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4-Aminoantipyrine as corrosion inhibitor for zinc in phosphoric acid

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ABSTRACT

The corrosion of zinc in phosphoric acid containing 4-aminoantipyrine has been studied at different acid concentrations, inhibitor concentration and temperatures. Corrosion increases with the concentration of acid and the temperature. Inhibition efficiency (I.E.) of 4-aminoantipyrine increases with the concentration of inhibitor and decreases with the increase in concentration of acid. As temperature increases, percentage of inhibition decreases. The plot of log (θ/1-θ) versus log C results in a straight line suggest that the inhibitors cover both the anodic and cathodic regions through general adsorption following Longmuir isotherm. Galvenostatic polarization curves show polarization of both anode as well as cathode.

Key words: Corrosion, zinc, phosphoric acid, 4-aminoantipyrine.

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. Phosphoric acid is a major chemical product, which has uses many important especially in the production of fertilizers. 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. Lin Wang et al. [5] has studied the corrosion inhibition of zinc in phosphoric acid solution by 2 –mercaptobenzimidazole. Sivaraju and Kannan [6] have studied the corrosion of mild steel in 1 N phosphoric acid with plant extract. S. S. Abd el-rehim et al. [7] has studied 4-Aminoantipyrine as an inhibitor of mild steel corrosion in HCl solution. R.T.Vashi et al. [8] studied ethylamines as corrosion inhibitors on zinc in (HNO_3+H_3PO_4). R.T. Vashi et al. [9] studied aniline as corrosion inhibitor for zinc in phosphoric acid. In the present work, the corrosion of zinc by phosphoric acid containing 4-aminoantipyrine has been reported.

MATERIALS AND METHODS

To study the corrosion of zinc in phosphoric acid, weight loss method, temperature effect, potential as well as polarization measurements have been used.

Rectangular specimens (4.50 x 2.03 x 0.17 cm) of zinc having an area of 0.2053 dm^2 were taken and cleaned by buffing and immersed in 0.01, 0.05, 0.10 and 0.15 M Phosphoric acid concentration with and without inhibitor containing 230 ml test solution at 301 + 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 [10]. 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 0.05 M H_3PO_4, the specimens were immersed in 230 ml of corrosive solution and corrosion rate was determined at various temperatures like 303, 313, 323 and 333 K for an immersion period of 3 h with and without inhibitor. From the data, I.E. (in %), energy of activation (Ea) and heat of adsorption (Q_{ads}) were calculated and shown in Table- 2.

For polarization study, metal specimens having an area of 0.0268 dm^2 were immersed in 230 ml corrosive solution without and with 80 mM inhibitor concentration in 0.01 M H_3PO_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 (Ecorr) [11].

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, 4-aminoantipyrine is added as inhibitor.

I.E. has been calculated as follows:

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

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

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].

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

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 [12].

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

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 [13].

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

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

The enthalpy of adsorption (ΔH°_a) and entropy of adsorption (ΔS°_a) are calculated using the equation.

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

Corrosion in acid: The rate of corrosion increases with the increase in acid concentration. The corrosion rate was 365.2, 1887.6, 3580.9 and 5205.2 mg/dm^2 in 0.01, 0.05, 0.10 and 0.15 M H_3PO_4 concentrations respectively for a period of 24 h at 301 ± 1 K as shown in Table -1.
Corrosion in presence of inhibitor: To assess their protective value 4-aminoantipyrine was added in 20, 40, 60 and 80 mM concentration in a solution of 0.01, 0.05, 0.10 and 0.15 M H_3PO_4 acid for 24 h duration period (Table -1).

Effect of inhibitor concentration: At constant acid concentration, the I.E. of the 4-aminoantipyrine increases with the inhibitor concentration, e.g. in case of 4-aminoantipyrine in 0.01 M H_3PO_4 the I.E. was found to be 88.0, 90.7, 94.7 and 97.3 % with respect to 20, 40, 60 and 80 mM inhibitor concentration respectively [Table -1].

Effect of acid concentration: At constant inhibitor concentration, the I.E. decreases with the increase in acid concentration. At 80 mM inhibitor concentration, the I.E. of 4-aminoantipyrine is 97.3, 95.9, 78.9 and 59.7 % with respect to 0.01, 0.05, 0.10 and 0.15 M acid concentration respectively [Table -1].

Effect of temperature: As the temperature increases, corrosion rate increases while percentage of I.E. decreases [Table-2]. Mean 'Ea' values were calculated by using eq.2 for zinc in 0.05 M H_3PO_4 is 12.7 $kJmol^{-1}$ while in acid containing inhibitor, the mean Ea values are found to be higher 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 are almost similar. From Table 2, it is evident that in all cases, the Q_{ads} values are negative and ranging from –9.4 to –41.7 $kJmol^{-1}$.The mean ΔGa values are negative almost in all cases and lie in the range of –23.2 (20 mM) to –26.5 $kJmol^{-1}$ (80 mM). 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 (15.3 to 52.2 $kJmol^{-1}$) indicating the endothermic nature of the reaction [16] suggesting that higher temperature favours the corrosion process. The entropy (ΔS°_a) values are positive (0.13 to 0.26 $kJmol^{-1}$) confirming that the corrosion process is entropically favourable [17].

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

Mechanism of corrosion inhibitor: Generally, zinc dissolve in phosphoric acid solution 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)

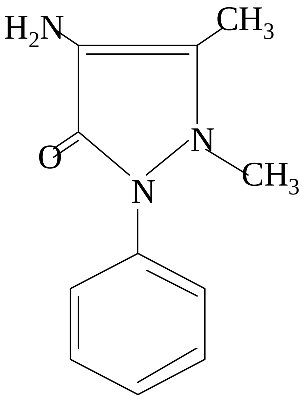
Reduction reaction is indicated by decrease in valence or the consumption of electrodes, as shown by the following equation.

$2H^+$ + $2e^-$ -------> $2H_{(ads.)}$ (cathodic reaction) --------(8)

or $H + H_3O^+ + e^-$ -------> $H_2\uparrow + H_2O$
or $O_2 + 4H^+ + 4e^-$ -------> $2H_2O$

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) is plotted against log C straight lines are obtained (Fig.1) 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.

Heterocyclic compound like 4-aminoantipyrine has low pka value (4.94) and it has a lower tendency of the dissociation and hence exhibited less inhibition than aliphatic amines.



4-aminoantipyrine is a weaker base than primary aliphatic amines. In 4-aminoantipyrine due to resonance, the lone pair of electrons on the nitrogen atom is less available for co-ordination with a proton than that in aliphatic amines. Due to presence of methyl and large molecule like benzene on heterocyclic ring, electron density of nitrogen becomes decreases, so basicity decreases due to steric effect.

Table – 1 . Corrosion rate (CR) and inhibition efficiency (I.E.) of zinc in 0.01, 0.05, 0.10 and 0.15 M H_3PO_4 acid containing 4-aminoantipyrine as inhibitor for an immersion period of 24 h at 301 ± 1 K.

System	Inhibitor Concentration mM	Acid concentration							
		0.01 M		0.05 M		0.10 M		0.15 M	
		CR mg/dm^2	I.E. %	CR mg/dm^2	I.E. %	CR mg/dm^2	I.E. %	CR mg/dm^2	I.E. %
A	--	365.2	-	1887.6	-	3580.9	-	5205.2	-
B	20	43.8	88.0	1007.9	46.6	2804.7	21.7	4367.7	16.1
	40	34.1	90.7	370.1	80.4	2079.2	41.9	3613.0	30.6
	60	19.5	94.7	112.0	94.1	1416.9	60.4	2785.2	46.5
	80	9.7	97.3	77.9	95.9	754.7	78.9	2098.6	59.7

A = H_3PO_4 *B = H_3PO_4 + 4-aminoantipyrine*

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 ($\Delta G°_a$) for zinc in 0.05 M H_3PO_4 acid containing inhibitor.

Inhibitor concentration = 80 mM *Immersion period = 3 h* *Effective area of specimen = 0.2053 dm^2*

System	Temperature, K								Mean E_a From Eq(1) kJ mol^{-1}	E_a From Arrhenius Plot kJ mol^{-1}	Q_{abs} (kJ mol^{-1})		
	303		313		323		333				303-313	313-323	323-333
	CR mg/dm^2	I.E. %	CR mg/dm^2	I.E. %	CR mg/dm^2	I.E. %	CR mg/dm^2	I.E. %					
A	832.6	-	993.3	-	1193.0	-	1314.7	-	12.7	15.3	-	-	-
B	14.6	98.2	29.2	97.1	43.8	96.3	53.6	95.9	35.6	36.0	-41.7	-19.2	-9.4

A = H_3PO_4 *B = H_3PO_4 + 4-aminoantipyrine*

Table-3. Polarisation data and inhibition efficiency (I.E.) of 4-aminoantipyrines for zinc 0.01 M H_3PO_4 at 301 ± 1 K.

Inhibitor concentration: 80 mM Effective area of specimen = 0.0268 dm^2

System	E_{corr} mV	CD I_{corr} mA/cm^2	Tafel slope (mV/decade)		B (mV)	I.E. (%) from methods	
			Anodic β_a	Cathodic $-\beta_c$		By Weight loss	By polarization
A	-940	0.560	88	117	22	-	-
B	-990	0.030	340	260	64	97.3	94.6

A = H_3PO_4 *B = H_3PO_4 + 4-aminoantipyrine*

β_a = Anodic Tafel constant, *β_C = Cathodic Tafel constant.*

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

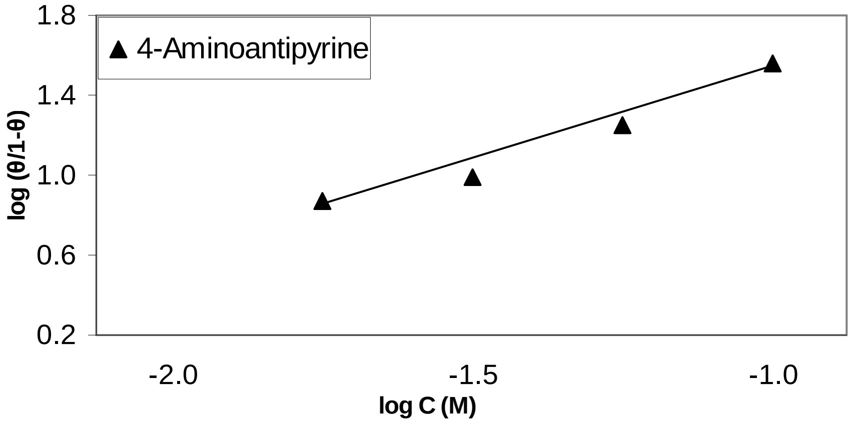


Fig. 1 : Plot of log (θ/1-θ) versus log C for inhibitors in 0.01 M phosphoric acid concentration.

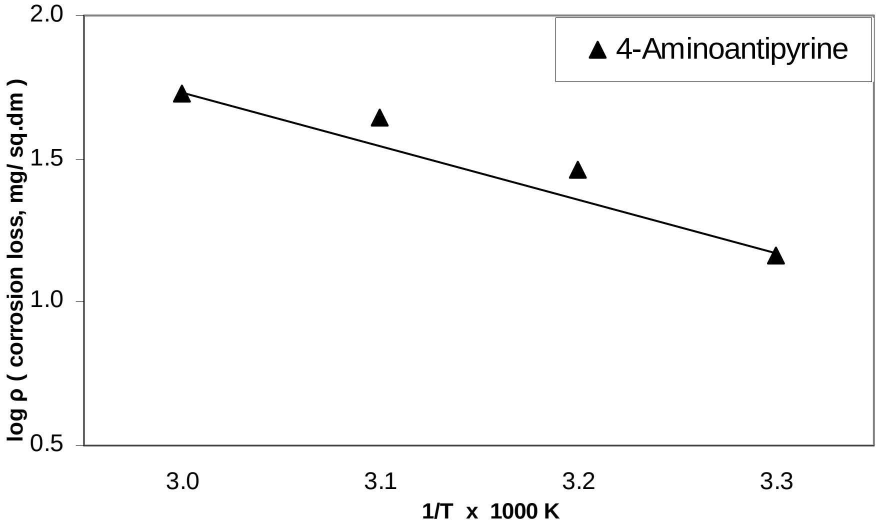


Fig. 2 : Arrhenius plots for corrosion of zinc in 0.05 M phosphoric acid in presence of 80 mM inhibitor concentration.

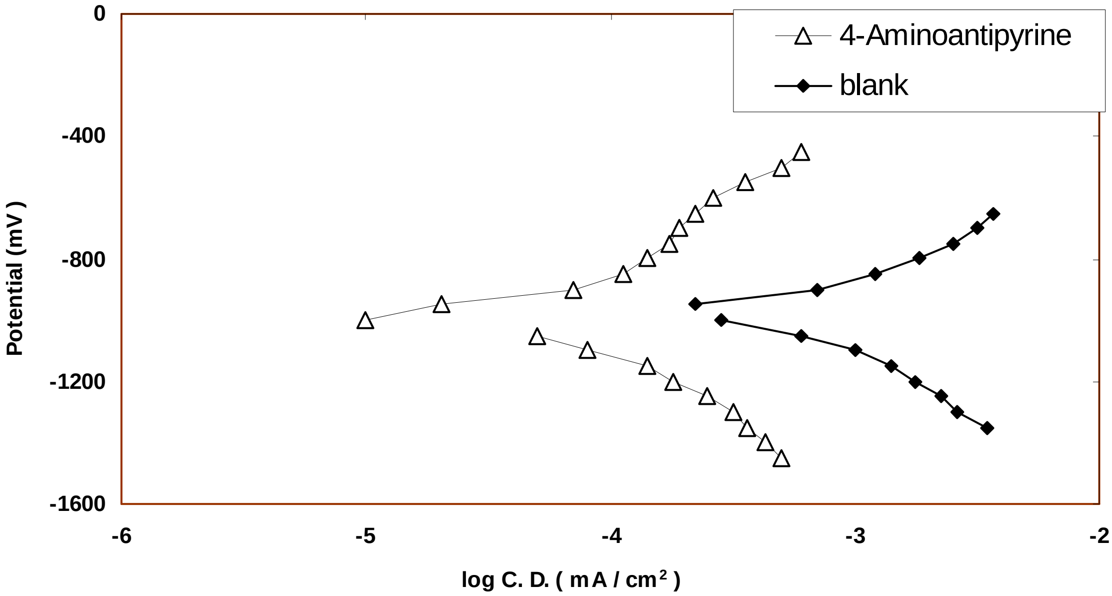


Fig : 3 : Polarisation cruves for corrosion of zinc in 0.01 M phosphoric acid containing 80 mM inhibitors .

CONCLUSION

* As the acid concentration increases the corrosion rate increases.
* I.E. of all inhibitor decreases as the concentration of acid increases.
* As the inhibitor concentration increases I.E. increases and corrosion rate decreases.
* Addition of inhibitor in corrosive media indicates that as the temperature increases corrosion rate increases while I. E. decreases.

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