

IMIDAZOLE AS A CORROSION INHIBITOR FOR MILD STEEL IN ACID MEDIUM**M. Sivaraju, K. Kannan*¹ and V. Chandrasekaran¹**

Department of Chemistry, Selvam Arts & Science College, Namakkal (India)

¹Department of Chemistry, Government College of Engineering, Salem - 636 001 (India)

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ABSTRACT

The inhibition effect of imidazole on the corrosion of mild steel in acid medium has been studied by mass loss and polarization techniques between 303 K and 333K. The inhibition efficiency increased with increase in concentration of inhibitor and temperature from 303 K to 318 K for both acids. But higher temperature at 333K the inhibition efficiency decreased. The corrosion rate increases with increase in temperature and decreases with increase in concentration of inhibitor compare to blank. The adsorption of this compound on the mild steel surface has been found to obey Temkin's adsorption isotherm. Potentiostatic polarization results reveal that imidazole is a mixed type inhibitor. The values of activation energy (E_a) and free energy of adsorption (ΔG_{ads}) were also calculated.

Keywords: Mild steel, sulphuric acid, hydrochloric acid, corrosion inhibitor, Temkin's adsorption, isotherm, potentiostatic polarization and imidazole.

INTRODUCTION

Iron and its alloys are extensively used in many engineering applications in various environments especially in inorganic and organic acid environments^{1,2} because of their excellent combination of properties³.

Concentrated mineral acids are used extensively in picking, cleaning, descaling and oil well acidizing of metallic materials cause corrosion damage to metals^{4,5}. It has been speculated that organic inhibitors are more effective with iron and that polar organic compounds containing sulphur and nitrogen are good corrosion inhibitors for the acidic dissolution of metals^{6,7}.

Many organic inhibitors with hetero atoms have been studied⁸⁻¹³. High electron density of the sulphur and nitrogen atoms in these hetero atoms, help the organic molecules to get chemisorbed onto the metal surface¹¹. Due to the aggressiveness of hydrochloric acid and sulphuric acid solutions against structural materials, such as carbon steel, the use of corrosion inhibitors are usually required to minimize the corrosion attack¹⁴⁻¹⁷.

So, in this investigation the corrosion of mild steel in 1N hydrochloric acid and 1N sulphuric acid solution in the absence and presence of imidazole at 303, 318, 333 K has been studied by weight loss method and polarization technique.

It is aimed to predict the corrosion rate, inhibition efficiency on mild steel corrosion and the thermodynamic feasibility of inhibition via surface coverage on mild steel by absorbed imidazole at various temperatures. The adsorption characteristic of imidazole was studied in order to access the adsorption isotherm(s).

EXPERIMENTAL**Mass loss measurements**

Mild steel specimens were cut to size of 5 cm x 1 cm from the mild steel sheets having the following percentage composition Fe =99.686, Ni = 0.013, Mo = 0.015, Cr = 0.043, S= 0.014, P = 0.009, Si = 0.007, Mn = 0.196, C=0.017. Mass loss measurements were performed as per ASTM method described previously¹⁸⁻²⁰. Mass loss measurements were carried out in 1 N sulphuric acid and 1 N hydrochloric acid with imidazole in

the concentration range of 0.1 % to 0.5 % as inhibitor and the temperature between 303 K and 33 K for and immersion period of 4 hours. All the solutions were prepared with AR grade chemicals in double distilled water.

Potentiostatic Polarization measurement

Polarization measurements were carried out in a conventional three-electrode cell. Mild steel strips coated with lacquer expect for and exposed area of 1 cm² was used as the working electrode.

Table - 1 : Calculated Corrosin rate, inhibition efficeincy (I.E.%) and surface coverage (θ) for imidazol from mass loss studies in 1N Sulphuric Acid and 1N Hydrochloric Acid

Temperatue (K)	Concertration of imidazole (%)	1N Sulphuric acid			1N Hydrochloric acid		
		Corrosin Rate (mmpy)	Surface Coverage (θ)	Inhibition Efficiency (%)	Corrosion Rate (mmpy)	Surface Coverage (θ)	Inhibition Efficiency (%)
303	Blank	63.1552	-	-	15.00	-	-
	0.1	23.9246	0.6211	62.11	7.2814	0.5146	51.46
	0.2	19.6895	0.6882	68.82	5.7954	0.6140	61.40
	0.3	16.4203	0.7400	74.00	4.7552	0.6833	68.33
	0.4	15.2315	0.7588	75.88	4.3837	0.7080	70.80
	0.5	14.9343	0.7635	76.35	0.7626	0.7626	76.26
318	Blank	455.5348	-	-	371.6526	-	-
	0.1	122.2239	0.7317	73.17	17.7577	0.9523	95.23
	0.2	104.0203	0.7716	77.16	13.0768	0.9647	96.47
	0.3	73.7058	0.8381	83.81	12.9282	0.9651	96.51
	0.4	70.8081	0.8445	84.45	12.7796	0.9657	96.57
	0.5	68.1333	0.8504	85.04	12.3338	0.9668	96.68
333	Blank	634.3012	-	-	507.92	-	-
	0.1	363.7740	0.4264	42.64	60.6290	0.8806	88.06
	0.2	347.6508	0.4480	44.80	55.5022	0.8907	89.07
	0.3	317.5592	0.4943	49.43	51.1185	0.8993	89.93
	0.4	312.5068	0.5073	50.73	38.2646	0.9247	92.47
	0.5	309.7577	0.5116	51.16	32.9150	0.9352	93.52

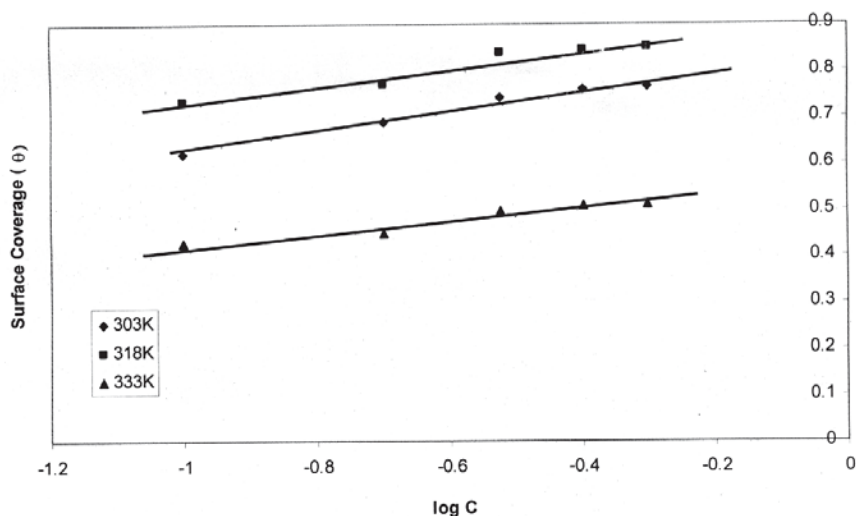


Fig. - 1 : Temkin's adsorption isotherm for corrosion behaviour of mild steel in 1N sulphuric acid with imidazole

The saturated calomel electrode and the platinum foil were used as reference and counter electrodes respectively. The potentiostatic was carried out using BAS – 100 A model instruments

RESULTS AND DISCUSSION

Mass loss Studies

Table -1 shows the value of inhibition efficiency [IE%] surface coverage (θ) and corrosion Rate obtained at different concentration of the inhibitors in 1 N sulphuric acid and 1 N hydrochloric acid solution for an immersion period of 4 hours. From the mass value, the inhibition efficiency [IE%] and surface coverage (θ) were calculated using the following equation^{12, 22}.

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

$$\theta = \frac{W_u - W_i}{W_u} \quad (2)$$

Where W_u and W_i are the corrosion rates for mild steel in the absence and presence of inhibitor respectively at the same temperature

It is clear that the addition of inhibitor to the acid has reduced the corrosion rate. The inhibition efficiency is increased with increase in the concentration of inhibitor and increased with temperature from 303 K to 318 K and then decreased. The values of the corrosion rate and inhibition efficiency of the inhibitor are known to depend on the molecular structure of the inhibitor. The maximum efficiency of imidazole was found to be 85.04% in 1N sulphuric acid and 96.68% in 1 N hydrochloric acid at 0.5% inhibitor concentration at 318 K

Thermodynamic / Kinetic Consideration

Table -2 shows that the calculated values of activation (E_a) and free energy of absorption (G_{ads}) for mild steel corrosion in 1 N sulphuric acid and 1 N hydrochloric acid with and without inhibitor. Energy of activation (E_a) was calculated from Arrhenius equation 23-25

$$\log P_2/P_1 = E_a/2.303 R [1/T_1 - 1/T_2]$$

Where P_1 and P_2 are the corrosion rates at temperatures T_1 and T_2 respectively. E_a values for the corrosion of mild steel in 1 N sulphuric acid at temperatures of 303 K, 318K and 333K are 105.542 KJ/Mole, 19.434 and 64.519/mole

Table - 2 : Calculated values of energy of activation (E_a) and free energy change (ΔG_{ads}) for mild steel in 1N sulphuric acid and 1N hydrochloric acid with imidazole

Temperature (K)	Concentration of imidazole (%)	1N Sulphuric acid E_a KJ/mole	ΔG_{ads} KJ/mole	1N Hydrochloric acid E_a KJ/mole	ΔG_{ads} KJ/mole
303-318	Blank	105.542	-	171.415	-
	0.1	87.117	-17.166	47.619	-16.06
	0.2	88.910	-16.169	43.468	-15.34
	0.3	80.2506	-15.788	53.242	-15.09
	0.4	82.078	-15.316	57.152	-14.65
	0.5	81.074	-14.818	66.277	-14.80
318-333	Blank	19.434	-	18.384	-
	0.1	64.027	-19.362	72.086	-24.63
	0.2	70.833	-18.095	84.861	-23.54
	0.3	85.742	-18.152	80.702	-22.58
	0.4	87.155	-17.517	64.380	-21.86
	0.5	88-893	-17.048	57.623	-21.36
303.333	Blank	64.519	--	98.509	-
	0.1	76.117	-16676	59.275	-23.03
	0.2	80.297	-14.999	63.188	-21.37
	0.3	82.843	-14.447	66.420	-20.51
	0.4	84.497	-13.739	60.595	-20.60
	0.5	84.801	-13.168	62.154	-20.43

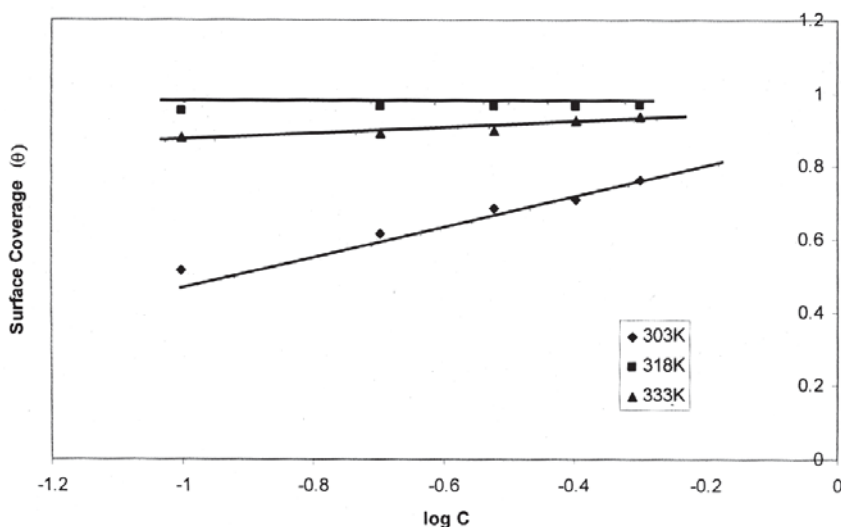


Fig. - 2 : Temkin's adsorption isotherm for corrosion behaviour of mild steel in 1N hydrochloric acid with imidazole

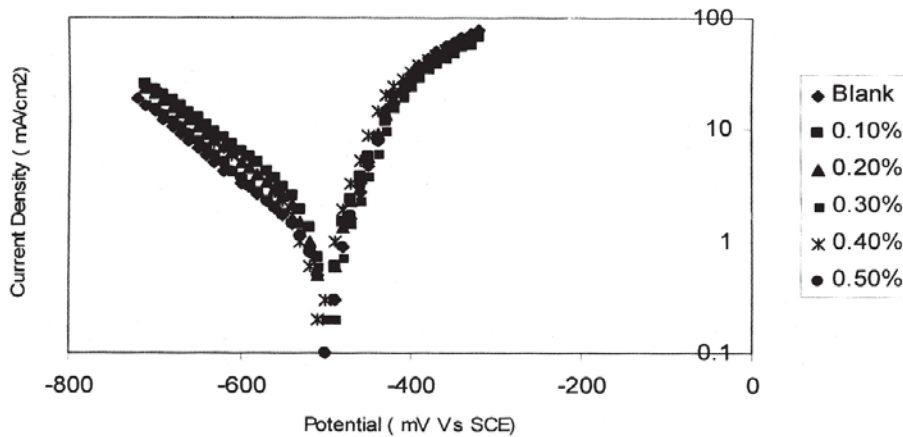


Fig. - 3 : Typical potentiostatic curves for mild steel in 1N sulphuric acid with imidazole

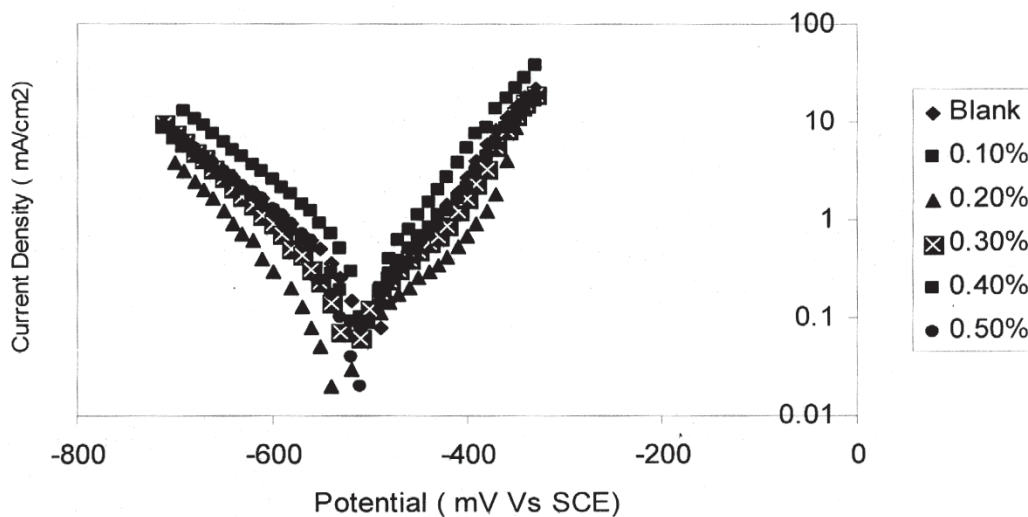


Fig. - 4 : Typical potentiostatic curves for mild steel in 1N hydrochloric acid with imidazole

Table - 3 : Electrochemical poplarization parameters for the corrosion behaviour of mild in 1N Sulphuric acid and 1N Hydrochloric acid with and without imidazole

Concentration inhibitor (%)	E _{cor} Vs SCE (mv)	1N Sulphuric acid				IE (%)	E _{cor} Vs SCE (mv)	1N Hydrochloric acid				IE (%)
		I _{cor} $\mu\text{A}/\text{cm}^2$	Tafel Constant mv/decade	b _a	-b _c			I _{cor} $\mu\text{A}/\text{cm}^2$	Tafel Constant mv/decade	b _a	-b _c	
Blank	-500	360	45	65	-	-	-495	110	60	80	-	-
0.1	-500	300	25	30	16.66	16.66	-505	95	45	30	13.63	13.63
0.2	-495	250	30	35	30.55	30.55	-515	90	50	65	18.18	18.18
0.3	-495	220	30	45	38.88	38.88	-525	80	90	55	27.27	27.27
0.4	-490	180	20	30	50.00	50.00	-510	70	55	50	36.36	36.36
0.5	-505	150	20	20	58.33	58.33	-515	50	55	45	54.54	54.54

respectively. And the Ea values for the corrosion of mild steel in 1 N hydrochloric acid at temperatures of 3.3 K, 318 K and 333 K are 171.415 KJ/ mole and 98.509 KJ/ mole respectively

In acid containing the inhibitor, the Ea values are found to be a lower than that in the uninhibited system at 303 K and 33 K only. At 318 K the Ea values are found to be higher than that in the uninhibited system. The higher values of Ea indicate physical adsorption of the inhibitor on metal surface²⁶.

The free of adsorption (ΔG_{ads}) at different temperature was calculated from the following equation²⁷.

$$\Delta G_{\text{ads}} = -RT \ln (55.5 K) \quad (4)$$

Where K is given by

$$K = \frac{\theta}{C(1-\theta)} \quad (5)$$

Where θ is surface coverage on the metal surface C is concentration of inhibitor in mole/lit and K is equilibrium constant.

The negative values of (ΔG_{ads}) indicated the spontaneous adsorption of inhibitor. This is usually characteristic of strong interaction with the metal surface. It is found that the ΔG_{ads} values are more positive than -40 KJ/mole^{-1} indication that inhibitor is physically adsorbed on the metal surface^{28,29}.

Adsorption isotherms

The plot of surface coverage (θ) obtained by mass loss method versus $\log C$ at different concentration of the inhibitors shows a straight line

indicating that the adsorption of the inhibitor from acid on mild steel surface follows the Timken's adsorption²⁷. This also points out that the corrosion inhibition by imidazole compound is a result of its adsorption on the metal surface. Fig. 1 and 2 shows the Timken's adsorption plots for imidazole.

Potentiostatic Polarization studies

The Polarization behaviors of mild steel functioning as cathode as well as anode in the test solutions is shown in Fig. 3 and 4 for 1N sulphuric acid and 1N hydrochloric acid at room temperature. The electrochemical data obtained are shown in Table -3. It is evident that imidazole bring about considerable polarization of cathode as well as anode. It was therefore inferred that the inhibitive action is of a mixed type. The cathodes and anodic Tafel slopes increase with increasing inhibitor concentration. The increase predominant in the case of the former Indicating that the cathodes inhibition is dominating through the inhibitive action is of mixed nature.

The corrosion parameters deduced from Tafel polarization such as corrosion current I_{cor} Corrosion potential E_{cor} , Tafel constant b_a and $-b_c$ and inhibition efficiency are given in Table III The I_{cor} values decreased with increasing concentration of the inhibitor. The inhibition efficiencies were determined from the values of corrosion current.

Conclusion

The following conclusion were made from the studies:

- 1) Corrosion rates of mild steel 1N sulphuric acid greater than 1N hydrochloric acid at all temperature.
- 2) Corrosion rates of mild steel in sulphuric acid and hydrochloric acid decreased with

- increasing concentration of imidazole.
- 3) The inhibition efficiency increased with respect to the concentration of imidazole as is assumed that the inhibition efficiency is equal to surface coverage.
 - 4) The inhibition efficiency of imidazole in sulphuric acid and hydrochloric acid increased with rise in temperature up to 318 K and then decreased.
 - 5) The maximum inhibition efficiency is found to be 85.04% and 96.68% at 318K for imidazole in 1N sulphuric acid and 1N hydrochloric
 - 6) The adsorption of imidazole on mild steel surface from the acid solution follows Temken's adsorption isotherm.
 - 7) The low and negative value of ΔG_{ads} indicated that the imidazole is physically adsorbed and spontaneous adsorption of inhibitor on the surface of mild steel.
 - 8) It is found that the imidazole acting as mixed type inhibitor.
 - 9) E_a values indicated physical adsorption of the inhibitor on metal surface

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