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2-Methyl Imidazole as a Corrosion Inhibitor for Mild Steel in Acid Medium

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The inhibition effect of 2-methyl imidazole on the corrosion of mild steel in acid medium has been studied by mass loss and polarization techniques between 303 and 333 K. The inhibition efficiency increased with increase in concentration of inhibitor and temperature from 303–318 K for both acids. But at higher temperature (333 K) the inhibition efficiency decreased. The corrosion rate increased with increase in temperature and decreased with increase in concentration of inhibitor compared 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 2-methyl imidazole is a mixed type inhibitor. The values of activation energy (E_a) and free energy of adsorption (ΔG_{ads}) were also calculated.

Key Words: **Mild steel, Sulphuric acid, Hydrochloric acid, Corrosion inhibition, Temkin's adsorption isotherm, Potentiostatic polarization, 2-Methyl imidazole.**

INTRODUCTION

Iron and its alloys are extensively used in many engineering applications in various environments, especially in inorganic and organic acid environments[1–3] because of their excellent combination of properties. Concentrated mineral acids are used extensively in pickling, cleaning, descaling and oil well aciding of metallic materials which 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 studied[8–13]. High electron density of the sulphur and nitrogen atoms in these hetero atoms helps the organic molecules to get chemisorbed on to the metal surface[11]. 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 attack[14–17].

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In view of this, in the investigation the corrosion of mild steel in hydrochloric acid and sulphuric acid solutions in the absence and presence of 2-methyl imidazole at 303, 318 and 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 2-methyl imidazole at various temperatures. The adsorption characteristic of 2-methyl imidazole was studied in order to access the adsorption isotherm [S].

EXPERIMENTAL

Mass loss measurements: Mild steel specimens were cut to size of 5 × 1 cm from 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 previously[18, 19]. Mass loss measurements were carried out in 1 N sulphuric acid and 1 N hydrochloric acid with 2-methyl imidazole in the concentration range of 0.1–0.5% as inhibitor and the temperature between 303 and 333 K for an immersion period of 4 h. All the solutions were prepared with AR grade chemicals in double distilled water.

Potentiostatic polarization measurements: Polarization measurements were carried out in a conventional three electrode cell. Mild steel strips coated with lacquer except for an exposed area of 1 cm^2 were used as working electrodes. The saturated calomel electrode and the platinum foil were used as reference and counter electrodes, respectively. The potentiostatic polarization was carried out using BAS-100 A model instrument.

RESULTS AND DISCUSSION

Mass loss studies

Table-1 shows the value of inhibition efficiency [IE%] surface coverage (θ) and corrosion rate obtained at different concentrations of the inhibitor in 1 N sulphuric acid and 1 N hydrochloric acid solutions for an immersion period of 4 h. From the mass value, the inhibition efficiency [IE%] and surface coverage (θ) were calculated using the following equation[20, 21].

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

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

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 can be seen from Table-1, that the addition of inhibitor to the acid has reduced the corrosion rate. The inhibition efficiency is increased with increase in concentration of inhibitor in temperature range from 303 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 inhibition efficiency of 2-methyl imidazole was found to be 82.10% in 1 N sulphuric acid and 97.51% in 1 N hydrochloric acid at 0.5% of inhibitor concentration at 318 K.

TABLE-1
CALCULATED CORROSION RATE, INHIBITION EFFICIENCY (I.E.%) AND SURFACE COVERAGE (θ) FOR 2 METHYL IMIDAZOLE FROM MASS LOSS STUDIES IN 1 N SULPHURIC ACID AND 1 N HYDROCHLORIC ACID

Temp. (K)	Concentration of 2-Methyl imidazole (%)	1 N Sulphuric acid			1 N Hydrochloric acid		
		Corosion rate (mmpy)	Surface coverage (θ)	Inhibition efficiency (%)	Corosion rate (mmpy)	Surface coverage (θ)	Inhibition efficiency (%)
303	Blank	38.8590	—	—	6.4641	—	—
	0.1	31.5776	0.1873	18.72	6.0183	0.0689	6.89
	0.2	29.7201	0.2352	23.52	5.4982	0.1494	14.94
	0.3	24.1475	0.3785	37.85	5.1267	0.2069	20.69
	0.4	21.8442	0.4378	43.78	4.2351	0.3448	34.48
	0.5	19.1694	0.5067	50.67	4.0865	0.3678	36.78
318	Blank	455.5348	—	—	371.3526	--	—
	0.1	106.0264	0.7672	76.72	16.5689	0.9553	95.53
	0.2	103.5745	0.7726	77.26	15.0086	0.9595	95.95
	0.3	101.3455	0.7775	77.75	11.2936	0.9695	96.95
	0.4	93.6183	0.7944	79.44	10.4020	0,9719	97.19
	0.5	81.5073	0.8210	82.10	9.2132	0.9751	97.51
333	Blank	634.3012	—	—	507.9165	—	—
	0.1	280.6320	0.5575	55.75	103.5745	0.7960	79.60
	0.2	274.6880	0.5669	56.69	103.1287	0.7969	79.69
	0.3	262.4284	0.5862	58.62	87.9715	0.8268	82.68
	0.4	247.0483	0.6 105	61.05	68.65634	0.8648	86.48
	0.5	183.4473	0.7107	71.07	67.2417	0.8676	86.76

Thermodynamic/Kinetic consideration

Table-2 shows that the calculated values of activation energy (E_a) and free energy of absorption (ΔG_{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[22–24]

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

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 303, 318 and 333K are 131.48, 19.43 and 78.10 kJ/mol, respectively and the E_a values for the corrosion of mild steel in 1 N hydrochloric acid at 303, 318 and 333 K are 216.38, 18.38 and 122.05 kJ/mol, respectively.

TABLE-2
CALCULATED VALUES OF ENERGY OF ACTIVATION (E_a) AND FREE ENERGY CHANGE (ΔG_{ads}) FOR MILD STEEL IN 1N SULPHURIC ACID AND 1 N HYDROCHLORIC ACID WITH 2-METHYL IMIDAZOLE

Temperature (K)	Concentration of 2-methyl imidazole (%)	1 N Sulphuric acid		1 N Hydrochloric acid	
		E_a (kJ/mol)	ΔG_{ads} (kJ/mol)	E_a (kJ/mol)	ΔG_{ads} (kJ/mol)
303–318	Blank	131.48	—	216.38	—
	0.1	64.70	–12.22	54.09	–9.36
	0.2	66.69	–11.20	53.60	–9.79
	0.3	76.62	–11.90	42.19	–9.77
	0.4	77.73	–11.80	47.99	–10.81
	0.5	77.31	–11.93	43.43	–10.50
318–333	Blank	19.43	—	18.38	—
	0.1	57.14	–20.06	107.59	–24.83
	0.2	57.25	–18.11	113.14	–23.27
	0.3	55.85	–17.11	120.59	–22.99
	0.4	56.96	–16.62	110.78	–22.44
	0.5	47.62	–16.48	116.68	–22.18
303–333	Blank	78.10	—	122.05	—
	0.1	61.10	–18.14	79.58	–21.27
	0.2	62.19	–16.32	81.99	–19.36
	0.,3	66.72	–15,42	79.50	–18.78
	0.4	67.84	–14.90	77.91	–18.79
	0.5	63.17	–15.53	78.33	–18.25

In acid containing the inhibitor, the E_a values are found to be lower than that in the uninhibited system at 303 and 333 K only. At 318 K the E_a values are found to be higher than that in the uninhibited system. The higher values of E_a indicate physical adsorption of the inhibitor on the metal surface[25].

The free energy of adsorption (ΔG_{ads}) at different temperatures was calculated from the following equation[26]:

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

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 mol/L and K is equilibrium constant.

The negative values of (ΔG_{ads}) indicate the spontaneous adsorption of the 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/mol indicating that the inhibitor is physically adsorbed on the metal surface[27, 28].

Adsorption isotherms

The plot of surface coverage (θ) obtained by mass loss method *vs.* log C at different concentration of the inhibitor shows a straight line indicating that the adsorption of the inhibitor from acid on mild steel surface follows the Temkin's adsorption isotherm[26]. This also points out that corrosion inhibition by 2-methyl imidazole compound is a result of its adsorption on the metal surface. Figs. 1 and 2 show the Temkin's adsorption isotherm plots for 2-methyl imidazole.

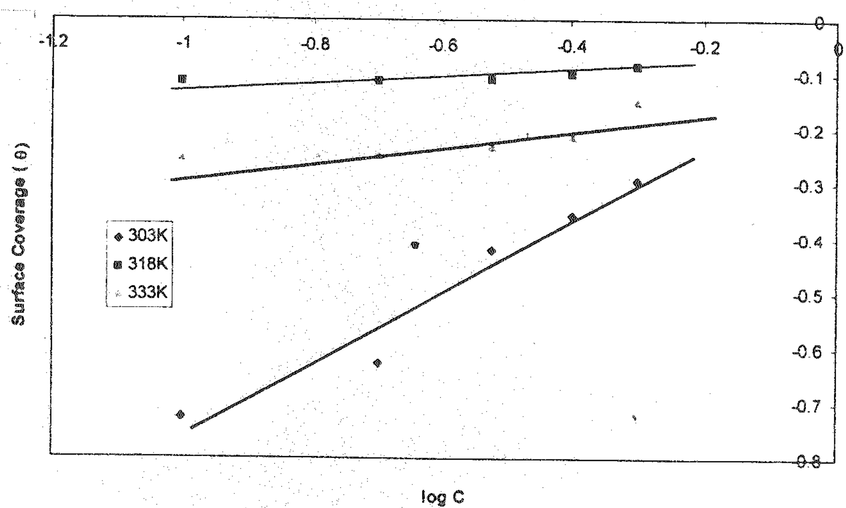

Fig. 1. Temkin's adsorption isotherm for corrosion behaviour of mild steel in 1 N sulphuric acid with 2-methyl imidazole

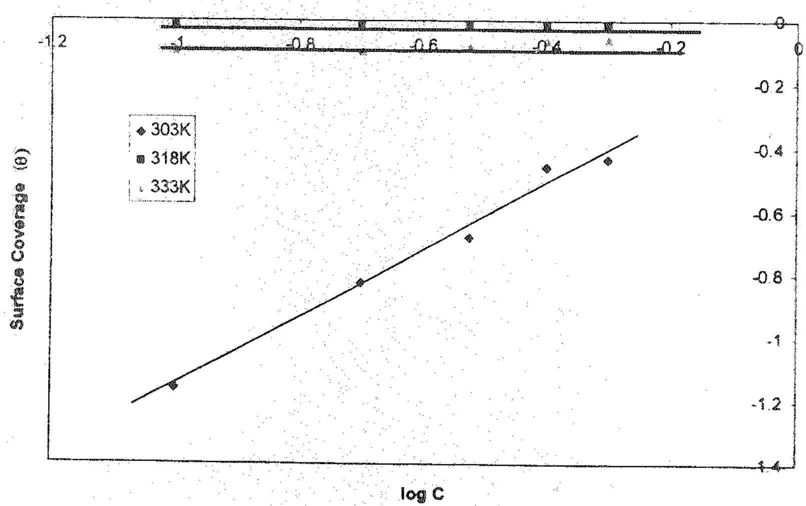

Fig. 2. Temkin's adsorption isotherm for corrosion behaviour of mild steel in 1 N hydrochloric acid with 2-methyl imidazole

Potentiostatic polarization studies

The polarization behaviour of mild steel functioning as cathode as well as anode in the test solution is shown in Figs. 3 and 4 for 1 N sulphuric acid and 1 N

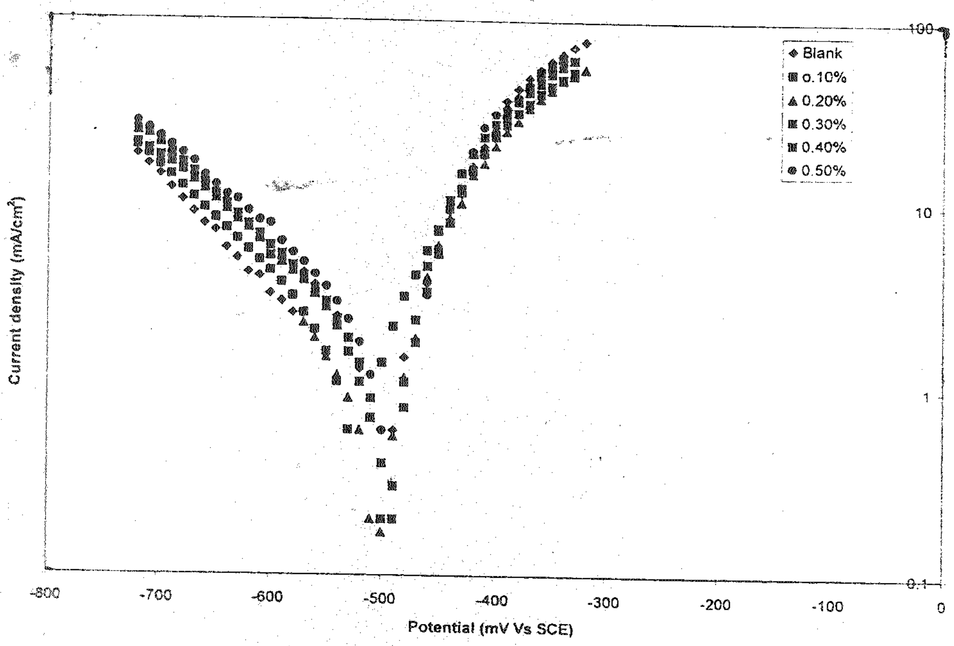

Fig. 3. Typical potentiostatic curves for mild steel in 1 N sulphuric acid with 2-methyl imidazole

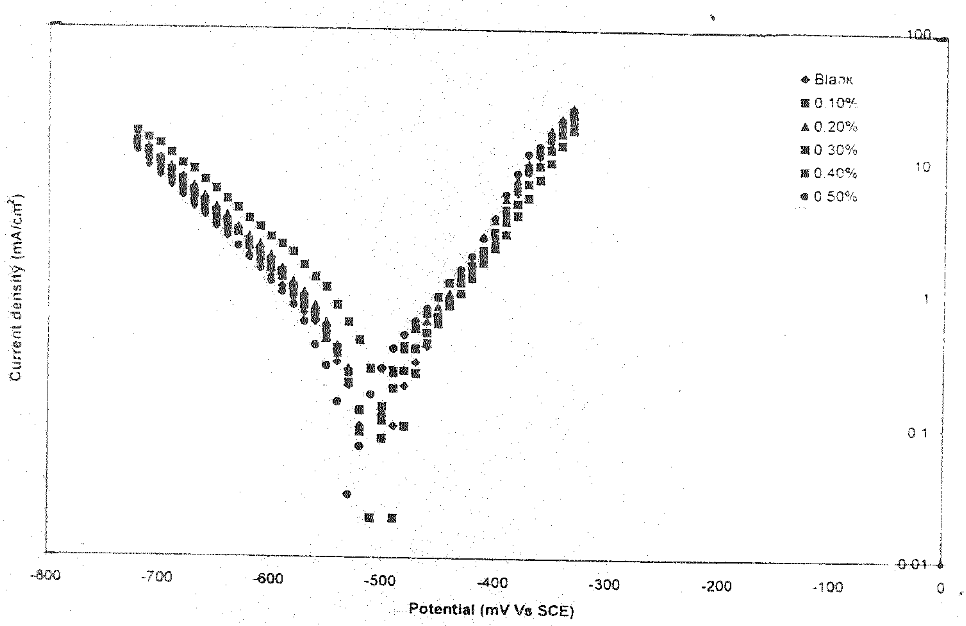

Fig. 4. Typical potentiostatic curves for mild steel in 1 N hydrochloric acid with 2-methyl imidazole

hydrochloric acid at room temperature. The electrochemical data obtained are shown in Table-3. It is evident that 2-methyl imidazole brings about considerable polarization of cathode as well as anode. It was therefore inferred that the inhibitive action is of a mixed type. The cathodic and anodic Tafel slopes increase with increase in inhibitor concentration. The increase is predominant in the case of the former indicating that the cathodic inhibition dominating through the inhibitive action is of mixed nature.

TABLE-3
ELECTROCHEMICAL POLARIZATION PARAMETERS FOR THE CORROSION BEHAVIOUR OF MILD STEEL IN 1N SULPHURIC ACID AND 1N HYDROCHLORIC ACID WITH AND WITHOUT 2-METHYL IMIDAZOLE

Concentration of inhibitor (%)	1 N sulphuric acid					1 N hydrochloric acid				
	E_{corr} *vs.* SCE (mV)	I_{corr} ($\mu A/cm^2$)	Tafel constant (mV/decade) b_a	Tafel constant (mV/decade) $-b_c$	IE (%)	E_{corr} *vs.* SCE (mV)	I_{corr} ($\mu A/cm^2$)	Tafel constant (mV/decade) b_a	Tafel constant (mV/decade) $-b_c$	IE (%)
Blank	–500	550	50	45	—	–505	95	70	70	—
0.1	–525	440	55	40	20.00	–515	90	70	35	5.26
0.2	–490	350	30	90	36.36	–510	85	45	50	10.52
0.3	–495	300	40	35	45.45	–510	75	40	35	21.05
0.4	–495	250	25	45	54.54	–500	64	30	35	32.63
0.5	–490	200	20	30	63.63	–530	62	45	40	34.73

The corrosion parameters deduced from Tafel polarization such as corrosion current i_{corr}, corrosion potential E_{corr}, Tafel constants b_a and $-b_c$ and inhibition efficiency are given in Table-3. The i_{corr} values decreased with increasing concentration of the inhibitor. The inhibition efficiencies were determined from the values of corrosion current. The inhibition efficiencies were found to be increased with increase in concentration of inhibitor.

Conclusions

The following conclusions were made from the studies:

- Corrosion rates of mild steel in 1 N sulphuric acid are greater than 1 N hydrochloric acid at all temperatures.
- Corrosion rates of mild steel in 1 N sulphuric acid and 1 N hydrochloric acid decreased with increase in concentration of 2-methyl imidazole.
- The inhibition efficiency increased with respect to the concentration of 2-methyl imidazole as it is assumed that the inhibition efficiency is equal to surface coverage.
- The inhibition efficiency of 2-methyl imidazole in 1 N sulphuric acid increased with rise in temperature up to 318 K and then decreased.
- The maximum inhibition efficiency was found to be 82.10 and 97.51% at 318 K for 0.5% of 2-methyl imidazole in 1 N sulphuric acid and 1 N hydrochloric acid, respectively.
- The adsorption of 2-methyl imidazole on mild steel surface from the acid solution follows Temkin's adsorption isotherm.
- The low and negative value of ΔG_{ads} indicates that the 2-methyl imidazole is physically adsorbed and there is spontaneous adsorption of inhibitor on the surface of mild steel.
- It was found that the 2-methyl imidazole acts as mixed type inhibitor.
- E_a values indicate physical adsorption of the inhibitor on metal surface.

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