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Study on the inhibition of mild steel corrosion by benzimidazole in binary acid mixture

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ABSTRACT

The inhibition effect of Benzimidazole on Mild Steel in (HNO_3 +HCl) binary acid mixture was studied by weight loss, Temperature effect methods and polarization techniques. Rate of Corrosion was increases with increase in concentration of acid mixture. The inhibition efficiency of Benzimidazole increased as the concentration of Benzimidazole Increased. The inhibitor is found to be an excellent corrosion inhibitor from the results obtained. The inhibition action depends on the chemical structure, concentration of the inhibitor and concentration of the corrosive medium. The values of activation energy (Ea), free energy of activation ($\Delta G°ads$), Heat of adsorption (Qads), enthalpy of adsorption (ΔH^0ads) and entropy of adsorption (ΔS^0ads) were calculated. Corrosion rate increases while I. E. decreases with rise in temperature.

Key words: Corrosion, Mild Steel, Nitric and Hydrochloric acid mixture, Benzimidazole.

INTRODUCTION

Mild steel is extensively used in industries because of its low cost and availability, as a result corrodes when exposed to various industrial environments and conditions. 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 researchers [1-4]. Most of the well known acid inhibitors are organic compounds containing O, S and/or N atoms [5-6]. Ethylamines, Xylenol orange, Pyridazine, Polyvinyl pyrrolidone, Ethanolamines, Neem (Azadirachta indica) mature leaves extract, biodegradable (VPAP and VOAP) etc. have been extensively investigated as corrosion inhibitors [7-13].

N-heterocyclic compounds act by adsorption on the metal surface, and the adsorption takes place through nitrogen atom, as well as with triple or conjugated double bonds or aromatic rings in their molecular structures. Many N-heterocyclic compounds, such as imidazoline, triazole, pyrimidine, pyrrole, pyridine, etc., derivatives [14-17], have been used for the corrosion inhibition of iron or steel in acidic media.

In this paper, the role of Benzimidazole 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 [18-19], washed with water, cleaned with acetone and dried in air.

To study the effect of temperature on corrosion of Mild Steel in binary acid mixture (0.01 M HNO_3 +0.01 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) + Benz 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, Benz imidazole was added as an inhibitor. I.E. was calculated by the following formula.

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

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 [20].

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

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

The values of heat of adsorption (Qads) were calculated by the following equation [20].

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

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 [21].

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

Where, log B = –1.74 – (ΔG^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 [22].

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

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

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 0.01 M Binary acid mixture is 20.934 $KJMol^{-1}$ 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 –42.598 to –20.830 $KJMol^{-1}$. Oguzje [23] explained that the degree of surface coverage decreased with rise in temperature. The higher negative values of heat of adsorption also show that the inhibition efficiency decreased with a rise in temperature**.**

From Table-3 the negativ ΔG^0ads values ranging from -19.37 to -16.05 $KJMol^{-1}$ 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^0ads) were positive indicating the endothermic nature of the reaction [24] suggesting that higher temperature favors the corrosion process. The entropy (ΔS^0ads) is positive confirming that the corrosion process is entropically favorable [25].

Anodic and cathodic polarization curve without inhibitor shown in figure -1 and with inhibitor shown in figure-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.

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 (HNO3 + HCl) acid mixture.

Table – 1 Corrosion Rate (CR) and Inhibition efficiency (I.E.) of Mild Steel in 0.01M, 0.05M, and 0. 1M binary acid mixture (HCl + HNO_3) containing Benzimidazole 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	366.07	17.17	1477.68	8.31	2602.68	6.12
	0.5	245.54	44.44	1125.00	30.19	2544.64	8.21
	1.0	89.29	79.80	357.14	77.84	2214.29	20.12

A= (HCl + HNO_3), B= (HCl + HNO_3) + Benzimidazole.

Table-2 Effect of temperature on corrosion rate (CR), inhibitive efficiency (IE %), energy of activation (Ea) for Mild Steel in 0.01 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	310-320K	320-330 K	300 K	310 K	320 K	330K	MeanΔG^0ads
A	-	-	-	-	-	-	-	-	-
B	0.1	-20.83	-21.26	-23.96	-19.37	-19.32	-19.26	-19.11	-19.26
	0.5	-33.69	-29.62	-36.27	-17.60	-17.07	-16.66	-16.05	-16.85
	1.0	-42.60	-23.74	-30.46	-18.07	-17.25	-17.04	-16.62	-17.25

A= (HCl + HNO_3), B= (HCl + HNO_3) + Benz imidazole.

Table -3 Heat of adsorption (Qads) and free energy of adsorption (ΔG^0ads) for Mild Steel in 0.01 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		165.18		209.82		267.86		352.68		18.499	20.145	24.157	20.934
B	0.1	31.25	81.08	49.11	76.60	75.89	71.67	120.54	65.82	34.958	35.901	40.629	37.163
	0.5	14.29	91.35	26.79	87.23	46.43	82.67	84.82	75.95	48.601	45.362	52.914	48.960
	1.0	6.25	96.22	13.39	93.62	22.32	91.67	40.17	88.61	58.980	42.088	51.622	50.900

A = (HNO_3+HCl), B = (HNO_3+HCl)+ Benzimidazole

Table -4 Polarization data and Inhibition efficiency (IE %) of Benz 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)			By Polarization method	
			Anodic (βa)	Cathodic (-βc)	B (mV)	C.R. (mpy)	IE (in %)
A	0.04310	-520.0	72.4	128.6	20.14	78.78	
B	0.00832	-470.0	62.8	341.1	23.08	15.21	80.70

A = (HNO_3+HCl), B = (HNO_3+HCl)+ Benzimidazole, βa = Anodic Tofel constant, βc = Cathodic Tofel constant, ***B(mV) = βa* βc/2.3(βa+ βc)***

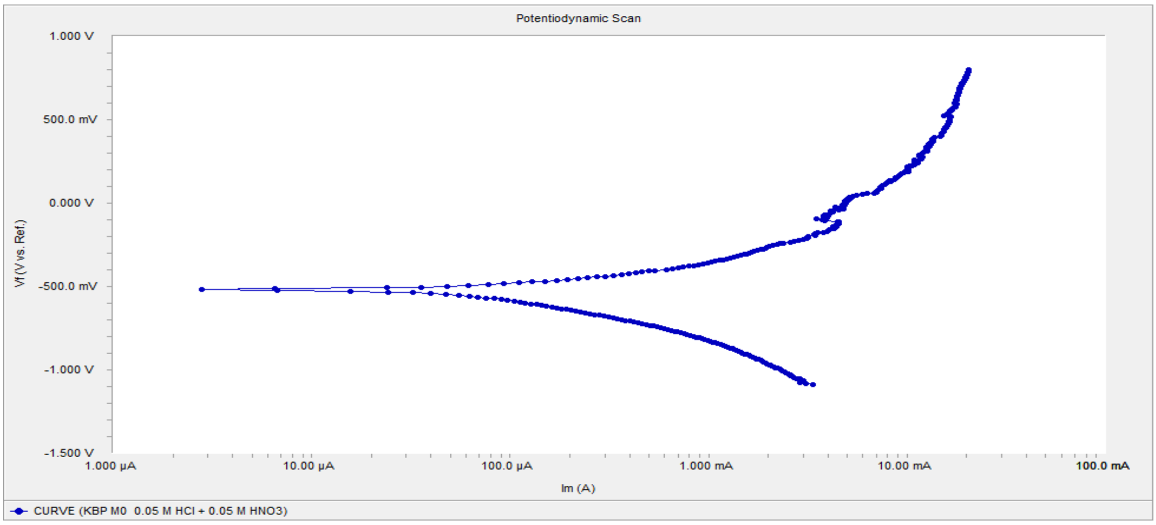

Figure-1 Polarization curve for corrosion of Mild Steel in (0.05 M HNO_3 + 0.05 M HCl) mix acid in absence of inhibitor

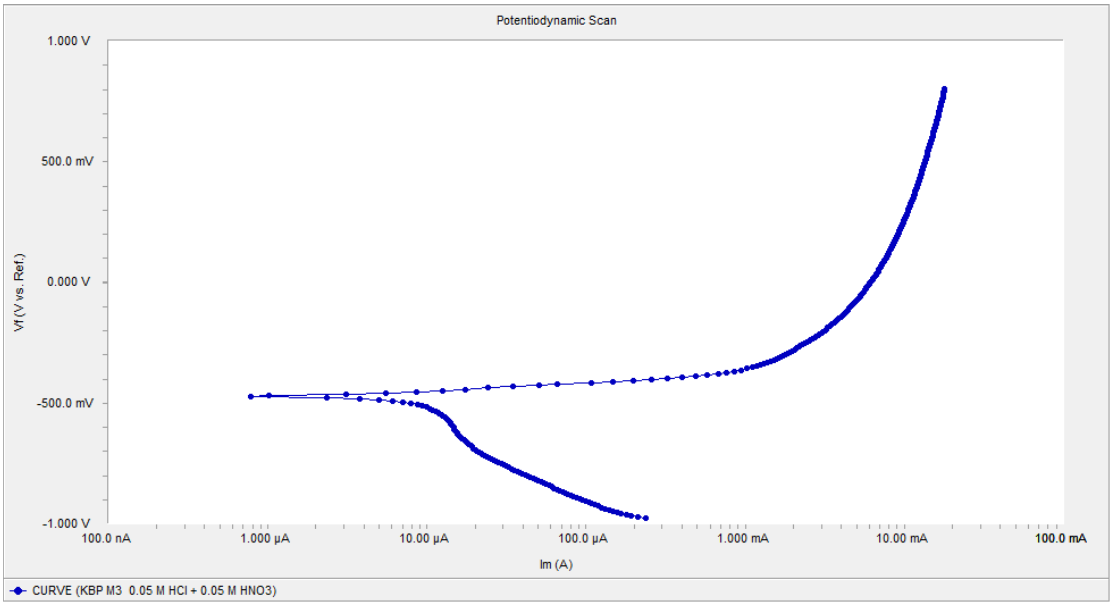

Figure-2 Polarization curve for corrosion of Mild Steel in (0.05 M HNO_3 + 0.05 M HCl) mix acid containing 1% inhibitor concentration

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