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Aniline as corrosion inhibitor for zinc in (HNO$_3$ + H$_2$SO$_4$) binary acid mixture

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ABSTRACT

The inhibition efficiency of aniline on zinc corrosion of zinc in (HNO$_3$ + H$_2$SO$_4$) binary acid mixture has been studied by weight loss method and polarization technique. Corrosion rate increases with the concentration of acid mixture and the temperature. Inhibition efficiency (I.E.) of aniline increases with the concentration of inhibitor while decreases with the increase in concentration of acid mixture. As temperature increases corrosion rate increases whereas percentage of I.E. decreases. The plot of log (θ/1-θ) versus log C results in a straight line suggest that the inhibitor cover both the anodic and cathodic regions through general adsorption following Longmuir isotherm. Galvenostatic polarization curves show polarization of both anodes as well as cathodes.

Key words: Corrosion, zinc, nitric and sulphuric acid mixture, aniline.
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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. Zinc corrodes in solution having pH lower than 6.0 and higher than 12.5, while within this range the corrosion is very slow [1]. Aromatic, aliphatic and heterocyclic amines have been extensively investigated as corrosion inhibitors [2-4]. According to Hackerman et al.[5] 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. Vashi et al. has studied the corrosion inhibition of zinc in (HNO$_3$ + H$_2$SO$_4$) by ethanolamines [6] and by ethyalamines [7] . According Patel et al.[8] the higher corrosion rate of brass in mixed acid (HNO$_3$ + H$_2$SO$_4$) may be due to the combined effect of sulphate ion and continuation of auto catalytic cycle of formation of nitrous acid. . In the present work, the role

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of aniline as inhibiting the corrosion of zinc in $(HNO_3 + H_2SO_4)$ binary acid mixture has been reported.

MATERIALS AND METHODS

To study the corrosion of zinc in binary acid mixture by various methods such as weight loss, temperature effect, potential as well as polarization measurements have been used.

Rectangular specimens (5.0 x 2.0 x 0.1 cm) of zinc having an area of 0.2935 dm^2 were taken and cleaned by buffing and immersed in 0.01, 0.05 and 0.1 N binary acid concentration with and without inhibitor containing 230 ml test solution at 301 $\pm$ 1 K for 24 h immersion period. After the test, specimens were cleaned by 10 % chromic acid solution having 0.2 % $BaCO_3$ for a period of about 2 minutes [9]. After cleaning, test specimens were washed with distilled water followed by acetone and dried with air drier. The mean value of weight loss was reported as mg/dm^2 shown in Table- 1. All chemicals used were of AR grade. The corrosive solution was prepared in double distilled water.

To study the effect of temperature on corrosion of zinc in binary acid mixture (0.05 N HNO_3 + 0.05 N H_2SO_4), the specimens were immersed in 230 ml of corrosive solution and corrosion rate was determined at various temperatures e.g. at 303, 313, 323 and 333 K for an immersion period of 3h with and without inhibitor. From the data, I.E.(in %), energy of activation (Ea), heat of adsorption (Qads), free energy of adsorption (ΔGa), change of enthalpy (ΔH) and entropy of adsorption (ΔS) were calculated .

For polarization study, metal specimens having an area of 0.047 dm^2 were immersed in 230 ml corrosive solution without and with 1.0 % inhibitor concentration in binary acid mixture (0.01 N HNO_3 + 0.01 M H_2SO_4). 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) as a reference electrode as well as Platinum electrode as an auxiliary electrode. The polarization study was made by using Potentio-Galvano-Scan (Weaving PGS 81) meter. 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 (Icorr) and the corrosion potential (E_{corr})[10].

RESULTS AND DISCUSSION

The results are presented in Tables 1 to 3 and in Figs.1 to 3. To assess the effect of corrosion of zinc in phosphoric acid, aniline is added as an inhibitor.
I.E. calculated as follows:

$$I.E.\ \% \quad = \quad \frac{W_u - W_i}{W_u} \times 100 \qquad \qquad ...\ (1)$$

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

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Energy of activation (Ea) has been calculated from the slope of log ρ versus 1/T (ρ = corrosion rate, T = absolute temperature) and also with the help of the Arrhenius equation [11].

$$\log \frac{\rho_2}{\rho_1} = \frac{Ea}{2.303R} \ [\ (1/T_1) - (1/T_2)\ ] \qquad\qquad ----- (2)$$

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

The value of heat of adsorption (Q_{ads}) were calculated by the following equation [11].

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

where, θ_1 and θ_2 [$\theta = (Wu - Wi)/Wi$] 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 [12].

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

Where, $\log B = -1.74 - (\Delta Ga\ /\ 2.303\ RT)$ and C is the inhibitor concentration.

The enthalpy of adsorption ($\Delta H^{°}_a$) and entropy of adsorption ($\Delta S^{°}_a$) are calculated using the equation [13].

$$\Delta H^{°}_a = E_a - RT \qquad --------- (5)$$
$$\Delta S^{°}_a = \Delta H - \Delta G\ /T \qquad --------- (6)$$

Table – 1   Corrosion rate (CR) and inhibition efficiency (I.E.) of zinc in 0.01, 0.05 and 0.10 N binary acid mixture (HNO₃ + H₂SO₄) containing aniline as inhibitor for an immersion period of 24 h at 01 ± 1 K.

System	Inhibitor Concentration (%)	(HNO$_3$ + H$_2$SO$_4$)Binary acid mixture concentration					
		0.01 N		0.05 N		0.10 N	
		CR	I.E.	CR	I.E.	CR	I.E.
		mg/dm^2	%	mg/dm^2	%	mg/dm^2	%
A	--	213.7	-	975.2	-	1921.4	-
B	0.10	185.0	13.4	725.9	25.6	1364.6	28.9
	0.50	151.6	29.1	619.4	36.5	1004.3	47.7
	1.00	131.9	38.3	583.7	40.2	763.8	60.3

A = (HNO₃ + H₂SO₄)   B = aniline + (HNO₃ + H₂SO₄)

Corrosion in acid: The rate of corrosion increases with the increase in concentration of binary acid mixture . The corrosion rate was 213.7, 975.2 and 1921.4 mg/dm^2 in 0.01, 0.05 and 0.10 N (HNO₃+ H₂SO₄) mixed acid concentrations respectively for a period of 24 h at 301 ± 1 K as shown in Table -1.

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Table – 2: Effect of temperature on corrosion rate (CR), inhibitive efficiency (IE%), energy of activation (Ea), heat of adsorption (Qads) and free energy of adsorption ($\Delta G°_a$) for zinc in 0.05 N binary acid mixture containing inhibitor.

Inhibitor concentration = 1.0%   Immersion period = 3 h   Effective area of specimen = 0.2935 dm^2

| System	Temperature, K								Mean Ea from eq.1	Ea from Arrhenius Plot	Q$_{abs}$ (kJ mol^{-1})			$\Delta G°_a$(kJ mol^{-1})
	303		313		323		333				303-313	313-323	323-333	
	CR	I.E.	CR	I.E.	CR	I.E.	CR	I.E.						
	mg/dm^2	%	mg/dm^2	%	mg/dm^2	%	mg/dm^2	%	kJ mol^{-1}	kJ mol^{-1}				
A	700.5	-	783.2	-	832.0	-	895.36	-	6.8	7.7	-	-	-	-
B	190.5	72.8	272.8	65.2	380.5	54.3	520.6	41.8	28.1	27.4	-28.1	-38.3	-44.8	-17.6

A = (HNO$_3$ + H$_2$SO$_4$)   B = aniline + (HNO$_3$ + H$_2$SO$_4$)
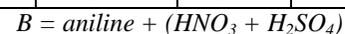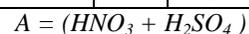
Table – 3: Polarization and inhibition efficiency (IE)of aniline for zinc in (0.01 N HNO$_3$ + 0.01 N H$_2$SO$_4$) binary acid at 301$\pm$ 1 K.

Inhibitor concentration: 1.0 %   Effective area of specimen = 0.047 dm^2

System	E$_{corr}$ mV	CD	Tafel slope (mV/decade)			I.E. (%) from methods	
		I$_{corr}$ mA/cm^2	Anodic	Cathodic	B (mV)	By Weight loss	By polarization
			βa	-βc			
A	-1140	0.30	466.0	200.0	60.9	-	-
B	-1090	0.23	233.0	411.0	64.8	27.2	23.3

A = (HNO$_3$ + H$_2$SO$_4$)   B = aniline + (HNO$_3$ + H$_2$SO$_4$)
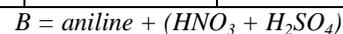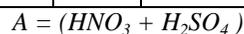
βa = Anodic Tafel constant,   βc = Cathodic Tafel constant.

CD = Corrosion current density from interception of anodic and cathodic lines.

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Fig.1: Plot of log (θ / 1-θ) versus log C for verious nhibitors in (0.05 N HNO₃ + 0.05 N H₂SO₄) mix acid concentration.

Fig : 2 : Arrhenius plots for corrosion of zinc in (0.05 N HNO₃ + 0.05 N H₂SO₄) mix acid in presence of 1.0 % inhibitor concentration.
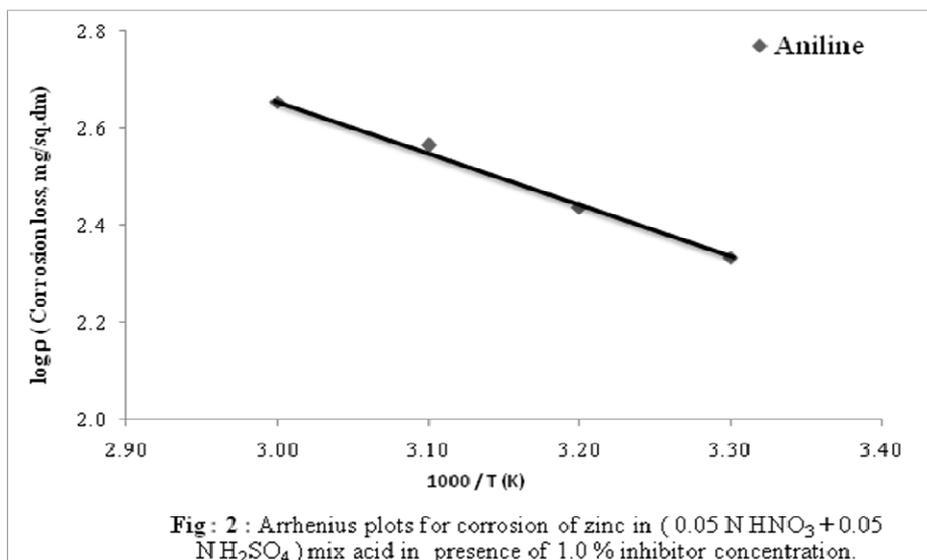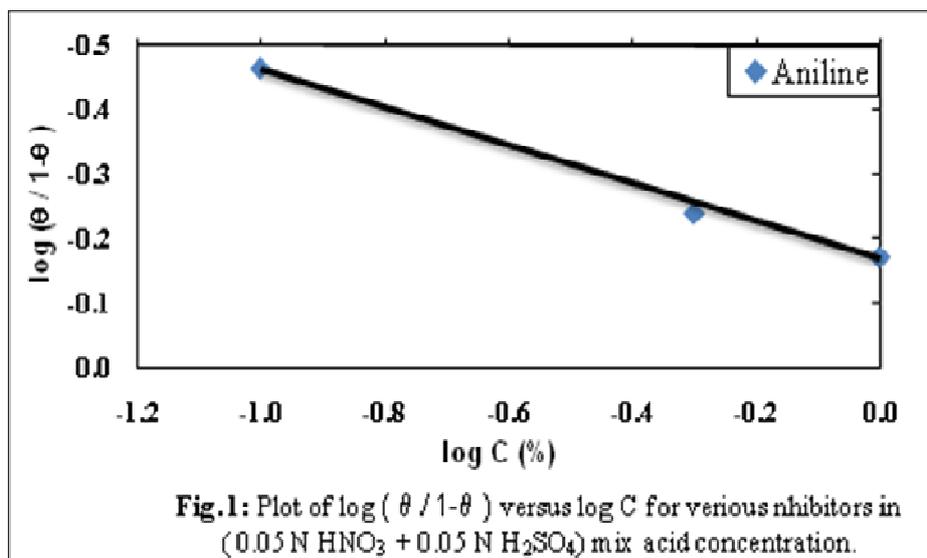
Corrosion in presence of inhibitor: To assess their protective value aniline was added in 0.1, 0.5 and 1.0 % concentration in 0.01, 0.05 and 0.10 N binary acid mixture concentrations for 24h duration period. I.E. of the aniline increases with the inhibitor concentration. In case of aniline in 0.1 N HNO_3 + 0.1 N H_2SO_4 acid mixture the I.E. of aniline was found to be 28.9, 47.7 and 60.3% with respect to 0.1, 0.5 and 1.0% inhibitor concentration respectively [Table -1].

Effect of acid concentration: I.E. increases with the increase in mix acid concentration. At 1.0 % inhibitor concentration, the I.E. of aniline is 38.3, 40.2 and 60.3 % with respect to 0.01, 0.05 and 0.10 N binary acid mixture concentration respectively [Table -1].

Effect of temperature: Table 2 show that as the temperature increases, corrosion rate increases while percentage of I.E. decreases. Mean 'Ea' values were calculated by using eq.2 for zinc in

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0.05 N binary acid mixture is 6.8 kJmol^{-1} while in acid containing inhibitor, the mean Ea values were found to be higher (28.1 kJmol-1) than that of uninhibited system (Table -2). The higher values of mean Ea indicate physical adsorption of the inhibitors on metal surface [14]. The values of Ea calculated from the slope of Arrhenius plot (Fig.2) and using eq.2 were almost similar. From Table 2, it is evident that in all cases, the Q_{ads} values are negative and ranging from –28.1 to –44.8 $^{-1}$. The mean ΔGa value was negative –17.6 kJmol-1. This suggests that they are strongly adsorbed on the metal surface. This statement was supported by the work of Talati and Darji [15]. The enthalpy changes (ΔH$^{°}_{a}$) are positive (25.8 kJmol^{-1}) indicating the endothermic nature of the reaction [16] suggesting that higher temperature favours the corrosion process. The entropy (ΔS$^{°}_{a}$) values are positive (0.15 kJmol^{-1}) confirming that the corrosion process is entropically favourable [17].
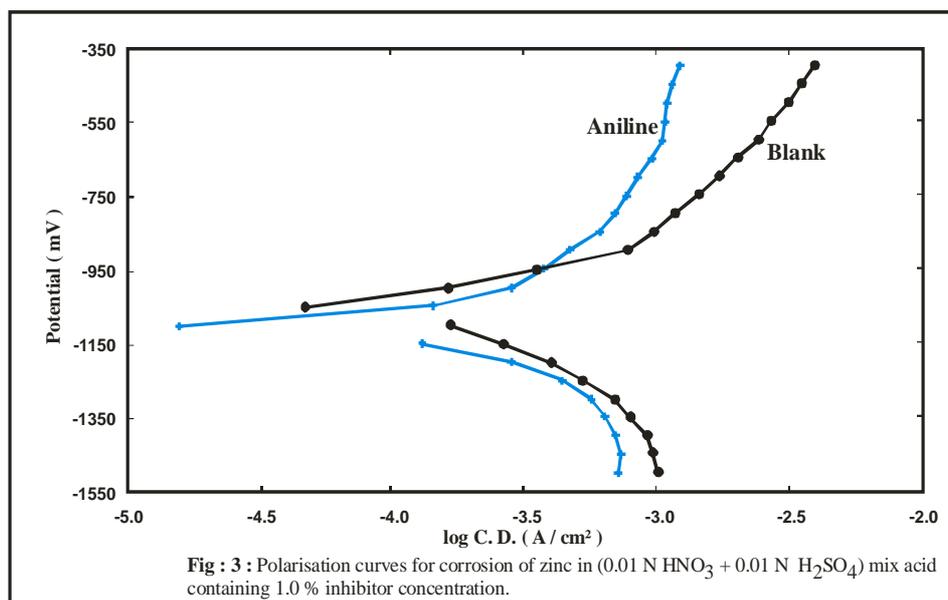

Fig : 3 : Polarisation curves for corrosion of zinc in (0.01 N HNO$_3$ + 0.01 N H$_2$SO$_4$) mix acid containing 1.0 % inhibitor concentration.

Polarization behaviour: Anodic and cathodic galvenostatic polarization data for shown in Table-3. Fig.3 shows polarisation of both anodes as well as cathodes. In almost all the cases, the I.E. from Tafel plots agree well (within ± 4 %) with the values obtained from weight loss data.

Mechanism of corrosion inhibition: Generally, zinc dissolve in (HNO$_3$+ H$_2$SO$_4$) binary acid mixture due to somewhat hydrogen type of attack, the reaction taking place at the microelectrodes of the corrosion cell being represented as,

Zn -------> Zn^{+2} + 2e$^-$ (anodic reaction)   --------(7)
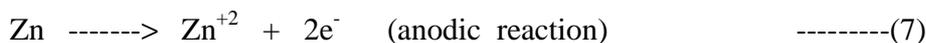
Reduction reaction is indicated by decrease in valence or the consumption of electrodes, as shown by the following equation.

2H$^+$ + 2e$^-$ -------> 2H $_{(ads.)}$ (cathodic reaction)   --------(8)
or   H + H$_3$O$^+$ + e$^-$ ------->   H$_2$ ↑ + H$_2$O   -------(9)

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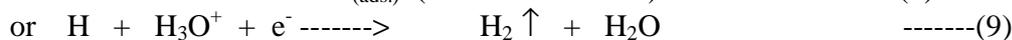
The mechanism of inhibitor of corrosion is believed to be due to the formation and maintenance of a protective film on the metal surface. Further, when log (θ /1-θ) was plotted against log C straight line is obtained in the case of aniline. (Fig.1). This suggests that the inhibitor cover both the anodic as well as cathodic regions through general adsorption following Langmuir isotherm.

It appears that nitrogen atom of amino group (-NH$_2$) in aniline acts as the reaction centre (polar function) because of its higher electron density. This reaction centre forms a monolayer on the zinc surface. Moreover, aniline assumes a small positive charge in acid solutions due to protonation of amino (-NH$_2$) group, higher electron density of the nitrogen atom facilitates the protonation. As the concentration increases the rate of protonation also increases. The successive increase in protonation may be responsible, in many cases, for the enhancement of the I.E.

CONCLUSION

*   As the acid concentration increases the corrosion rate increases.
*   At constant inhibitor concentration, the I.E. increases with increase in the binary acid mixture concentration.
*   As the inhibitor concentration increases I.E. increases while corrosion rate decreses.
*   Addition of inhibitor in corrosive media indicates that as the temperature increases corrosion rate increases while I. E. decreases.

Acknowledgement

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