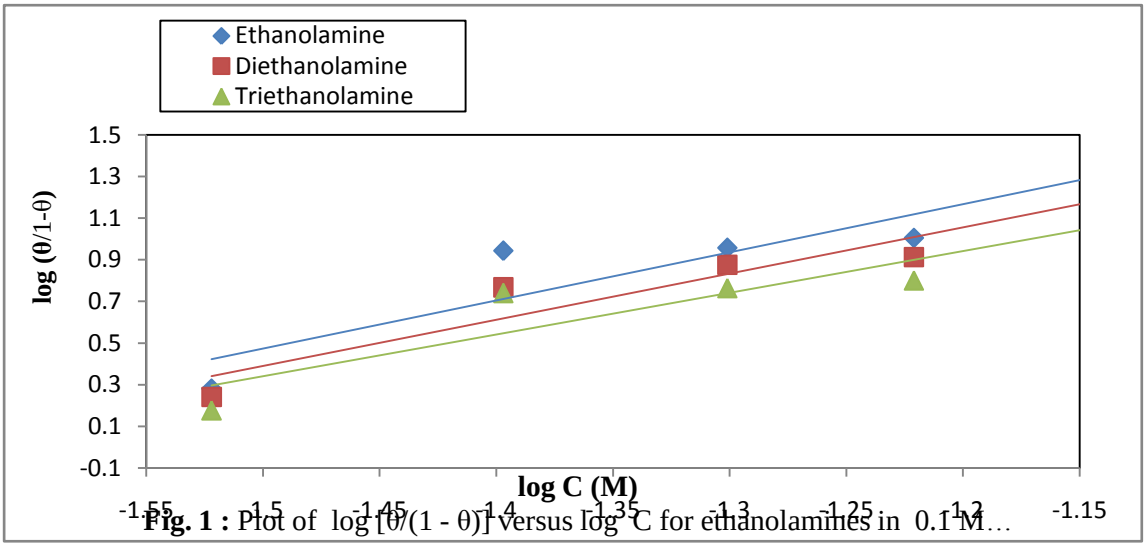


Fig. 1 : Plot of log [θ/(1 - θ)] versus log C for ethanolamines in 0.1 M…

Energy of activation (Ea) has been calculated from the slope of log ρ versus 1/T (ρ = corrosion rate, T = absolute temperature) (Fig. 1) and also with the help of the Arrhenius equation [17].

$$\log\frac{\rho_2}{\rho_1} = \frac{\text{Ea}}{2.303\text{R}}\left[\left(\frac{1}{\text{T}_1}\right) - \left(\frac{1}{\text{T}_2}\right)\right] \quad \ldots\ldots\ldots (2)$$

Where, ρ_1 and ρ_2 are the corrosion rate at temperature T_1 and T_2 respectively.

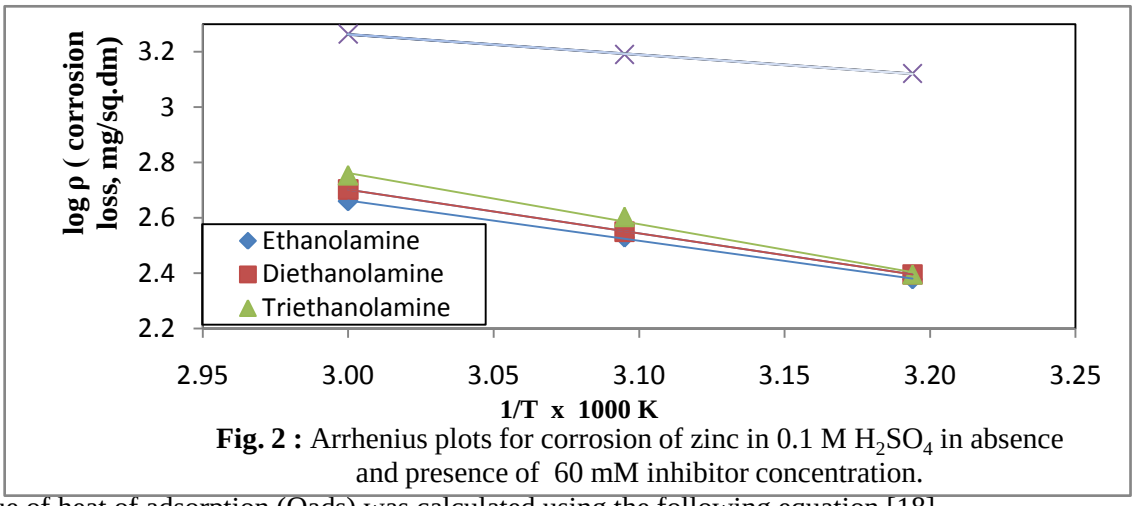


Fig. 2 : Arrhenius plots for corrosion of zinc in 0.1 M H_2SO_4 in absence and presence of 60 mM inhibitor concentration.

The value of heat of adsorption (Qads) was calculated using the following equation [18].

$$Q_{ads} = 2.303\ R\left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)\right] \times \left[\frac{T_1 \times T_2}{T_2 - T_1}\right] \quad \ldots\ldots\ldots (3)$$

Where, θ_1 and θ_2 [θ = (Wu – Wi)/Wi] are the fractions of the metal surface covered by the inhibitor at temperature T_1 and T_2 respectively.

Table 2: Effect of temperature on Corrosion rate (CR), Energy of activation (E_a) and Heat of adsorption (Q_{ads}) for zinc in 0.1 M H_2SO_4 in absence and presence of inhibitors for an immersion period of 3 h.

Inhibitor	Inhibitor Conc. mM	Temperature (K)						Mean E_a kJ mol^{-1}	'Ea' from Arrhenius Plot	Heat of adsorption, Q_{ads} (kJ mol^{-1})	
		313		323		333					
		CR mg dm^{-2}d^{-1}	I.E. (%)	CR mg dm^{-2}d^{-1}	I.E. (%)	CR mg dm^{-2}d^{-1}	I.E. (%)			313-323 K	323-333 K
Blank	-	10594.08	-	12399.60	-	14709.52	-	14.25	14.06	-	-
Ethanolamine	30	4513.76	57.39	5814.80	53.10	7460.96	49.27	21.79	21.36	-14.59	-13.71
	40	3372.00	68.17	4673.04	62.31	6266.16	57.40	26.83	26.57	-24.45	-18.28
	50	2602.00	75.43	3664.08	70.45	4805.84	67.32	26.52	26.31	-21.25	-13.07
	60	1911.68	81.95	2708.24	78.15	3664.08	75.09	28.15	27.89	-20.04	-15.28
Diethanolamine	30	4832.32	54.38	6584.72	46.89	8602.72	41.51	24.95	24.73	-18.49	-26.69
	40	4009.28	62.15	5357.20	57.60	6903.36	53.06	23.57	23.36	-15.93	-19.43
	50	2708.24	74.43	3903.04	68.52	5443.04	62.99	30.23	29.93	-24.45	-21.99
	60	1991.36	81.20	2840.96	77.08	4035.84	72.56	30.63	30.27	-21.04	-21.50
Triethanolamine	30	5336.80	49.62	7089.20	42.82	9133.68	37.90	23.26	23.04	-23.02	-18.31
	40	3770.32	64.41	3016.48	75.67	7328.24	50.18	28.74	28.51	-28.53	-22.05
	50	2495.84	76.44	3796.88	69.37	5682.00	61.37	35.66	35.26	-30.22	-31.71
	60	1991.36	81.20	3212.72	74.09	4540.32	69.13	35.57	35.36	-34.66	-21.85

The values of the free energy of adsorption (ΔGa) were calculated with the help of the following equation [18].

$$\log C = \log\left(\frac{\theta}{1-\theta}\right) - \log B \quad \ldots\ldots\ldots (4)$$

Where, log B = -1.74- $\left(\frac{\Delta Ga}{2.303\ RT}\right)$ and C is the inhibitor concentration. The enthalpy of adsorption (ΔH°_{a}) [19] and entropy of adsorption [20] (ΔS°_{a}) were calculated using the equation.

$$\Delta Ha^{0} = Ea - RT \quad \ldots\ldots\ldots (5)$$

$$\Delta Sa^{0} = \frac{\Delta H - \Delta G}{T} \quad \ldots\ldots\ldots (6)$$

Inhibitor efficiency (I.E.) from I_{corr} were calculated using following equation.

$$I.E.(\%) = \frac{i_{corr\ (uninh\ )} - i_{corr\ (inh\ )}}{i_{corr\ (uninh\ )}} \times 100 \quad \ldots\ldots\ldots (7)$$

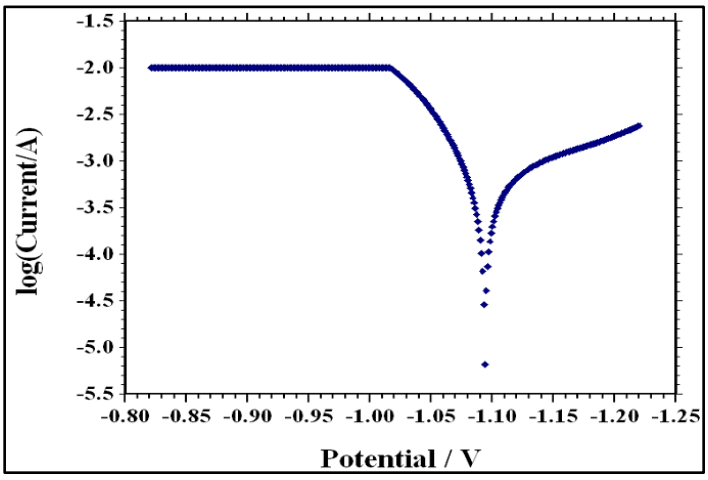


Fig 3: Polarization curve for corrosion of zinc in 0.1 M H_2SO_4 in absence of inhibitor

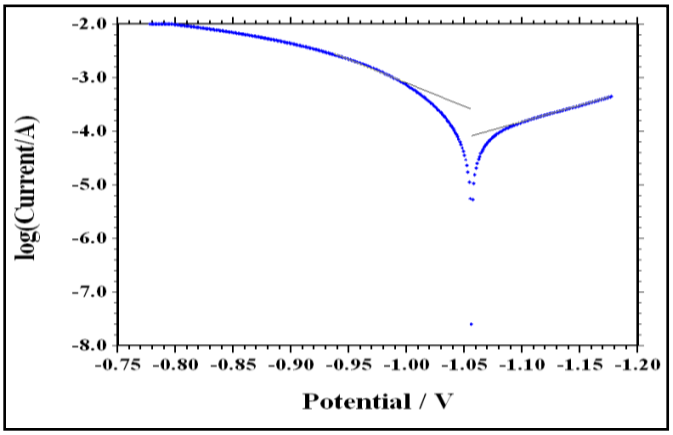


Fig 4: Polarization curve for corrosion of zinc in 0.1 M H_2SO_4 containing 60 mM ethanolamine

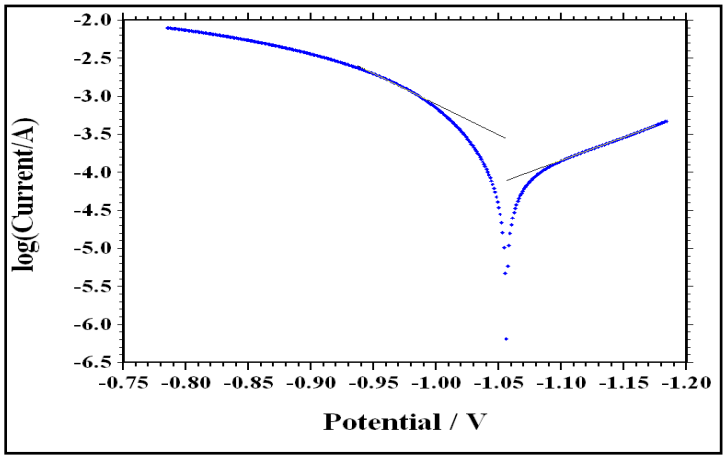


Fig 5: Polarization curve for corrosion of zinc in 0.1 M H_2SO_4 containing 60 mM diethanolamine

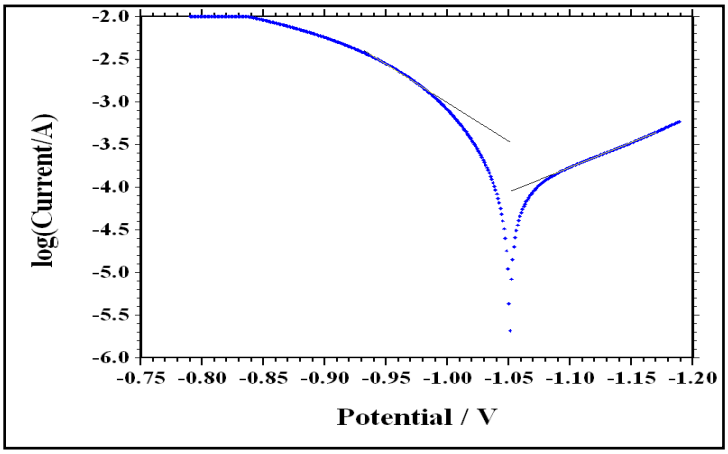


Fig 6: Polarization curve for corrosion of zinc in 0.1 M H_2SO_4 containing 60 mM triethanolamine

Table 3: Polarization data and inhibition efficiency (IE %) of 60 mM ethanolamines for zinc in 0.1 M H_2SO_4.

System	E_{corr} (V)	I_{corr} (μA/cm^2)	Tafel slope (mV/decade)		B (V)	IE (%)	
			+βa	- βc		Weight Loss	By polarization
Blank	-1.094	2.232	0.4133	0.2191	0.0622	-	-
Ethanolamine	-1.056	0.1617	0.1148	0.1630	0.0295	91.01	92.75
Diethanolamine	-1.057	0.1648	0.1248	0.1657	0.0309	89.12	92.61
Triethanolamine	-1.050	0.1869	0.1104	0.1728	0.0293	86.37	91.62

βa = Anodic Tafel constant, βc = Cathodic Tafel constant,
CD = Corrosion current density from interception of anodic and cathodic lines.

The charge transfer resistance (R_{ct}) values were calculated from the difference in impedance at lower and higher frequencies. To obtain the double layer capacitance (C_{dl}), the frequency at which the imaginary component of the impedance maximum was found as presented in the following equation [21].

$$C_{dl} = \frac{1}{2 \pi f R_{ct}} \quad \ldots\ldots\ldots\ldots (8)$$

Where, f is the frequency at the maximum height of the semicircle on the imaginary axis and R_{ct} is the charge transfer resistance [22]. I.E. from C_{dl} values were calculated using following equation.

$$\text{I. E. } (\%) = \frac{C_{dl\,(uninh\,)} - C_{dl\,(inh\,)}}{C_{dl\,(uninh\,)}} \times 100 \quad \ldots\ldots\ldots (9)$$

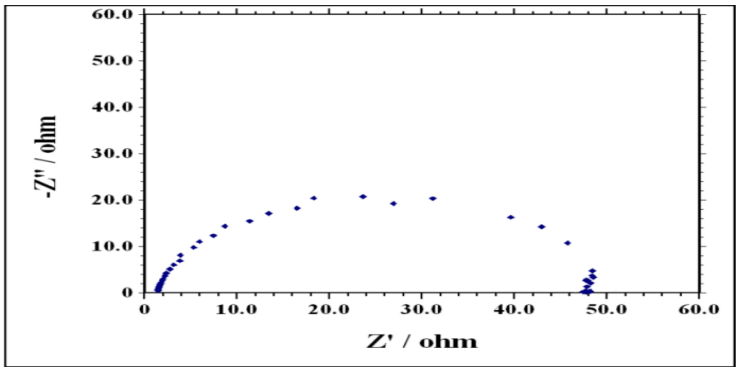


Fig 7: Nyquist plot for corrosion of zinc in 0.1 M H_2SO_4 without inhibitor

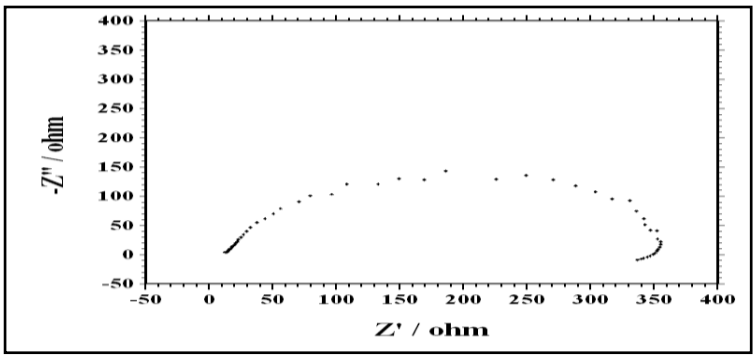


Fig 8: Nyquist plot for corrosion of zinc in 0.1 M H_2SO_4 containing 60 mM ethanolamine

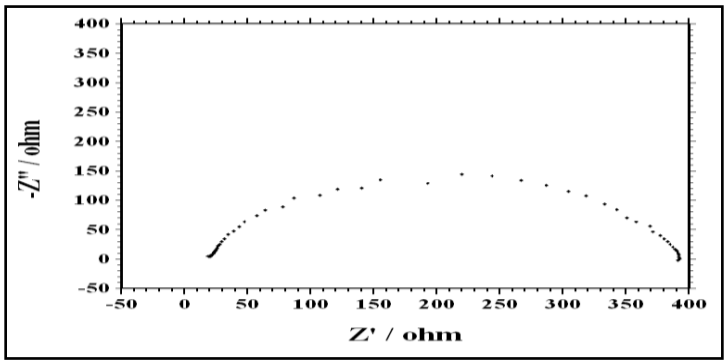


Fig 9: Nyquist plot for corrosion of zinc in 0.1 M H_2SO_4 containing 60 mM diethanolamine

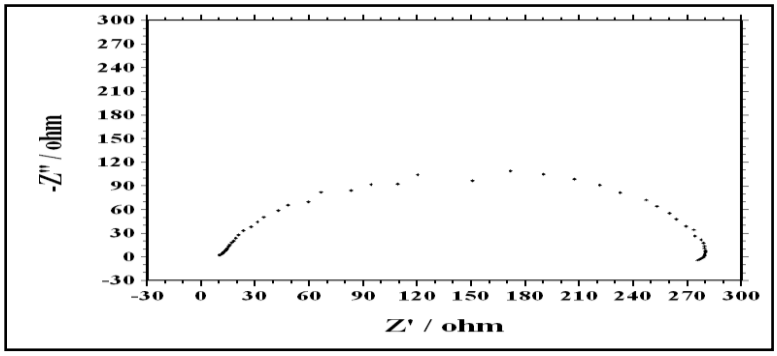


Fig 10: Nyquist plot for corrosion of zinc in 0.1 M H_2SO_4 containing 60 mM triethanolamine.

Table 4: EIS parameters for the corrosion of zinc in 0.1 M H_2SO_4 in absence and presence of 60 mM ethanolamines

System	R_{ct} (Ω cm^2)	C_{dl} (μF cm^{-2})	IE (%) Calculated from	
			EIS method	Weight loss method
Blank	49.5	151.84	-	-
Ethanolamine	340.0	3.12	97.94	91.01
Diethanolamine	373.0	2.84	98.12	89.12
Triethanolamine	270.0	5.36	96.94	86.37

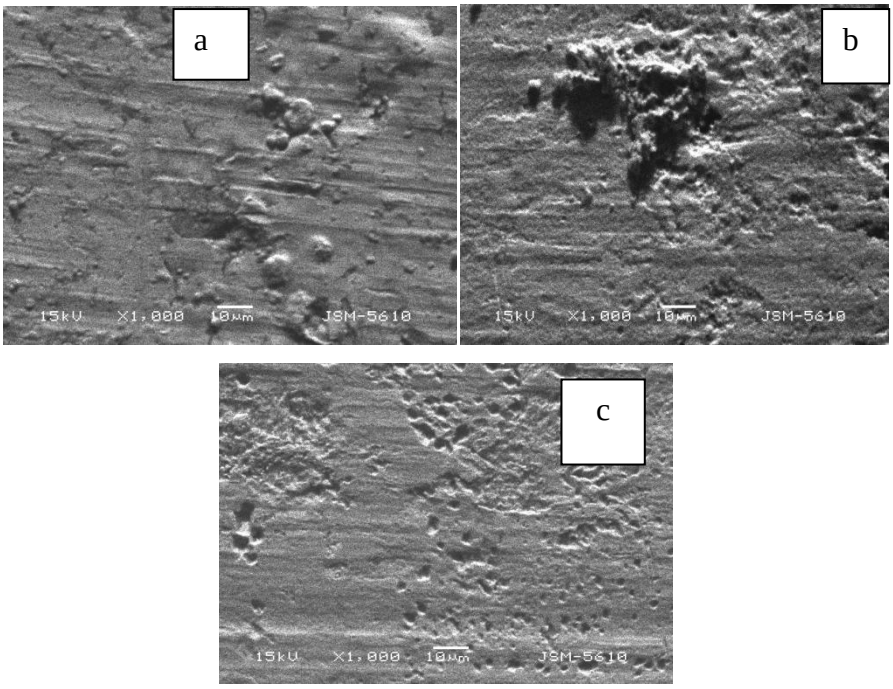


Figure 11: SEM micrograph of zinc (a) polished zinc plate (1000X), immersion in 0.1 M zinc in absence of inhibitor (1000X), (c) immersion in 0.1 M zinc in presence of 60mM ethanolamine inhibitor after 24h (1000X).

Corrosion by sulphuric acid: The corrosion rate increases with the increase in acid concentration. The corrosion rate was 1035.50, 2880.84 and 6179.88 mg dm^{-2} d^{-1} correspond to 0.1, 0.3 and 0.5 M H_2SO_4 concentrations respectively for a period of 24 h at 301 ± 1 K as shown in table-1.

Effect of inhibitor concentration: At constant acid concentration, the I.E. of the ethanolamines increases with the inhibitor concentration, e.g. In 0.1 M H_2SO_4 the I.E. for ethanolamine were found to be 65.66, 89.77, 90.06 and 91.01%, for diethanolamine I.E. were 63.55, 85.42, 88.27 and 89.12% and for triethanolamine I.E. were 61.05, 84.62, 85.31 and 86.37% correspond to 30, 40, 50 and 60 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 60 mM inhibitor concentration, the I.E. of ethanolamine were 91.01, 94.08 and 95.38 %, for diethanmolamine it was 89.12, 92.98 and 94.02% and for triethanolamine it were 86.37, 91.52 and 93.67% correspond to 0.1, 0.3 and 0.5 M acid concentration respectively (Table-1).

Effect of temperature: To determine the effect of temperature on corrosion, corrosion loss was measured in 0.1 M sulphuric acid containing 30, 40, 50 and 60 mM inhibitor concentration at solution temperature of 313, 323 and 333 K for an immersion period for 3 h. As the temperature is increases, corrosion loss

increases while percentage of I.E. decreases (Table- 2). Corrosion loss increases with temperature may be due to the desorption of the adsorbed molecules inhibitor and/ or aggressive at higher temperature and thus exposing the fresh metal surface to further attack [23], which results in intensification of the kinetic of electrochemical reaction [24] and thus explains the higher corrosion rate at elevated temperature, The addition of ethanolamines in corrosive media indicates that as the temperature increases I.E. decreases, e.g. in 0.1 M H_2SO_4 at 60 mM inhibitor concentration, the I.E. for ethanolamine was 81.95, 78.15 and 75.09% at 313, 323 and 333 K respectively.

Energy of activation (Ea): The mean 'Ea' value calculated from equation (2) for zinc in 0.1 M H_2SO_4 was 14.25 kJ mol $^{-1}$. A comparison of the values of the Ea for the corrosion process in inhibited (in the range 21.79 to 35.66 kJ mol^{-1}) which indicates that the "Ea" values were higher in inhibited than in uninhibited acid (Table-2). The higher values of mean Ea, indicates physical adsorption of the inhibitors on metal surface [25]. The value of Ea calculated from the slop of Arrhenius plot (Fig. 1) and using equation 2 were almost similar.

Heat of adsorption (Q_{ads}): From table 2 it was evident in all cases Q_{ads} values were negative and ranging from -13.07 kJ mol^{-1} to -34.66 kJ mol^{-1}. As the temperature increases values of Q_{ads} decreases (become more negative). The negative Q_{ads} values shows that the adsorption and hence the I.E. decreases with rise in temperature [26].

Adsorption isotherm: The graph of log [θ / (1 - θ)] *vs.* log C for aliphatic amines (ethanolamine, diethanmolamine and triethanolamine) in 0.1 M H_2SO_4 was depicted in figure 2. A straight line was obtained proving the fact that the adsorption of these three inhibitors on the zinc surface obeys the Langmuir adsorption isotherm.

Free energy of adsorption ($\Delta G°_a$): The values of mean $\Delta G°_a$ were calculated. In all cases mean $\Delta G°_a$ values were negative and lie in the range of -19.45 (30 mM triethanolamine) to -21.78 (60 mM ethanolamine). The negatives values of ($\Delta G°_a$) indicated the spontaneous adsorption of the inhibitor. This is usually characteristic of strong interaction with metal surface. It was found that the $\Delta G°_a$ values more positive than -40 kJ mol^{-1}, indicating that inhibitor is physically adsorbed on the metal surface [19].

Enthalpy of adsorption ($\Delta H°_{ads}$): The enthalpy of adsorption ($\Delta H°_{ads}$) were positive as 18.68 kJ mol^{-1} (for 30 mM ethanolamine) to 37.61 kJ mol^{-1} (for 60 mM triethanolamine) indicating the endothermic nature of the reaction [19] suggesting that higher temperature favors the corrosion process.

Entropy of adsorption ($\Delta S°_{ads}$): The entropy ($\Delta S°_{ads}$) values were positive as 0.12 kJ mol^{-1} (for 30 mM ethanolamine) to 0.18 kJ mol^{-1} (for 60 mM triethanolamine) confirming that the corrosion process is entropically favorable [20].

Potentiodynamic Polarization measurements: Potentiodynamic polarization curve for zinc in 0.1 M H_2SO_4 in absence and presence of 60 mM ethanolamines were shown in fig.-3 to fig-6. Associated electrochemical parameters such as corrosion potential (E_{corr}), corrosion current density (i_{corr}) anodic Tafel slope (β_a), cathodic Tafel slope (β_c) and percentage inhibition efficiency (I.E.) were given in Table 3. The curves show polarization of both, the cathodes as well as anodes. (Fig. 3-6) I.E. calculated from corrosion current obtained by the extrapolation of the cathodic and anodic Tafel lines were given in table 3. In almost all the cases, the I.E. from Tafel plots agree well (within ± 4%) with the values obtained from weight loss data.

Electrochemical impedance spectroscopy (EIS) measurements: Corrosion of zinc in 0.1 M H_2SO_4 in presence of ethanolamines was investigated by EIS measurement at room temperature. Nyquist plots for zinc obtain in absence and presence of ethanolmines were shown in (Fig. 7-10) and table-4. The addition

of inhibitor increase R_{ct} value while C_{dl} decrease. This decrease in C_{dl} value was due to the adsorption of inhibitor on metal surface. The results suggest that the inhibitor acts by the formation of a protective layer on the surface, which modifies the metal/solution interface. It was observed that from that the impedance diagram was almost semicircular in appearance, but not perfect semicircle. The difference has been attributed to frequency dispersion [27]. The semicircle nature of the plots indicates that the corrosion of zinc is mainly controlled by charge transfer process.

Scanning electron microscope (SEM) measurement: To understand the surface conditions of the metal specimen in the absence and presence of inhibitors SEM images are taken. The morphology of the polished zinc plate is very smooth and shows no corrosion (a) while zinc specimens dipped in a 0.1 M sulphuric acid in the absence of inhibitor (b) is very rough and the surface was damaged due to metal dissolution, However, the presence of 60 mM of ethanolamine inhibitors suppresses the rate of corrosion and surface damaged has been diminished considerably (c) as compared to the blank solution (b) which suggest the formation of a protective inhibitor film at the zinc surface. As the inhibitor gets adsorbed by physisorption and binds on the metal surface, it shows less abrasion as compared to uninhibited conditions.

Mechanism of corrosion and inhibition: Sulphuric acid acts as strong acid. The probable chemical reaction taking place in sulphuric acid is as under. It undergoes hydrolysis in aqueous solution.

$$2H_2SO_4 + 2H_2O \rightarrow 2H_3O^+ + 2HSO_4^- \quad \text{... (10)}$$

Generally, zinc dissolves in sulphuric acid solution due to somewhat hydrogen type of attack, the reaction taking place at the microelectrodes of the corrosion cell being represented as,

$$Zn \rightarrow Zn^{2+} + 2e^- \text{ (anodic reaction)} \quad \text{… (11)}$$

Reduction reaction is indicated by a decrease in valence or the consumption of electrons.

$$2H^+ + 2e^- \rightarrow 2H_{(ads)} \text{ (Cathodic reaction)} \quad \text{… (12)}$$

H_2 gas is liberated by any of the two following reactions:

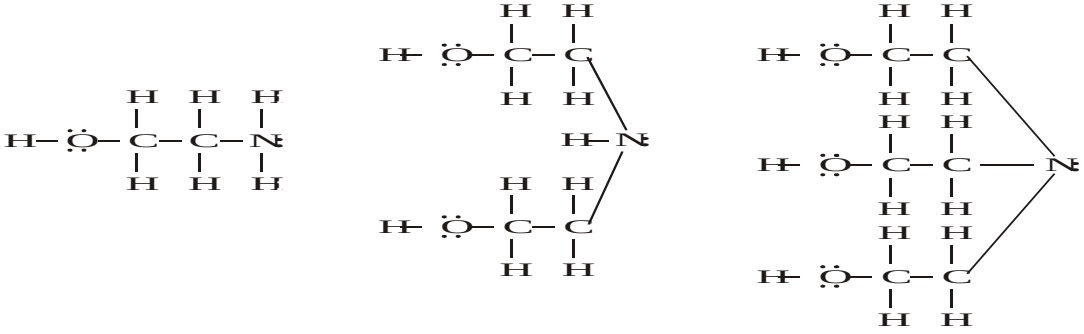
$$H + H = H_2 \uparrow \quad \text{… (13)}$$

$$\text{or } H + H+ + e^- = H_2 \uparrow \quad \text{… (14)}$$

$$\text{or } H + H_3O+ + e^- = H_2 \uparrow + H_2O \quad \text{… (15)}$$

Corrosive attack of sulphuric acid on zinc may be mainly due to the formation of HSO_4^- during the ionization of acid. However, inhibitors prevent the auto-catalytic cycle of the formation of HSO_4^- which results into inhibitor of the corrosion of zinc in sulfuric acid.

In sulphuric acid generally at all inhibitor concentration the order of I.E. of these three amines was as follows: ethanolamine > diethanolamine > triethanolamine.



Ethanolamine >	Diethanolamine >	Triethanolamine
pka = 9.50	pka = 8.88	pka = 7.77
l. p. = 3	l. p. = 5	l. p. = 7

Among ethanolamines the pka value decreases in the following order: 9.50 (ethanolamine) > 8.88 (diethanolamine) > 7.77 (triethanolamine). The result shows that higher the pka value higher will be the basicity and higher the I.E.

Lone pair is increases in the following order: 3 (ethanolamine) < 5 (diethanolamine) < 7 (triethanolamine). This indicates that as the lone pair increases corrosion rate also increases and I.E. decreases.

As the number of ethanol groups increases on nitrogen atom, it increases crowding around nitrogen atom. This crowding result in strain 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 reduced. Because of this effect ethanolamine gave higher inhibition than di and triethanolamine in H_2SO_4.

The results are in agreement with the work of Vashi and Champaneri [28], Vashi and Diksha Naik [29], Vashi and Bhajiwala [30], and Vashi et al. [9] and found percentage inhibition in the order: ethanolamine > diethanolamine > triethanolamine.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 [31]. The order can be explained on the basis of the influence of electron withdrawing ability of OH group in alkanol group and the overcrowding on the nitrogen atom [32].

CONCLUSIONS

- As the acid concentration increase the corrosion rate increases.
- At constant inhibitor concentration, the I.E. of ethanolamines increases as the concentration of acid increases. At all concentration of acid, as the inhibitor concentration increases I.E. increases and corrosion rate decreases.
- At 60 mM inhibitor concentration and 0.1 M acid concentration ethanolamine shows better I.E. while triethanolamine shows less effective.
- As the temperature increases corrosion rate increases while I.E. decreases.
- In all cases, the value of heat of adsorption (Q_{ads}) and the value of free energy of adsorption (ΔG_a) were negative. Value of change of enthalpy (ΔH) and entropy of adsorption (ΔS) were positive.
- Mean value of 'Ea' in inhibited acid were higher than the value of 'Ea' in acid only, which shows that chemisorption of the inhibitor molecule.
- log (θ/1-θ) Vs log C (inhibitor concentration) shows straight line, which indicate that the inhibition action appears to be the chemisorption and inhibitors cover both anodic and cathodic region through general adsorption following Langmuir isotherm.
- Results obtained from polarization method and EIS methods were in good agreement with weight loss method.
- Polarization curves shows somewhat less cathodic polarization and greater anodic polarization in presence of inhibitor.
- SEM shows smoother surface of inhibited metal samples than inhibited samples due to the formation of a protective layer on inhibited metal sample.

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