

INHIBITION OF CORROSION OF ZINC IN (HNO₃ + HCl) ACID MIXTURE BY ANILINE

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Received: 09 February 2015 / Accepted: 21 April 2015 / Published online: 01 May 2015

ABSTRACT

Corrosion of Zinc metal in (HNO₃ + HCl) binary acid mixture and inhibition efficiency of aniline 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. As temperature increases corrosion rate increases while percentage of I.E. decreases. A plot of $\log (1 - \eta)$ versus $\log C$ results in a straight line suggest that the inhibitor cover both the anodic and cathodic regions through general adsorption following Langmuir isotherm. Galvanostatic polarization curves show polarization of both anodes as well as cathodes.

Key words: Corrosion, zinc, (HNO₃ + HCl) binary acid mixture, aniline, inhibition.

1. 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.

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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. Vashi and Diksha Naik [7] has studied aniline as corrosion inhibitor for zinc in phosphoric acid. Vashi et al.[8-9] studied the corrosion inhibition of zinc in ($\text{HNO}_3 + \text{H}_2\text{SO}_4$) and ($\text{HNO}_3 + \text{H}_3\text{PO}_4$) binary acid mixture by aniline. In the present work, the role of aniline as inhibitor for corrosion of zinc in ($\text{HNO}_3 + \text{HCl}$) binary acid mixture has been reported.

2. 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 ($5.0 \times 2.0 \times 0.1$ 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 $301 \pm 1 \text{ K}$ 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 [10]. After cleaning, test specimens were washed with distilled water followed by acetone and dried with air drier. The mean value of corrosion rate 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 ($0.05 \text{ N HNO}_3 + 0.05 \text{ N HCl}$), 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 (E_a), heat of adsorption (Q_{ads}), free energy of adsorption (ΔG_{a}), change of enthalpy (ΔH) and entropy of adsorption (ΔS) were calculated and shown in Table- 2.

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 ($0.01 \text{ N HNO}_3 + 0.01 \text{ N HCl}$). 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 (I_{corr}) and the corrosion potential (E_{corr}) [11].

3. RESULTS AND DISCUSSION

The results are presented in Tables 1 to 3 and in Fig.1. To assess the effect of corrosion of zinc in ($\text{HNO}_3 + \text{HCl}$) acid mixture, aniline is added as an inhibitor.

I.E. calculated as follows:

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

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

W_i is the weight loss of metal in inhibited acid.

Energy of activation (E_a) has been calculated from the slope of \log versus $1/T$ ($=$ corrosion rate, T = absolute temperature) and also with the help of the Arrhenius equation[12].

$$\log \frac{r_2}{r_1} = \frac{E_a}{2.303R} \left[\left(\frac{1}{T_1} \right) - \left(\frac{1}{T_2} \right) \right] \quad \text{-----} (2)$$

where, r_1 and r_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 [12].

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

where, θ_1 and θ_2 [$= (W_u - W_i)/W_i$] are the fractions of the metal surface covered by the inhibitor 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 equation [13].

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

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

The enthalpy of adsorption (ΔH_a°) and entropy of adsorption (ΔS_a°) are calculated using the equation [14].

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

$$\Delta S_a^\circ = \Delta H - \Delta G / T \quad \text{-----} (6)$$

Table 1. Corrosion rate (CR) and inhibition efficiency (I.E.) of zinc in 0.01, 0.05 and 0.10 N (HNO₃ + HCl) binary acid mixture containing aniline as inhibitor for an immersion period of 24 h at 301 ± 1 K.

System	Inhibitor Concentration (%)	(HNO ₃ + HCl) 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	--	176.49	-	1011.75	-	2112.77	-
B	0.10	92.29	47.7	471.27	53.4	923.07	56.3
	0.50	86.43	51.0	402.17	60.3	704.40	66.7
	1.00	71.76	59.3	346.42	65.8	610.17	71.1

A = (HNO₃ + HCl)B = Aniline + (HNO₃ + HCl)

Table 2. Effect of temperature on corrosion rate (CR), inhibitive efficiency (I.E. %), energy of activation (E_a), heat of adsorption (Q_{ads}) and free energy of adsorption (ΔG°_a) for zinc in (0.05 N HNO₃ + 0.05 N HCl) binary acid mixture containing inhibitor.

System	Temperature, K								Mean Ea from eq.2	Ea from Arrhenius Plot	Q _{abs} (kJ mol ⁻¹)		
	303		313		323		333						
	CR	I.E.	CR	I.E.	CR	I.E.	CR	I.E.			303-313	313-323	323-333
	mg/dm ²	%	mg/dm ²	%	mg/dm ²	%	mg/dm ²	%			kJ mol ⁻¹	kJ mol ⁻¹	
A	703.12	-	774.35	-	836.79	-	931.35	-	7.91	7.66	-	-	-
B	227.95	67.6	294.52	62.0	359.32	57.1	454.96	51.2	19.35	19.13	19.43	17.16	21.32

A = HNO₃ + HCl, B = aniline + (HNO₃ + HCl), Inhibitor concentration = 1.0 %, Immersion period = 3 h, Effective area of specimen = 0.2935 dm²

Table 3. Polarization data and inhibition efficiency (IE) of aniline for zinc in (0.01 N HNO₃ + 0.01 N HCl) binary acid mixture at 301± 1 k.

System	E _{corr} mV	CD	Tafel slope (mV/decade)		B (mV)	I.E. (%) from methods	
		I _{corr} mA/cm ²	Anodic	Cathodic		Weight loss	By Polarization
			a	- c			
A	-882	0.210	545.0	1600.0	176.8	-	-
B	-920	0.130	650.0	800.0	155.9	38.1	40.3

A = HNO₃ + HCl, B = aniline + (HNO₃ + HCl), Inhibitor concentration: 1.0%, Effective area of specimen = 0.047 dm²

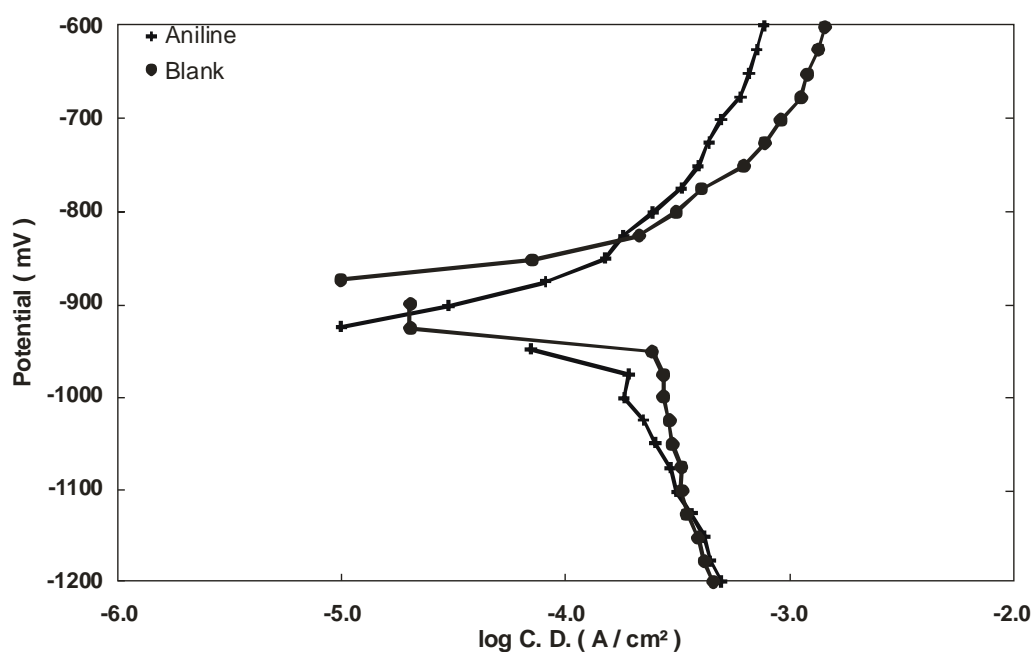


Figure 1 : Polarisation curves for corrosion of zinc in (0.01 N HNO₃ + 0.01 N HCl) mix acid containing 1.0 % inhibitor concentration.

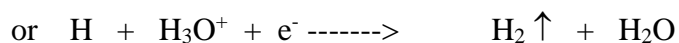
- **Corrosion in acid:** The rate of corrosion increases with the increase in binary acid mixture concentration. The corrosion rate was 176.49, 1011.75 and 2112.77 mg/dm² in 0.01, 0.05 and 0.10 N (HNO₃+ HCl) mixed acid concentrations respectively for a period of 24h at 301 ± 1 K as shown in Table -1.
- **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 24 h duration period (Table -1).

- **Effect of inhibitor concentration:** I.E. of the aniline increases with the inhibitor concentration, e.g. in case of aniline in 0.1 N HNO₃ + 0.1 N HCl acid mixture the I.E. was found to be 56.3, 66.7 and 71.1% 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 59.3, 65.8 and 71.1% 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 0.05 N binary acid mixture is 7.91 kJmol⁻¹ containing inhibitor, which is higher than that of uninhibited system (19.13 kJmol⁻¹) (Table -2). The higher values of mean Ea indicate physical adsorption of the inhibitors on metal surface [15]. The values of Ea calculated from the slope of Arrhenius plot and using eq.2 were almost similar. The Q_{ads} values are negative and ranging from -17.16 to -21.32 kJmol⁻¹ [Table-2]. The mean G_a values were negative in all cases and lie in the range of -12.38 (0.1%) to -17.75 kJmol⁻¹ (1.0 %). This suggests that they are strongly adsorbed on the metal surface. This statement was supported by the work of Talati and Darji [16]. The enthalpy changes (ΔH_a^o) are positive (17.70 kJmol⁻¹) indicating the endothermic nature of the reaction [17] suggesting that higher temperature favours the corrosion process. The entropy (ΔS_a^o) values are positive (0.12 kJmol⁻¹) confirming that the corrosion process is entropically favourable [18].
- **Polarization behaviour:** Anodic and cathodic galvanostatic polarization data for shown in Table-3. Fig.1 shows polarisation of both anodes as well as cathodes. In almost all the cases, the I.E. from Tafel plots agree well (within ± 2%) with the values obtained from weight loss data.
- **Mechanism of corrosion inhibition:** Generally, zinc dissolve in (HNO₃+ HCl) binary acid mixture due to somewhat hydrogen type of attack, the reaction taking place at the microelectrodes of the corrosion cell being represented as,



Reduction reaction is indicated by decrease in valence or the consumption of electrodes, as shown by the following equation.





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 $\log (1 - \theta)$ is plotted against $\log C$ straight lines are obtained in the case of inhibitor used. 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 ($-\text{NH}_2$) 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 ($-\text{NH}_2$) 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.

4. CONCLUSIONS

- 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 decreases.
- As the temperature increases corrosion rate increases while I. E. decreases.

5. ACKNOWLEDGEMENT

The authors are thankful to Department of Chemistry, Navyug Science College, Surat for providing laboratory facilities.

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How to cite this article

Vashi R T, Bhajiwala M H, Prasanna Rathod K N. Inhibition of corrosion of zinc in (HNO_3 + HCl) acid mixture by aniline. J Fundam Appl Sci. 2015, 7(2), 290-297.