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Research Article

Corrosion Inhibition and Adsorption Properties of 1-Methyl Imidazole on Mild Steel in Binary Acid Mixture of (HNO_3+HCl)

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ABSTRACT

1-Methyl imidazole (N-Methyl imidazole) is tested as corrosion inhibitor on Mild Steel in (HNO_3 + HCl) binary acid mixture by different methods. The inhibition action depends on the chemical structure, concentration of the inhibitor and concentration of the corrosive medium.Many N-hetero cyclic compounds with polar groups and/or π electrons are acting as efficient corrosion inhibitors in acidic solutions. Results obtained from weight loss method, temperature effect method and polarization technique revealed that N-hetero cyclic compound 1-Methyl imidazole act as good inhibitor on Mild Steel in (HNO_3 + HCl) binary acid mixture. Corrosion rate increases with rise in temperature and with rise in concentration of mix acid. Inhibition efficiency increases with rise in the concentration of inhibitor. Different values like activation energy, heat of adsorption, enthalpy of adsorption, entropy of adsorption etc. were calculated.

Key Words: Corrosion, Mild Steel, Nitric acid, Hydrochloric acid , 1-Methyl imidazole.

INTRODUCTION

Mild steel is widely employed in industry because of its low cost and availability. Acid solutions are generally used for the removal of undesirable scale and rust in several industrial processes. Inhibitors are generally used to control metal dissolution. The inhibition of corrosion in acid solutions can be secured by the addition of a variety of organic compounds and has been investigated by several workers[1-4]. Most of the well known acid inhibitors are organic -compounds containing O, S and/or N atoms[5,6]. Aliphatic amines, heterocyclic amines, aromatic amines and phenolic compounds have been extensively investigated as corrosion inhibitors[7-13]. In this paper, the role of 1-Methyl imidazole in inhibiting the corrosion of Mild steel in (HNO_3 + HCl) binary acid mixture has been reported.

MATERIALS AND METHODS

The mild steel used had the following chemical composition (0.025% C, 0.013% Si, 0.010% S, 0.014% P, 0.210% Mn, 0.008% Ni, 0.007%Cr, 0.002% Mo, 0.006% Cu, 0.059% Al and balance Fe).

Rectangular specimens of Mild Steel of size (5.10 cm x 2.04 cm x 0.12 cm thickness) with a small hole of ~2 mm diameter just near one end of the specimen were used for the determination of corrosion rate. All the specimens were cleaned by buffing and wrapped in plastic bag to avoid atmospheric corrosion. A specimen, suspended by a glass hook, was immersed in 200 ml of three different concentration test solution at 300 ± 1 K for 24 h. After the test, the specimens were cleaned by using wash solution prepared by adding 2% Sb_2O_3 (antimony Oxide), 5% $SnCl_2$ (stannous chloride) in concentrated HCl (100 ml) at room temperature with constant stirring about 15-20 mins[14,15], washed with water, acetone and dried in air.

To study the effect of temperature on corrosion of Mild Steel in binary acid mixture (0.05 M HNO_3 +0.05 M HCl), the specimens were immersed in 200 ml of corrosive solution and corrosion rate was determined at various temperatures e.g. at 300, 310, 320 and 330 K for an immersion period of 3hr with and without inhibitor. From the data, I.E.(in %), energy of activation (Ea), heat of adsorption (Qads), free energy of adsorption (ΔG^0ads), change of enthalpy (ΔH^0ads) and entropy of adsorption (ΔS^0ads) were calculated.

For polarization study, metal specimen having an area of 0.0025 dm^2 was used. Corrosion behavior of Mild steel samples were tested in (0.05M HNO_3 + 0.05M HCl) &

(0.05M HNO_3 + 0.05M HCl) + 1-Methyl imidazole solutions using potentiostat Gamry Reference 600. Corrosion cell which consists of Calomel electrode as reference electrode, graphite rod as counter electrode and test samples as working electrode.

RESULTS AND DISCUSSION

The results are given in Tables 1 to 4. To assess the effect of corrosion of Mild steel in (HNO_3+ HCl) binary acid mixture, 1-Methyl imidazole was added as an inhibitor. I.E. was calculated by the following formula.

$$\text{I.E. (\%)} = [(W_u - W_i) / W_u] \times 100 \quad \text{------------- (1)}$$

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

Wi is the weight loss of metal in inhibited acid.

Energy of activation (Ea) has been calculated with the help of the Arrhenius equation [16].

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

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

The values of heat of adsorption (Qads) were calculated by the following equation [16].

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

Where, θ_1 and θ_2, [θ = (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 (ΔG^0ads) were calculated with the help of the following equation [17].

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

Where, log B = –1.74 – (□G^0a / 2.303 RT) and C is the inhibitor concentration.

The enthalpy of adsorption (ΔH^0ads) and entropy of adsorption (ΔS^0ads) are calculated using the following equation [18].

$$\Delta H^0ads = Ea - RT \quad \text{----- (5)}$$

$$\Delta S^0ads = [\Delta H^0ads - \Delta G^0ads] / T \quad \text{---------(6)}$$

Table-1 shows that corrosion rate increases with increase in concentration of mix acid while % of I.E. decreases. Also as concentration of inhibitor increases corrosion rate decreases while % of I.E. increases.

Table-2 shows that as the temperature increases, Corrosion rate increases while % of I.E. decreases. Mean Ea values were calculate by using equation 2 for mild steel in 0.05 M Binary acid mixture is 27.532 $KJMol^{-1}$ while acid containing inhibitors the mean Ea values were 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.

From Table-3 it is evident that the values of Qads were found to be negative and lies in the range of –51.61 to –12.12 $KJMol^{-1}$. Oguzje explained that the degree of surface coverage decreased with rise in temperature[19]. The higher negative values of heat of adsorption also show that the inhibition efficiency decreased with a rise in temperature**.**

From Table-3 the negative mean ΔG^0ads values ranging from-16.93 to -12.07 $KJMol^{-}$indicate that the adsorptions of the inhibitors are spontaneous. The most efficient inhibitor shows more negative ΔG^0ads value. This suggests that they are strongly adsorbed on the metal surface. The values of enthalpy changes (ΔH) were positive indicating the endothermic nature of the reaction[20] suggesting that higher temperature favors the corrosion process. The entropy (ΔS) is positive confirming that the corrosion process is entropically favorable[21].

Polarization behaviour: Anodic and cathodic polarization curve without inhibitor shown in fig -1 and with inhibitors shown in fig - 2 indicates polarization of both anodes and cathodes. I.E. calculated from corrosion current obtained by extrapolation of the cathodic and anodic Tafel constants are given in Table 4. The I.E. obtained from weight loss and polarization measurement were in fairly good agreement.

Mechanism: The mechanism of inhibition of corrosion is generally believed to be due to the formation and maintenance of a protective film on the metal surface. Mild Steel dissolves in (HNO_3 + HCl) acid mixture.

CONCLUSION

The present study shows that 1-Methyl imidazole is an efficient inhibitor for the corrosion of Mild Steel in (HNO_3 + HCl) binary acid mixture. It appears that an efficient inhibitor is characterized by negative value of free energy of adsorption, positive value of entropy of adsorption and higher (more negative) heat of adsorption.Corrosion rate increases with increase in the concentration of binary acid mixture. Inhibition efficiency increases with increase in concentration of 1-Methyl imidazole.

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Table - 1

Corrosion Rate (CR) and Inhibition efficiency (I.E.) of Mild Steel in 0.01M, 0.05M, and 0. 1M binary acid mixture (HNO_3 + HCl) containing 1-Methyl imidazole as inhibitors for an immersion period of 24 hr at 300 ± 1 K

System	Inhibitor Conc. (%)	Acid Concentration					
		0.01 M		0.05 M		0.1 M	
		CR mg/dm^2	IE %	CR mg/dm^2	IE %	CR mg/dm^2	IE %
A		441.96		1611.61		2772.32	
B	0.1	241.07	45.45	1267.86	21.32	2285.71	17.55
	0.5	17.86	95.96	897.32	44.32	1852.68	33.17
	1.0	4.46	98.99	183.03	88.64	1522.32	45.08

A = (HNO_3 + HCl), B = (HNO_3 + HCl) + 1-Methyl imidazole.

Table -2

Effect of temperature on corrosion rate (CR), inhibitive efficiency (IE %), energy of activation (Ea) for Mild Steel in 0.05 M binary acid mixture containing inhibitor.

System	Inhi. Con. In %	Temperature								Energy of Activation (Ea) $KJMol^{-1}$			
		300 K		310 K		320 K		330 K					
		CR mg/ dm^2	IE %	CR mg/dm^2	IE %	CR mg/dm^2	IE %	CR mg/dm^2	IE %	300-310 K	310-320K	320-330 K	Mean Ea
1	2	3	4	5	6	7	8	9	10	11	12	13	14
A		491.1		687.5		1054		1344		26.02	35.21	21.36	27.53
B	0.1	398.7	18.82	574.1	16.49	901.8	14.4	1172	12.79	28.20	37.25	23.01	29.49
	0.5	147.3	70.00	234.4	65.91	401.8	61.9	564.7	57.97	35.91	44.46	29.89	36.75
	1.0	17.9	96.36	40.2	94.16	102.7	90.3	218.8	83.72	62.70	77.40	66.41	68.84

A = (HNO_3 + HCl), B = (HNO_3 + HCl) + 1-Methyl imidazole.

Table -3

Heat of adsorption (Qads) and free energy of adsorption (ΔG^0ads) for Mild Steel in 0.05 M binary acid mixture containing inhibitor.

System	Inhibitor Conc. %	Heat of Adsorption Qads $KJmol^{-1}$			Free Energy of Adsorption ΔG^0ads $KJMol^{-1}$				
		300-310 K	310-320 K	320-330 K	300 K	310 K	320 K	330K	Mean ΔG^0ads
A	-	-	-	-	-	-	-	-	-
B	0.1	-12.41	-13.15	-12.12	-12.09	-12.08	-12.05	-12.05	-12.07
	0.5	-14.54	-14.50	-14.23	-13.84	-13.81	-13.79	-13.78	-13.81
	1.0	-38.35	-45.78	-51.61	-18.17	-17.49	-16.58	-15.49	-16.93

A = (HNO_3 + HCl), B = (HNO_3 + HCl) + 1-Methyl imidazole.

Table - 4
Polarization data and Inhibition efficiency (IE %) of 1-Methyl imidazole for Mild Steel in (0.05 M HNO_3 + 0.05 M HCl) at 300 ± 1 K with 1% inhibitor concentration

System	Icorr (mA/sq.cm)	Ecorr (mV)	Tafel Slope (mV/decade)			IE(in %) from methods	
			Anodic βa	Cathodic -βc	B mV	By polarization	Weight Loss
A	0.04310	-520.0	72.4	128.6	20.14		
B	0.00407	-590.0	63.3	92.8	64.99	90.56	88.64

A = (HNO_3+HCl), B = (HNO_3+HCl) + 1-Methyl imidazole, βa = Anodic Tofel constant,
βc = Cathodic Tofel constant, **B(mV) = βa* βc/2.3(βa+ βc)**

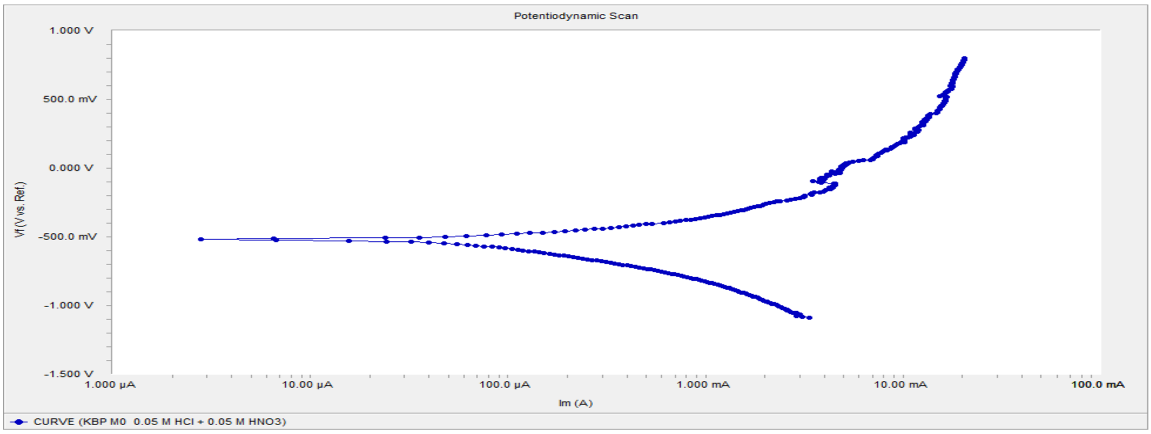

Figure-1
Polarization curve for corrosion of Mild Steel in (0.05 M HNO_3 + 0.05 M HCl) mix acid in absence of inhibitor

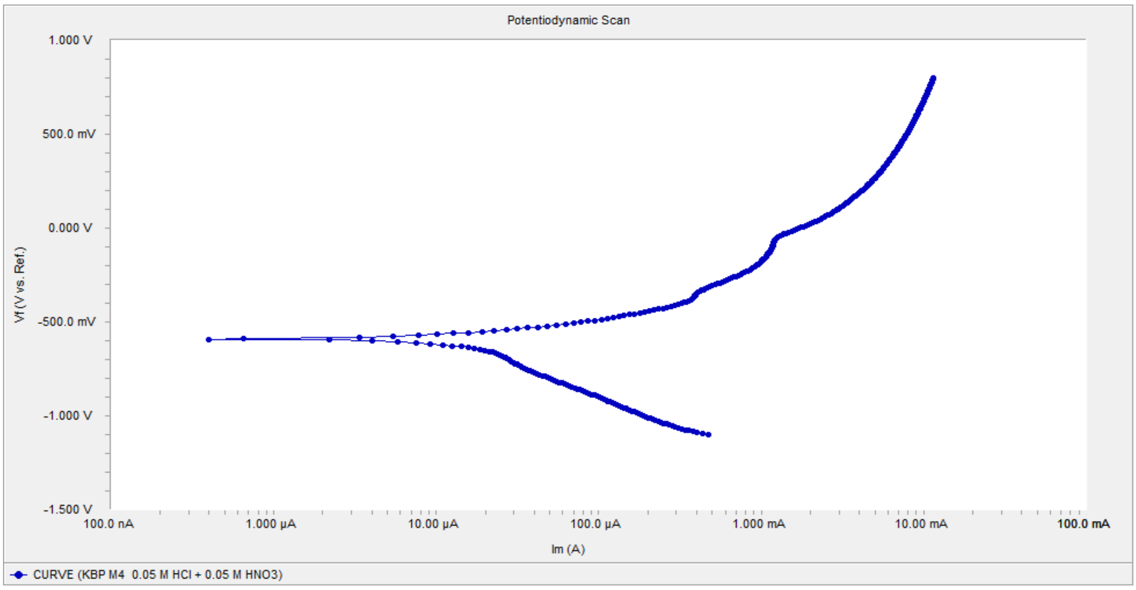

Figure-2
Polarization curve for corrosion of Mild Steel in (0.05 M HNO_3 + 0.05 M HCl) mix acid containing 1% inhibitor concentration

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