



Hexamine as Corrosion Inhibitors for Zinc in Phosphoric Acid

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Abstract: The corrosion of zinc in phosphoric acid containing hexamine has been studied at different acid concentrations, inhibitor concentration and temperatures. Corrosion increases with the concentration of acid and the temperature. The inhibition efficiency (IE) of hexamine increases with the concentration of inhibitor. The IE decreases with the increase in concentration of acid. As temperature increases, percentage of inhibition decreases. The plot of $\log (\theta/1-\theta)$ versus $\log C$ results in a straight line suggest that the inhibitors 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.

Keywords: Corrosion, Zinc, Phosphoric acid, Hexamine.

Introduction

The problem of corrosion is of considerable importance, nowadays 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 inhibitors¹⁻³. 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-mercapto benzimidazole. Vashi *et al.* studied ethanolamines⁶ and ethylamines⁷ as corrosion inhibitors for zinc in phosphoric acid. Hexamine was reported as effective corrosion inhibitor for various metals in acid.⁸⁻¹⁰ In the present work, the corrosion of zinc by phosphoric acid containing isomer of hexamine has been reported.

Experimental

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 0.205 dm² were cleaned by buffing and immersed in 0.01, 0.05, 0.10 and 0.15 M acid concentration with and without inhibitor containing 230 mL test solution at 301±1 K for 24 h duration period. After the test, specimens were cleaned by 10% chromic acid solution having 0.2% BaCO₃ for a period of about 2 minutes¹¹. After cleaning, test specimens were washed with distilled water followed by acetone and dried with air drier. Triplicate experiments were performed in each case and the mean value of weight loss was reported in form of corrosion rate. All chemicals used were of AR grade. The test solution was prepared in double distilled water.

To study the effect of temperature on corrosion of zinc in 0.05 M H₃PO₄, the specimens were immersed in 230 mL of corrosive solution and corrosion rate was determined at solution temperature of 303, 313, 323 and 333 K for an immersion period of 3 h with and without inhibitors.

For polarization study, metal specimens having an area of 0.0268 dm² were immersed in 230 ml corrosive solution without and with 80 mM inhibitor concentration in 0.01 M H₃PO₄. 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). Tafel lines correspondingly. The intersect point of cathodic and anodic Tafel lines gives the corrosion current (I_{corr}) and the corrosion potential (E_{corr})¹².

IE has been calculated as follows:

$$\text{IE (\%)} = \{(W_u - W_i) / W_u\} \times 100 \quad (1)$$

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 $\log \rho$ versus $1/T$ (ρ = corrosion rate, T = absolute temperature) and also with the help of the Arrhenius equation¹³.

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

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 equation¹³.

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

Where, θ_1 and θ_2 [$\theta = (W_u - W_i)/W_i$] 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 (ΔG_a) were calculated with the help of the following equation¹⁴.

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

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.

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

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

Results and Discussion

The results are presented in Tables 1 & 2 and Figures 1 & 2. To assess the effect of corrosion of zinc in phosphoric acid, hexamine was added as inhibitor.

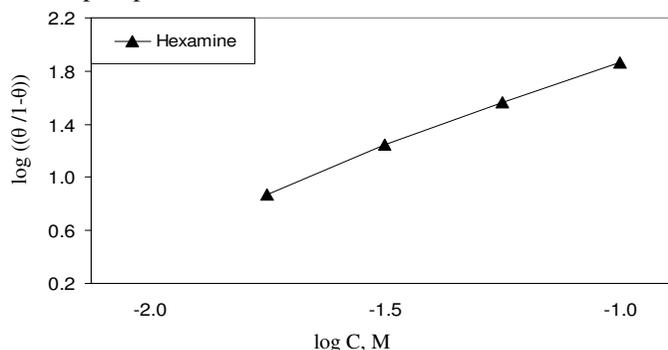


Figure 1. Plot of $\log(\theta / (1-\theta))$ versus $\log C$ for hexamine in 0.01 M phosphoric acid concentration

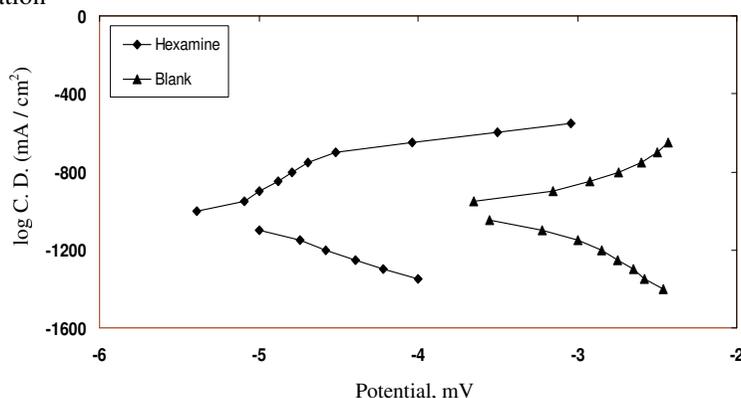


Figure 2. Polarisation curves for corrosion of zinc in 0.01 M phosphoric acid containing 80 mM inhibitors

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.

Effect of inhibitor concentration

The IE of the hexamine increases with the inhibitor concentration, *e.g.* in case of hexamine in 0.01 M H_3PO_4 the IE was found to be 88.0, 94.7, 97.3 and 98.7% with respect to 20, 40, 60 and 80 mM inhibitor concentration respectively (Table 1).

Effect of acid concentration

The IE decreases with the increase in acid concentration. At 80 mM inhibitor concentration, the IE of hexamine was 98.7, 97.4, 93.3 and 88.5% with respect to 0.01, 0.05, 0.10 and 0.15 M acid concentration respectively Table 1.

Table 1. Corrosion rate (CR) and inhibition efficiency (IE) of zinc in 0.01, 0.05, 0.10 and 0.15 M H_3PO_4 acid containing hexamine as inhibitors for an immersion period of 24 h at 301 ± 1 K

System	Conc. of Inhibitor mM	Acid concentration, M							
		0.01		0.05		0.10		0.15	
		CR mg/dm ²	IE %						
A	--	365.2	-	1887.6	-	3580.9	-	5205.2	-
B	20	43.8	88.0	628.1	66.7	1918.5	46.4	3160.1	39.3
	40	19.5	94.7	131.5	93.0	1343.9	62.5	2215.5	57.4
	60	9.7	97.3	68.2	96.4	516.1	85.6	1363.4	73.8
	80	4.9	98.7	48.7	97.4	238.6	93.3	598.9	88.5

A = H_3PO_4 B = H_3PO_4 + Hexamine

Effect of temperature

In 0.05 M H_3PO_4 corrosion rate increases as temperature increases *i.e.* corrosion rate was 832.6, 993.3, 1193.0 and 1314.7 mg / dm² for 3 h immersion period. Inhibition efficiency was found to decrease with temperature. The IE for hexamine at 80 mM concentration was 98.8, 98.5, 98.3 and 97.7 % at 303, 313, 323 and 333 K respectively for 3 h immersion period.

Value of E_a calculated from eq.2 was found to be higher (30.8 kJ mol⁻¹) than that of uninhibited system (12.7 kJ mol⁻¹). This suggests that the presence of reactive centres on the inhibitor can block the active sites for corrosion, resulting¹⁵ in an increase in E_a . The values of E_a calculated from the slope of Arrhenius plot and using eq.2 are almost similar. It was evident that in all cases, the Q_{ads} values were negative and ranging from -28.0 to -9.3 kJ mol⁻¹. Oguzie¹⁶ explained that the negative values of Q_{ads} also signify that the degree of surface coverage decreased with rise in temperature.

The mean ΔG_a values was -28.2 kJ mol⁻¹. This suggests that they are strongly adsorbed on the metal surface. This statement was supported by the work of Talati and Darji¹⁷. The enthalpy changes (ΔH_a) was positive (28.2 kJ mol⁻¹) indicating the endothermic nature of the reaction¹⁸ suggesting that higher temperature favours the corrosion process. Adeyen¹⁹ described that if the $\Delta H < 10$ kJ mol⁻¹ the adsorption is probably physisorption and if the $\Delta H > 10$ kJ mol⁻¹ values indicate that the hexamine strongly adsorbed on zinc is chemisorption. The entropy (ΔS_a°) values was positive (0.18 kJ mol⁻¹) confirming that the corrosion process is entropically favourable²⁰.

Polarization behaviour

Anodic and cathodic galvanostatic polarization curves for zinc in 0.01 M H_3PO_4 acid, alone and containing 80 mM concentration of hexamine is shown in Figure 2. The curves show polarization of both, the cathodes as well as anodes. IE calculated from corrosion current obtained by extrapolation of the cathodic and anodic Tafel lines are given in Table 2. The IE calculated from Tafel plots agree well (within $\pm 0.2\%$) with the values obtained from weight loss data.

Table 2. Polarisation data and inhibition efficiency (IE) of hexamine for zinc in 0.01 M H_3PO_4 at 301 ± 1 K, Inhibitor concentration: 80 mM, Effective area of specimen = 0.0268 dm²

System	E_{corr} mV	CD	Tafel slope (mV/decade)		IE, % from methods	
		I_{corr} mA/cm ²	Anodic	Cathodic	B, mV	Weight loss By polarization
			β_a	$-\beta_c$		
A	-940	0.560	88	117	22	-
B	-995	0.006	415	250	68	98.7

A = H_3PO_4 , B = H_3PO_4 + Hexamine, β_a = Anodic Tafel constant, β_c = Cathodic Tafel constant,

$\beta = (\beta_a \times \beta_c) / [2.3 (B_a + \beta_c)]$ CD = Corrosion current density from intersection of anodic and cathodic lines

Mechanism of corrosion

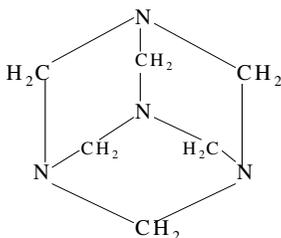
Generally, zinc dissolve in phosphoric acid solution due to somewhat hydrogen type of attack, the reaction taking place at the microelectrodes of the corrosion cell being represented as,



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 $\log (\theta / 1-\theta)$ is plotted against $\log C$ straight line was obtained (Figure 1). This suggests that the inhibitor cover both the anodic as well as cathodic regions through general adsorption following Langmuir adsorption isotherm.



Scheme 1. Structure of hexamine

Macro molecular size and higher number²¹ of *N*-atoms of hexamine (Scheme 1) might have covered almost all active source of zinc. Four nitrogen atom of the hexamine having high electron density must have functioned as the reaction center²² and the hexamine molecules might have been chemisorbed to form a thin monolayer on the zinc surface.

Hexamine (hexamethylenetetramine) consists of four nitrogen atoms and six CH₂ groups. Because of the presence of three nitrogen atoms electrons are disposed easily in the ring and therefore it is expected to be an effective inhibitor. The inhibitor action can be accounted by the interaction of lone pair of electrons in the nitrogen atom on the positively charged metal surface. The presence of six methylene groups also helps to lead to an enhancement of electron density at the nitrogen atom, which enhances its adsorption on the metal surface. This in turn leads to an increase in the value of IE.

The protective effect of the inhibitor is probably due to formation of an insoluble film²³. Hence the mechanism of the inhibitive action is possibly due to the blocking of anodic and cathodic sites by adsorption, which enables the formation of a protective insoluble film.

Conclusion

- As the acid concentration increase the corrosion rate increases and IE of inhibitor decreases.
- At all concentration of acid, as the inhibitor concentration increases IE increases and corrosion rate decreases.
- Mean value of *E_a* in inhibited acid are higher than the value of *E_a* in acid only, which shows that chemisorptions of the inhibitor molecule.

- As the temperature increases corrosion rate increases while IE decreases.
- Hexamine act as mixed type of inhibitor.

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References

1. Champaneri V A and Vashi R T, *Asian J Chem.*, 2010, **22(3)**, 1799-1807.
2. Vashi R T, Bhajiwala H M and Desai S A, *Oriental J Chem.*, 2009, **25(3)**, 555-560.
3. Unni V K V and Ramachar J C, *J Electrochem Soc.*, 1970, **10**, 809.
4. Hackerman N and Hurd R M, Proc 1st Int Congr Met Corros., Butterworths, U K. 1961, 166-172.
5. Wang Lin, Pu Jian-Xin and Luo Hui-Chun, *Corros Sci.*, 2003, **45(4)**, 677-683.
6. Vashi R T, Naik Diksha and Bhajiwala H M, *Bull Electrochem.*, 2005, **21(9)**, 415-421
7. Vashi R T and Naik Diksha, *Trans SAEST*, 2006, **41**, 68-73.
8. Putilova I N, *Zhur. Fis Khim.*, 1959, **33**, 26.
9. Mehta G N, *Bull Electrochem.*, 1988, 4(2), 111.
10. Mehta G N, *Bull Electrochem.*, 1988, **4(2)**, 111.
11. Stroud E G, *J Appl Chem.*, 1951, **1**, 93.
12. Uhlig H H, *Corrosion Corrosion Control*, Wiley USA, 1967, 18.
13. Subramanian N and Ramakrishnaiah K, *Indian J Tech.*, 1970, **8**, 369.
14. Abdel A M S and Saied A E L, *Trans SAEST*, 1981, **16**, 197.
15. Abdel Aal M S and Morad M S, *Br Corr J.*, 2001, **36**, 253.
16. Oguzie E E, *Mater Chem Phys.*, 2004, **87**, 212.
17. Talati J D and Darji J M, *J Indian Chem Soc.*, 1988, **LXV**, 94 -99.
18. Agrawal A K, Singhal D, Chadha S and Gulati A, *Trans SAEST*, 2003, **38**, 111-114.
19. Adeyen O O, *Bull Electrochem.*, 2005, **21**, 363.
20. Issa R M, El-Sonbati A Z, El-Bindary A A and Kera H M, *Eur Polym J.*, 2002, **38**, 561.
21. Finar I L, *Organic Chemistry*, Vol II, ELBS and Longman, 1959, 153.
22. Ayers R C and Hackerman N, *J Electrochem Soc.*, 1963, **110**, 507.
23. Rawat N S and Singh A K, *Bull. Electrochem.*, 1987, **3**, 7.

