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Aliphatic amines as corrosion inhibitors for zinc in hydrochloric acid

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ABSTRACT

The inhibition of corrosion of zinc in hydrochloric acid by aliphatic amines like, triethylamine, triethanolamine and ethanolamine has been studied with respect to inhibitor concentration and temperature. The inhibition efficiency of aliphatic amines increased as the concentration of the inhibitor increased, while decrease with the increase in concentration of the acid and temperature. Weight loss data at different temperatures was used to determine activation energy. The activation energies in inhibited acid are higher than that in plain acid. For all inhibitors, the heat of adsorption (ΔH_{ads}) and free energy of adsorption are negative. The plot of log (θ/1-θ) versus logC results in a straight line, suggest that, the inhibitors appears to function through adsorption following Langmuir isotherm. Galvanostatic polarization curves show polarization of both anodes as well as cathodes.

key words: Corrosion, Zinc, Hydrochloric Acid, Aliphatic Amine.

INTRODUCTION

Corrosion resistance property of zinc is so important that nearly half the word's annual consumption of the metal is used to protect steel from rusting. Due to various industrial applications and economic importance of zinc, it's protection against corrosion attracted much attention. The corrosion behavior of zinc is affected by both, alkaline and acid solution, the corrosion being more sever at P^H values below 6 and above 12.5[1]· Hydrochloric acid is a strong inorganic acid that used in many industrial processes. Aliphatic amine, aromatic amine and heterocycliccompound have been extensively investigated as corrosion inhibitor[2-6]. According to Hackerman et al[7], the percentage of π- orbital of free electron on the nitrogen atom of secondary aliphatic and cyclic amines controlles the inhibitive properties of these compounds. The efficiency of few Schiff bases as corrosion inhibitor [8-9] has been also reported.

In the present work, the effect of aliphatic amines like triethylamine, triethanolamine and thanolamine as corrosion inhibitor for zinc in hydrochloric acid has been reported.

MATERIALS AND METHODS

To study the corrosion of zinc in hydrochloric acid, methods such as weight loss and polarization have been used. Rectangular specimens (5.25cmx2.50cmx0.2cm) of 99.90 % pure zinc with a small hole of about 3 mm diameter just near the one end of the specimen have been used. The specimens were polished by buffing, clean with distilled water several times, then degreased by acetone and dried by air drier. Each specimen was suspended to the same depth using pyrex glass hook. The volume of corrosive solution taken was 200 ml for all experiment. Only one specimen was suspended in a pyrex beaker of 250 ml capacity. The weight loss experiment was carried out in various concentration of hydrochloric acid with and without inhibitors of different concentration (5 to 25 mM) at temperature 302 ± 1 k, for 24 hours. To study the effect of temperature on corrosion of zinc, the weight loss experiment was carried out in 0.025 N hydrochloric acid at different temperature, 303, 313, and 323 K for an immersion period of 3 hours with and without inhibitor. After the test, the specimen was cleaned by 10% chromic acid solution having 0.2 % $BaCO_3$[10]. After cleaning, the test specimens were washed with distilled water followed by acetone and dried by air drier. The mean value of weight loss was reported as mdd. All the chemicals used were of A. R. grade. The corrosive solution was prepared in double distilled water. From the data, inhibition efficiency (IE %), energy of activation (E_a), heat of adsorption (Q_{ads}) and free energy of adsorption (ΔG_{ads}) were calculated.

For polarization study, metal specimens having an area of 1 cm^2 where immersed in 200 ml corrosive solution without and with 25 mM inhibitor concentration in 0.01 N hydrochloric acid. The test cell include the metal specimen as a working electrode, corrosive solution in which the specimen was to be tested, and saturated calomel electrode (SCE) as a reference electrode as well as platinum electrode as an auxiliary electrode. The polarization study was made by using Potentio – Galvano – Scan meter. Polarization curves were plotted with potential against log current density (called Tafel plot). 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})[11]

RESULTS AND DISCUSSION

To study the effect of inhibitor concentration on inhibition efficiency of the inhibitors, weight loss were determined in 0.01 N, 0.025 N and 0.050 N hydrochloric acid, containing various concentrations of inhibitor at 302 ± 1 K for exposure period of 24 hours. The inhibition efficiency (I.E %) was calculated as follows:

$$IE\% = \left(\frac{W_u - W_i}{W_i}\right) \times 100 \qquad \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_(1)$$

Where, W_u= weight loss in uninhibited acid, and W_i = weight loss in inhibited acid.

The results given in table-1, show that a specimen of zinc immersed in plain acid suffers a weight loss of 307.33, 611.24 and 1157.41 mdd in 0.01 N, 0.025 N and 0.050 N HCl respectively.

The results show that for all the three concentrations of the acid, the concentration of the inhibitor is increased, the weight loss due to corrosion decreases. The order of efficiency of the different inhibitor at 25 mM concentrations is found to be:

(a) In 0.01 N HCl :
ethanolamine (98.45 %) > triethylamine (95.34 %) > triethanolamine (70.84 %)

(b) In 0.025 N HCl :
ethanolamine (89.80 %) > triethylamine (83.27 %) > triethanolamine (64.49 %)

(c) In 0.05 N HCl :
triethylamine (47.72 %) > ethanolamine (40.45 %) > triethanolamine (38.33 %)

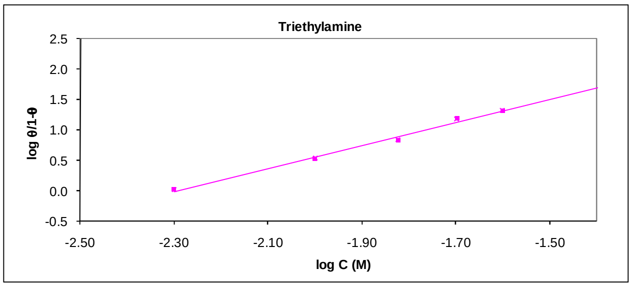
When the plot of log (θ/1- θ) versus log C (θ = fraction of the metal surface covered by the inhibitor, C = inhibitor concentration) were drown, straight lines were obtained (fig.-1). This suggests that the inhibitors get adsorbed on the metal surface following Langmuir adsorption isotherm[12].

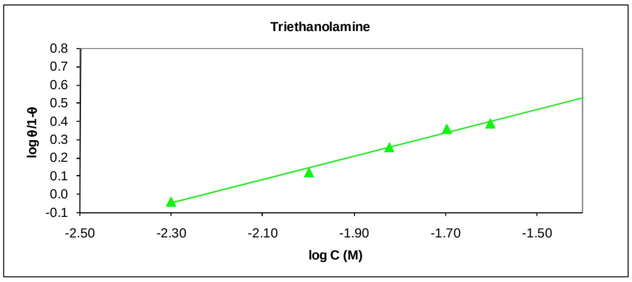
Table 1 : Weight Loss Data for Corrosion of Zinc in Hydrochloric Acid Solution : Effect of Aliphatic Amines.

Surface area of specimen : 29.35 cm^2 Temperature : 29 ± 1°C

immersion period : 24 hrs

acid concentration :		0.01 N		0.025 N		0.050 N	
Inhibitor and its concentration in mM		**Corrosion rate (mdd)**	**Inhibition Efficiency (IE%)**	**Corrosion rate (mdd)**	**Inhibitio n Efficiency (IE%)**	**Corrosion rate (mdd)**	**Inhibition Efficiency (IE%)**
Blank		307.33		611.24		1157.41	
Triethylamine	**5**	151.96	50.55	451.45	26.14	1019.76	11.89
	10	71.55	76.72	315.84	48.32	970.36	16.16
	15	40.20	86.91	248.38	59.36	847.70	26.68
	20	19.42	93.68	186.71	69.45	766.27	33.79
	25	14.31	95.34	102.21	83.27	605.11	47.72
Triethanolamine	**5**	161.16	47.56	494.03	19.18	1060.99	8.33
	10	132.53	56.87	396.25	35.17	971.38	16.07
	15	109.71	64.30	274.62	55.07	878.71	24.08
	20	93.70	69.51	236.80	61.26	783.99	37.34
	25	89.61	70.84	217.04	64.49	713.80	38.33
Ethanolamine	**5**	112.10	63.53	481.43	21.24	1069.85	7.57
	10	62.35	79.71	382.28	37.45	887.56	23.31
	15	26.24	91.46	272.57	55.41	852.81	26.32
	20	17.72	94.24	147.87	75.81	698.13	39.69
	25	4.77	98.45	62.35	89.80	689.27	40.45





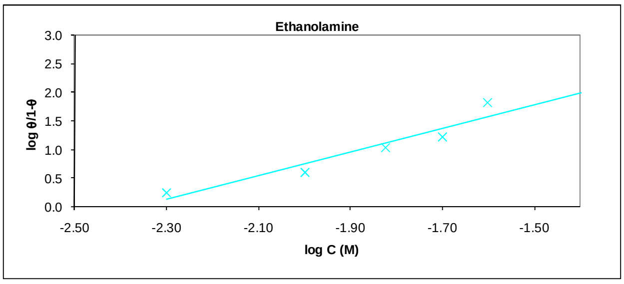


Fig 1 : Langmuir Adsorption Isotherm for Corrosion of Zinc in 0.01 N HCl Solution Containing Aliphatic Amine.

To study the effect of temperature on inhibitor efficiency, corrosion rate were determined in 0.025 N hydrochloric acid, plain as well as inhibited solution at temperature of 303, 313 and 323 K.

Energy of activation (E_a) has been calculated with the help of Arrhenius equation[12].

$$\log\frac{\rho_2}{\rho_1} = \frac{E_a}{2.303R}\left[\left(\frac{1}{T_1}\right) - \left(\frac{1}{T_2}\right)\right] \quad \text{\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_(2)}$$

Where, ρ_1 and ρ_2 are the corrosion rate (in mdd) at temperature T_1 and T_2 K respectively.

The values of the apparent energy of activation, Ea were also calculated from the slopes of plots of log ρ versus 1/T K following the Arrhenius equation.

$\rho = A\, e^{-Ea/RT}$

Where ρ = corrosion rate, A= constant, R= gas constant, e = base of the natural logarithm, and T = Kelvin temperature

The values given in table -2 show that the Ea values are low (8.27 k cal.mol^{-1}) in uninhibited acid whereas in inhibited acid they are higher. The higher value of activation energy (E_a) in the presence of inhibitor as compared to the activation energy in the absence of inhibitor in hydrochloric acid indicates that the inhibitor induces the energy barrier for the corrosion reaction, which leads to the decreasing of rate of corrosion of zinc in presence of inhibitor. The activation energy in inhibited acid is ranging from 8.76 k cal/mole to 14.95 k cal/mole, which indicates that the inhibitors are adsorbed physically. According to O. K. Aiola, B. B. Damaskin [13, 14], the value of activation energy less than 19.12 k cal/mole (80 k J/mole) and even smaller than 1.19 k cal/mole (5 k J/mole) represents physical adsorption.

The value of heat of adsorption (Q_{ads}) was calculated by the following equation [15].

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

Where, θ_1 and θ_2 [$\theta = W_u - W_i / W_i$] are the fraction of the metal surface covered by the inhibitors at temperature T_1 and T_2 K respectively.

The value of the free energy of adsorption (ΔG_{ads}) was calculated with the help of the following equation[16].

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

Where,

$$logB = -1.74 - \left(\frac{\Delta G^{\circ}_{ads}}{2.303RT}\right)$$

and C is the inhibitor concentration.

The results given in table -2 show that in all the cases, the corrosion rate increases with temperature. However, the efficiency of inhibitors decreases.

From the value of ΔG_{ads} and Q_{ads} given in table-2 it is evident that for all the inhibitors the heat of adsorption and free energies of adsorption are negative. This suggest that there is a strong interaction of the inhibitor molecules with the metal surface [17], forming a highly adherent film. The low ΔG_{ads} value in this case further confirms physical adsorption.

Table 2 : Effect of Temperature on Corrosion Rate (mdd), Inhibition Efficiency (IE%), Energy of Activation (Ea), Heat of Adsorption (Q_{ads}), and Free Energy of Adsorption (ΔG_a) for Zinc in 0.025 N Hydrochloric Acid containing Aliphatic Amine as Inhibitor.

surface area of specimen : 29.35 cm^2 Immersion period : 3 hours

inhibitor and its concentration in Mm		Temperature (K)						Energy of Activation (Ea) K Cal. mole $^{-1}$		Head of Adsorption Q_{ads} K.cal.mole^{-1}		Free Energy Of Adsorption ΔG_a K.cal.mole^{-1}
		303K		313K		323K		Mean E from eq.	E from Arhenius Plot	303-313 K	313-323 K	Mean
		CR	IE	CR	IE	CR	IE					
Blank		534.24	---	703.24	---	1237.48	---	8.27	8.35			
Triethylamine	**5**	212.61	60.20	346.17	50.78	970.36	21.58	14.95	15.09	-7.21	-26.55	-5.60
	25	68.14	87.24	95.40	86.43	174.45	85.90	9.23	9.34	-1.34	-0.89	-5.94
Triethanolamine	**5**	234.41	56.12	329.81	53.10	572.40	53.74	8.76	8.87	-2.30	0.52	-5.90
	25	65.42	87.78	92.67	86.82	193.53	84.36	10.68	10.78	-1.58	-4.02	-5.93
Ethanolamine	**5**	231.69	56.63	376.15	46.51	951.28	23.13	13.89	14.03	-7.66	-21.32	-5.56
	25	57.24	89.29	84.50	87.98	171.72	86.12	10.79	10.92	-2.45	-3.32	-6.02

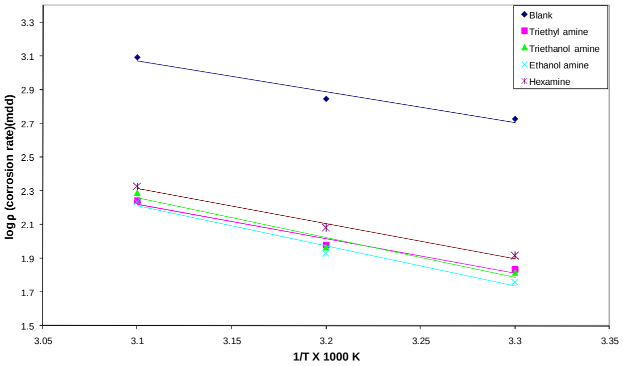


fig 2(b)Arrhenius Plots for Corrosion of Zinc in 0.025N HCl in Absence and Presence of 25mM Aliphatic Amine

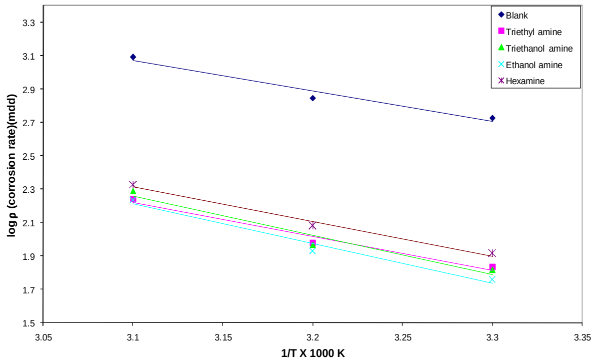


fig 2(b)Arrhenius Plots for Corrosion of Zinc in 0.025N HCl in Absence and Presence of 25mM Aliphatic Amine

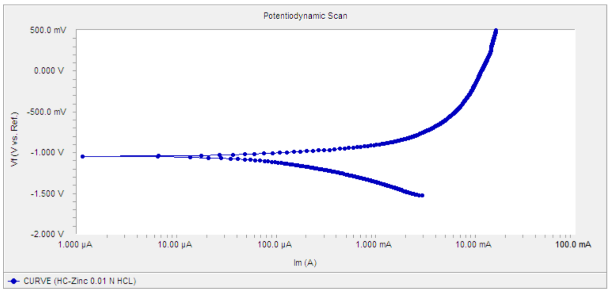
Galvanostatic cathodic and anodic polarization measurements were carried out in 0.01 N HCl solution, in presence and absence of triethylamine, triethanolamine and ethanolamine. In 0.01 N HCl solution the values of I_{corr}, Tafel parameters β_a and β_c obtained in presence and absence of aliphatic amines presented in table -3. In 0.01 N HCl solution, the value of I_{corr} obtained by Tafel extrapolation was 53.50 µA/cm^2 and the βc and βa values were 220.70 and 109.70 V/decade respectively. I_{corr} values in presence of aliphatic amines have narrow variation but more deviation from that in plain acid. The inhibitor adsorption shifted the corrosion potential E_{corr}, with respect to the blank, but this shift is not more than 85 mV. According to Riggs and others, the classification of a compound as an anodic or cathodic inhibitor is feasible when the potential displacement is at least 85 mV in relation to that measured for the blank solution. So it can be say that the inhibitors are mixed type inhibitor.

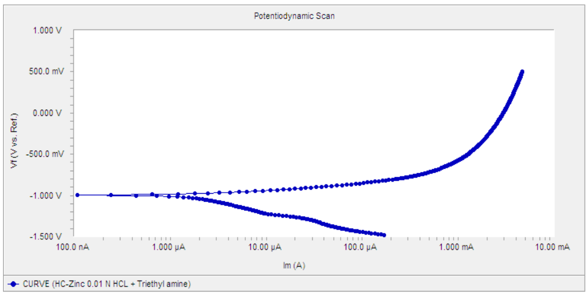
Table 3 : Tafel Parameters and Inhibition Efficiency (IE%) for Zinc in 0.01 N Hydrochloric acid solution containing Aliphatic amine.

Surface area of specimen : 1 cm^2 Temperature : 25°C

Inhibitor Concentration : 25 mM

Inhibitor	Open circuit potential (mV)	Corrosion current density I_{corr} (µA/cm^2)	Tafel slope (V/decade)		Inhibition effeciency (IE%) Calculated from	
			Cathodic β_c	Anodic β_a	Polarization method	Weight loss method
Blank	-1030.00	53.50	220.70	109.70		
Triethyl amine	-984.10	1.76	301.90	70.70	96.71	95.34
Triethanol amine	-1059.00	18.00	234.00	129.90	66.36	70.84
Ethanol amine	-933.60	1.23	231.70	72.40	97.77	98.45





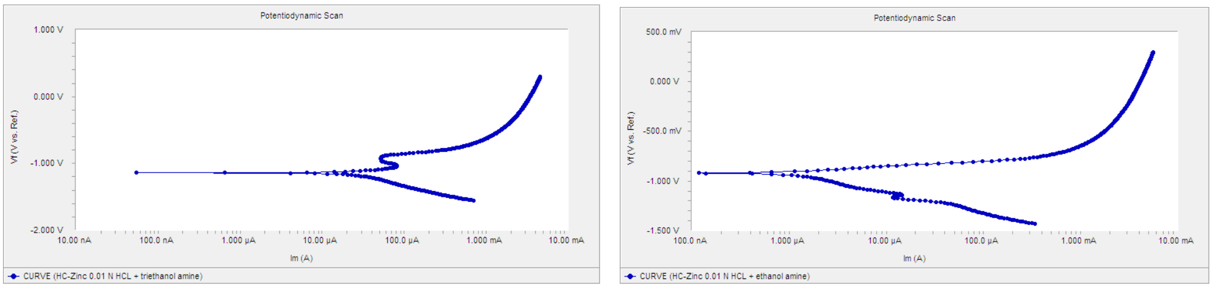


Fig. 3 : polarization Curves for Corrosion of Zinc in 0.01 N HCl Solution Containing 25 MmM Inhibitor Concentration

Mechanism of Corrosion Inhibition

As the evident from the results the higher inhibition efficiency (IE) at different concentration of the aliphatic amines can be attributed to the presence of nitrogen atom of amino group (-NH2). Nitrogen atom in aliphatic amines acts as the reaction centre, because of its higher electron density. This reaction centre terms and the same trend is maintained even at higher environment concentrations. In case of ethanolamine, somewhat higher inhibition efficiency is observed. This behavior may be mainly due to –OH group which act as electron repelling group and provides more electron density to the nitrogen atom and therefore increased electron density on the N atom results in higher inhibition action. It can be assume that a bond of lewis acid base type, generally with the inhibitor as electron donor and the metal as the electron acceptor may play important role in decreasing corrosion rate.

Somewhat less inhibition efficiency (IE) is observed with triethanolamine. As the number of ethanol groups increases on N atom, this crowding results in strain which is less in ehanolamine and more in triethanolamine. Due to this, the stability of molecule is high in ethanolamine than triethanolamine and so basicity is also reduce. Because of this effect, ethanolamine gave higher inhibition than triethanolamine in hydrochloric acid. High efficiency of triethylamine may be attributed to the presence of -C_2H_5 group in the vicinity of nitrogen atom of amino group (-NH_2). Presence of –C_2H_5 group increase the electron charge cloud density in amino (-NH_2) group and this increased electron density, which is responsible for the enhancement of inhibition efficiency (IE) of the compound. But the inhibition efficiency is not as high as for ethanol amine, it may be due to steric hindrance of it.

CONCLUSION

From the results of the study, the following conclusion may be drawn:

1. The corrosion rate of zinc increase with increase in acid concentration.
2. The extent of inhibition increases with the increase in concentration of inhibitors.
3. All the aliphatic amine provides protection through a physical adsorption.
4. The change in anodic and cathodic Tafel valued in presence of aliphatic amines indicate their effect on both anodic and cathodic process, however, somewhat less anodic polarization, but greater cathodic polarization in plain as well as in inhibited acid suggest that inhibitors function by general adsorption at cathodic as well as anodic regions of the metal surface.
5. There was good agreement in the value of inhibition efficiency calculated using polarization technique and weight loss data.

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